Adsorption of Pb2+ on magnetic modified hemp biochar prepared using microwave-assisted pyrolysis

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Adsorption of Pb(II) Ions from Wastewater by Magnetically Modified Biochars derived from Microwave-Assisted Pyrolyzed Biomass

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Biochar II: Production, Characterization and Applications
September 15-20, 2019, Cetraro (Calabria), Italy
Background

Why treat wastewater?

Rise in economic development

- Increase pollutions e.g. lead poisoning
- Death of aquatic lives and human
- 412 000 deaths recorded annually due to lead exposure in the USA

Increase demand for clean water

- Rapid urbanization
- Expanding industrial activities

Government Legislations
Background

Why treat wastewater?

Major water pollutants

- Pb$^{2+}$, Cu$^{2+}$
- As & Cd ions, etc.

Organic Pollutants

- Basic dyes (MB, MV)
- Anionic dyes (MO)

Industry:
Mining, textiles, polymer, chemical, etc.

Methylene Blue, Methyl Violet, Methyl Orange
Wastewater treatment technologies

- Adsorption
- Membrane separation, Reverse osmosis,
- Ion exchange, Chemical Precipitation, etc.

Types of Adsorbent

- Activated Carbon, Biochar
- Zeolites, Resins, Clay, Silica gel

Most effective in heavy metal ions adsorption from aqueous solution

✓ Universal & Cheap
✓ Most Convenient
✓ Fast & Efficient
✓ Low residue generation
✓ Potential to recover/reuse absorbent

Biochar Vs Activated Carbon

Alhashimi et. al investigated environmental and economic performance of biochar (BC) compared to activated carbon (AC) and demonstrated that:
1. Significantly less energy (90% less) is needed to produce biochar based adsorbents
2. The GHG emissions related to production for biochar are all negative as compared to all positive emissions for AC
3. Biochar is significantly cheaper than AC for metals removal

<table>
<thead>
<tr>
<th></th>
<th>Biochar</th>
<th>Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy Demand</td>
<td>6.1 MJ/kg</td>
<td>97 MJ/kg</td>
</tr>
<tr>
<td>GHG Emissions</td>
<td>-0.9 kg CO₂ e/kg</td>
<td>+6.6 kg CO₂ e/kg</td>
</tr>
<tr>
<td>Price *</td>
<td>USD $5.00/kg</td>
<td>USD $5.00/kg</td>
</tr>
</tbody>
</table>

*BC currently cost between $0.55 - $2.20/kg

<table>
<thead>
<tr>
<th></th>
<th>Biochar</th>
<th>Activated Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>3.03 - 123</td>
<td>$40</td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td>$200</td>
</tr>
<tr>
<td>Cadmium</td>
<td>1.5 - 51.41</td>
<td>$550</td>
</tr>
<tr>
<td>Copper</td>
<td>0.08 - 89</td>
<td>$600</td>
</tr>
<tr>
<td>Lead</td>
<td>0.07 - 256</td>
<td>$300</td>
</tr>
</tbody>
</table>

Studied under an equivalent functional unit to adsorb heavy metals.

What is Biochar?

A fine-grained, porous and carbon-rich material produced from the thermal degradation of organic materials under oxygen-limited conditions.

Production Methods

- Slow Pyrolysis
- Fast Pyrolysis
- Flash carbonization
- Gasification
- **Microwave-assisted pyrolysis**

Microwave-Assisted Pyrolysis

- Rapid heating of sample
- Reduces residence time and accelerates reaction
- Energy efficient
- More controllable
- Cost effective
Biochar Production

Microwave vs. Conventional Heating

Microwave:
- Direct
- Microwaves penetrate biomass and create rapidly changing electric fields
- Dipoles continually rotate to align, movement and collision generates heat
- Uniform heating

Conventional:
- Indirect
- Reactor is heated through electrical heating
- Biomass is heated through conduction and convection
- Uneven heating
Industrial Applications of Biochars

BC Application Routes

➢ Developed:
  ➢ Contaminant remediation
  ➢ Soil amendment
  ➢ Carbon sequestration

