Biochar adsorbents for the removal of heavy metals and volatile organics from an industrial paper mill's wastewater

Karina van der Merwe

REPS 2018

13 September 2018

Content

- Background and motivation
- Research aim
- Research objectives
- Objective 1: paper sludge analysis
- Objective 2: methodology, analysis and results
- Objective 3 – 5: planning
- Questions
- References

Background and Motivation

- Fresh water accounts for 0,30% of water available on earth [1]
  - Rivers, lakes and swamps
- Factors that contribute to global and local water shortages [2]
  - Population growth
  - Rapid industrialisation
  - Pollution by anthropogenic sources
  - Poor management of natural resources
- Industrial wastewater is discharged into the water [3]
  - 90% of wastewater produced

Background and Motivation

- Water contamination is a growing concern
  - Food security
  - Biodiversity
  - Water-energy nexus
- Industrial wastewater mainly contains inorganic and organic pollutants [4]
  - Heavy metals
  - Phenol derivatives

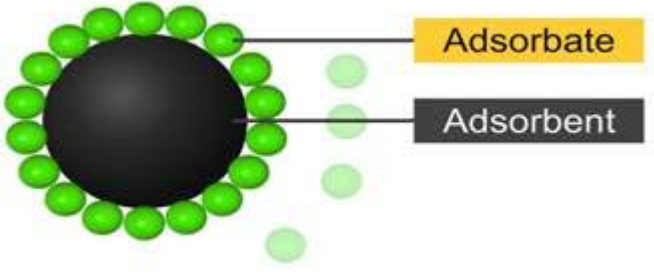
Background and Motivation

- Heavy metal sources
  - Mining , textile printing and smelting activities
- Phenolic compounds' sources
  - Paper and pulp, plastics and resins industries
- Characteristics of heavy metals and phenolic compounds [3] [5]
  - Non-biodegradable
  - Bioaccumulative
  - Leads to biomagnification

Background and Motivation

- Conventional methods of wastewater treatment [6] [7]
  - Chemical precipitation
    - Toxic sludge generation
    - Disposal costs
  - Membrane filtration
    - Fouling
    - High capital investment

- Adsorption is a **better alternative** [6] [8]
  - Effective
  - Simple operation
  - Adaptable



Background and Motivation

- Activated carbon is the most common adsorbent [9]
  - Large surface area
  - Porous structure
  - Functional groups
- Activated carbon disadvantages include [10] [11] [12]
  - High temperature
  - Expensive feedstocks
  - Requires additional treatment steps

Background and Motivation

- Biochar is an alternative to activated carbon
  - Produced from biomass
    - agricultural crops and waste
    - municipal waste
    - industrial waste
- Produced by the two main thermochemical processes
  - Hydrothermal liquefaction (HTL)
  - Pyrolysis
- Pyrolysis disadvantages [13]
  - Biochar produced has limited properties
  - Dry biomass must be used

Background and Motivation

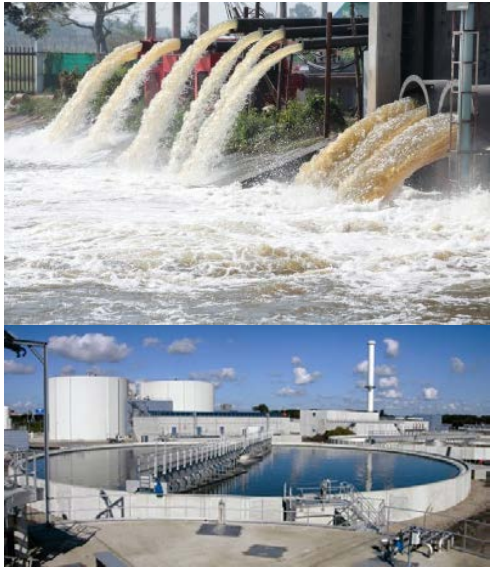
- Hydrothermal liquefaction is the preferred route[13] [14]
  - Low temperatures
  - Wet biomass can be used
  - Low cost feedstocks
  - Biochar produced has more properties
    - Better adsorption performance
      - Polar functional groups

Background and Motivation

- Paper sludge produced annually by the paper and pulp industry [15]
  - China: 12 million tons
  - United States: 8 million tons
  - Western Europe: 6 million tons
  - Japan: 3 million tons
- South Africa produces 0.50 million tons annually [16]
- Paper sludge landfilled or agricultural applications [17]
  - Additional disposal costs
  - Leaching of contaminants

Background and Motivation

- Paper sludge can be used for bio-processes
  - Reduced environment impact
    - Ground water sources: leaching
    - Waste management costs
- Limited literature of paper sludge
  - Biochar by hydrothermal liquefaction
  - Removal of heavy metals and organics
  - Synthetic and real industrial wastewater



Research Aim

The purpose of the study is to determine the effectiveness of paper sludge based biochar as a possible adsorbent to remove heavy metals and volatile organics from an industrial paper mill's wastewater stream.