➢ Biochar filler in composites:
  ➢ Low ash
  ➢ High C
  ➢ High SSA

➢ Diversified applications:
  ➢ Stable biochar market

Biochar Production Reactor, UNB

Scaled-up microwave reactor

- 3000 Watt max
- Large insulated single batch reactor
- Real time temperature data
- Volatiles exit through condenser
- Max. 5 kg sample

MW power supply (1), Magnetron head (2), Sub-tuner (3), Waveguide (4), SS 309 reactor (5), \( \text{N}_2 \) gas generator (6), Flow meter (7), Main power switch (8), Condenser (9), Bio-oil collector (10), Computer and data logging system (11), Temperature data acquisition system (12)
Problem Statements

• Characterize & evaluate the adsorption behaviour of modified biochar towards heavy metal ions in an aqueous environment

• Establish proper procedures for the separation & recovery of metal loaded adsorbents from an aqueous solution
Key Objectives

i. Understand the effects of pH, contact time, temperature, heavy metal ion concentration & adsorbent dose on the adsorption capacity of magnetically modified biochars.

ii. Assess the adsorption of heavy metal ions from synthetic wastewater using magnetically modified biochars.

iii. Undertake a comparable study on the adsorption capacity of biochars from two different biomass: maple (hardwood biomass) & hemp (agricultural biomass).
Significance

• Relief on traditional bio-sorbent like activated carbon
• Produce a cost effective and eco-friendly adsorbent with higher adsorption capacity and selectivity for heavy metal ions
• Enhance the recovery & reusability of metal loaded adsorbent via BC modification
• Provide a deeper insight into the sorption behaviour of heavy metal ions in aqueous solution
## Literature Reviews

### Biochar Modification

**Chemical**
- Modification of functional groups (amination, carboxylation)
- Acid/base treatment, etc.

**Physical**
- Steam activation
- Gas purging (CO₂/ammonia mixture)

**Impregnation with mineral oxides**
- Kaolinite
- Gibbsite

**Magnetic**
- Chemical co-precipitation of Fe³⁺/Fe²⁺
 Literary Reviews

- **Current Work on magnetic modification**
  - BC application is less attractive due to difficulty of separation & recovery after use
  - **Saravanan et. al** showed that magnetic BC is more thermally stable (gum kondagogu feedstock)
  - **Jiang et. al** reported high adsorption capacity of magnetic BC for MO – 398.08 mg/g. (chitosan-graphene oxide)
  - Competitive adsorption of Pb$^{2+}$ & Cd$^{2+}$ from aqueous solution by magnetic sorbent (sugarcane bagasse) showed that lead inhibits copper, **Yu et. al.**
  - **Devi & Saroha** showed that magnetic BC displays increased surface area for adsorption. (pentachlorophenol removal)
  - **Yuwei & Jianlong** showed that magnetic BC has adsorption capacity of 35.5 mg/g for Cu$^{2+}$(aq).
  - **NONE considered the current research activities**
Biochar application for wastewater treatment

Work done so far

• Mostly at lab scale, focusing on sorption of single metal spiked solution
• Few studies have assessed magnetic adsorbents
• ALL published work employed PRISTINE/MODIFY BC prepared by CONVENTIONAL PYROLYSIS

Selected work

• Yu et. al investigated competitive adsorption using magnetic sugarcane bagasse - not biochar
• Mohan et. al studied competitive sorption of lead & cadmium ions with magnetic oak bark BC – BC produced by conventional pyrolysis
Research Questions & Hypotheses

How does the adsorption capacity of MWAP BC from woody biomass compares to agric. Biomass?

E.g. Maple BC (woody biomass) vs Hemp BC (agricultural biomass).

Expected that maple BC will exhibit a higher adsorption capacity over hemp BC for heavy metal ions.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface areas, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maple BC 300µm 2.7kW, 1.5kg, 1.5 h</td>
<td>107.78</td>
</tr>
<tr>
<td>Hemp BC 300µm 2.7kW, 1.5kg, 1.5h</td>
<td>78.51</td>
</tr>
</tbody>
</table>
Research Methodology

Adsorbent preparation
- BC production
- BC modification

Biochar characterisation
- FT-IR, SEM, EDX, TGA, VSM & BET

Adsorption Characterisation
- Single metal system
- Batch mode
Biochar Characterization

- BET
- Batch Sorption
- SEM
- FT-IR
- TGA
- VSM

- Pore structure
- Adsorption capacity
- Surface morphology
- Surface functional groups
- Thermogravimetric Analysis (Thermal stability)
- Vibrating Sample Magnetometry (Magnetism)
Adsorption Characterization

**Independent variables**
- pH, contact time, Adsorbent dose
- Temperature, heavy metal concentration
- Comparative test (maple & hemp BC)

**Adsorption Kinetics**
- Estimates rate of adsorption
- Pseudo-first order
- Pseudo-second order

**Adsorption isotherms**
- Determines adsorption behaviour of ions by BC
- Langmuir model
- Freundlich model
Biochar Modification

H₂O₂ Impregnation
- Introduces O-containing functional group
- Enhances affinity for metal ions

Magnetic modification
- Introduces Fe oxides
- Enhances ease of separation
Biochar Modification

Results and Discussion

Characterizations

SEM

Unmodified maple BC (A), Magnetically modified maple BC (B)
Results and Discussion

Characterizations SEM

Unmodified Hemp BC (C), Magnetically modified Hemp BC (D)

- Hairy like particles on BC surfaces physically confirms successful Fe loading
• Percent weight of Fe on Hemp BC increased from 0.16 to 12.39. Fe loading confirmed.
Results and Discussion

Characterizations

EDX

- Percent weight of Fe on maple BC increased from 0 to 32.86. Fe loading confirmed.
Results and Discussion

Adsorption Isotherm – Magnetic Hemp Biochar

- Freundlich model has the best fit
- \( R^2 = 0.997 \)
- Heterogeneous adsorption surface and active sites of biochar

conditions: PH: 5.5, Time: 2h, Volume: 20 mL, Mass: 0.02g, Shaking: 300 rpm
Results and Discussion

Adsorption Isotherm – Magnetic Maple Biochar

- Langmuir model has the best fit
- $R^2 = 0.993$
- Sorption occurs at active sites uniformly distributed on biochar surface

Conditions: PH: 5.5, Time: 2h, Volume: 20 mL, Mass: 0.02g, Shaking: 300 rpm
Results and Discussion

Adsorption Kinetics – Magnetic Hemp Biochar

- Pseudo-second order model fits better
- $R^2 = 0.962$
- Pb$^{2+}$ ions removed by chemisorption
Results and Discussion

Adsorption Kinetics – Magnetic Maple Biochar

- Pseudo-second order model fits better
- \( R^2 = 0.941 \)
- \( \text{Pb}^{2+} \) ions removed by chemisorption

Experimental Data

- PSO
- PFO

Adsorption \( q_e \) (mg/g)

Time (Min)
Results and Discussion

Desorption Study – Magnetic Hemp Biochar

- Adsorbent maintained over 70% adsorption efficiency for Pb (II) even after 5 cycles
- Magnetic Hemp Biochar is recyclable
Results and Discussion

Desorption Study – Magnetic Maple Biochar

- Adsorbent maintained over 55% adsorption efficiency for Pb (II) even after 5 cycles
- Magnetic Maple Biochar is recyclable
Conclusions

• Previously the use of biochar for wastewater treatment is less attractive as it is difficult to separate and expensive.

• This study successfully demonstrated and simplifies the recovery, recycling of metal-loaded biochar following the adsorption of heavy metal ions from aqueous suspension.

• Experimental results showed that magnetic hemp biochar exhibits a better adsorption performance for Pb (II) ions than magnetic maple biochar under the same operating conditions.
Summary

Wastewater

Adsorption Technology

Carbon-based Adsorbent

Microwave Assisted Pyrolysis

Biochar

Magnetic Modification

Heavy Metal Ions adsorption

Clean water
Acknowledgements
THANK YOU!

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