Research Objectives

- **Objective 1:** Characterisation of raw materials
  - Industrial wastewater
  - Waste paper sludge
- **Objective 2:** Prepare and characterise biochar
  - Biochar produced by HTL
  - De-ash the biochar produced
  - Homogeneous sample preparation
- **Objective 3:** Characterise adsorptive performance of biochar in a synthetic heavy metal environment
  - Calcium: highest concentration in industrial wastewater

Research Objectives

- **Objective 4:** Characterise adsorptive performance of biochar in a synthetic organic environment
  - Phenol: highest concentration in industrial wastewater
- **Objective 5:** Compare the performance of biochar with activated carbon
  - Synthetic wastewater
  - Real industrial wastewater

Objective 1: Paper Sludge Analysis

Analysis type	Purpose of analysis	Progress
FTIR analysis	Surface functional groups	Done
Proximate analysis	Moisture, volatile and ash content as well as the fixed carbon	Done
Calorific analysis	Higher heating value	Done
Fibre analysis	Cellulose, hemicellulose and lignin content	Done
SEM analysis	Physical morphology	Done
BET analysis	Surface area, average pore size distribution, average pore size and average porosity	To be done
Elemental analysis	C, H, N, S, O content	To be done

Paper Sludge Analysis

Proximate analysis (wt %)	
Moisture content	54.80
Volatile matter	15.60
Ash	26.60
Fixed carbon	3.00
Fibre analysis (wt %)	
Hemicellulose	12.47
Cellulose	35.32
Lignin	6.37

Objective 2: Biochar Production

- Biochar was produced by hydrothermal liquefaction
  - 316 Stainless steel autoclave
  - Feedstock: 200 g paper sludge
  - Temperature: 300°C and 280°C
  - Starting pressure: 5 bar
  - Residence time: 15 minutes
  - Nitrogen atmosphere

Objective 2: Biochar Production

Before

After

Objective 2: Biochar Production Results

Temperature	Basis	Yield (g/kg)
300°C	Wet	326 ± 38
300°C	Dry	722 ± 84
280°C	Wet	235 ± 24
280°C	Dry	520 ± 53

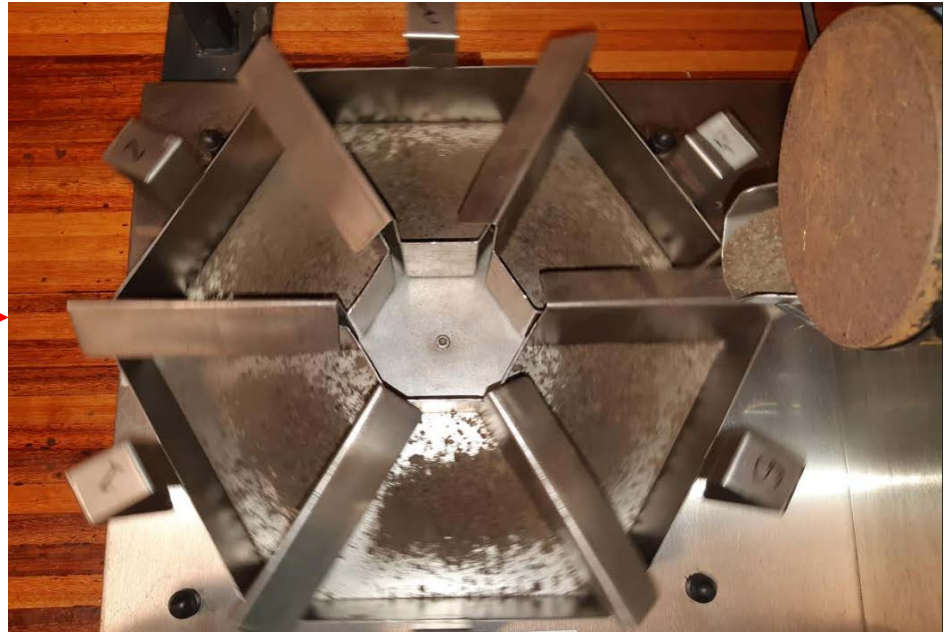
Objective 2: Biochar de-ashing

Washing with water

After filtration

Objective 2: Homogeneous sample preparation

Before splitting

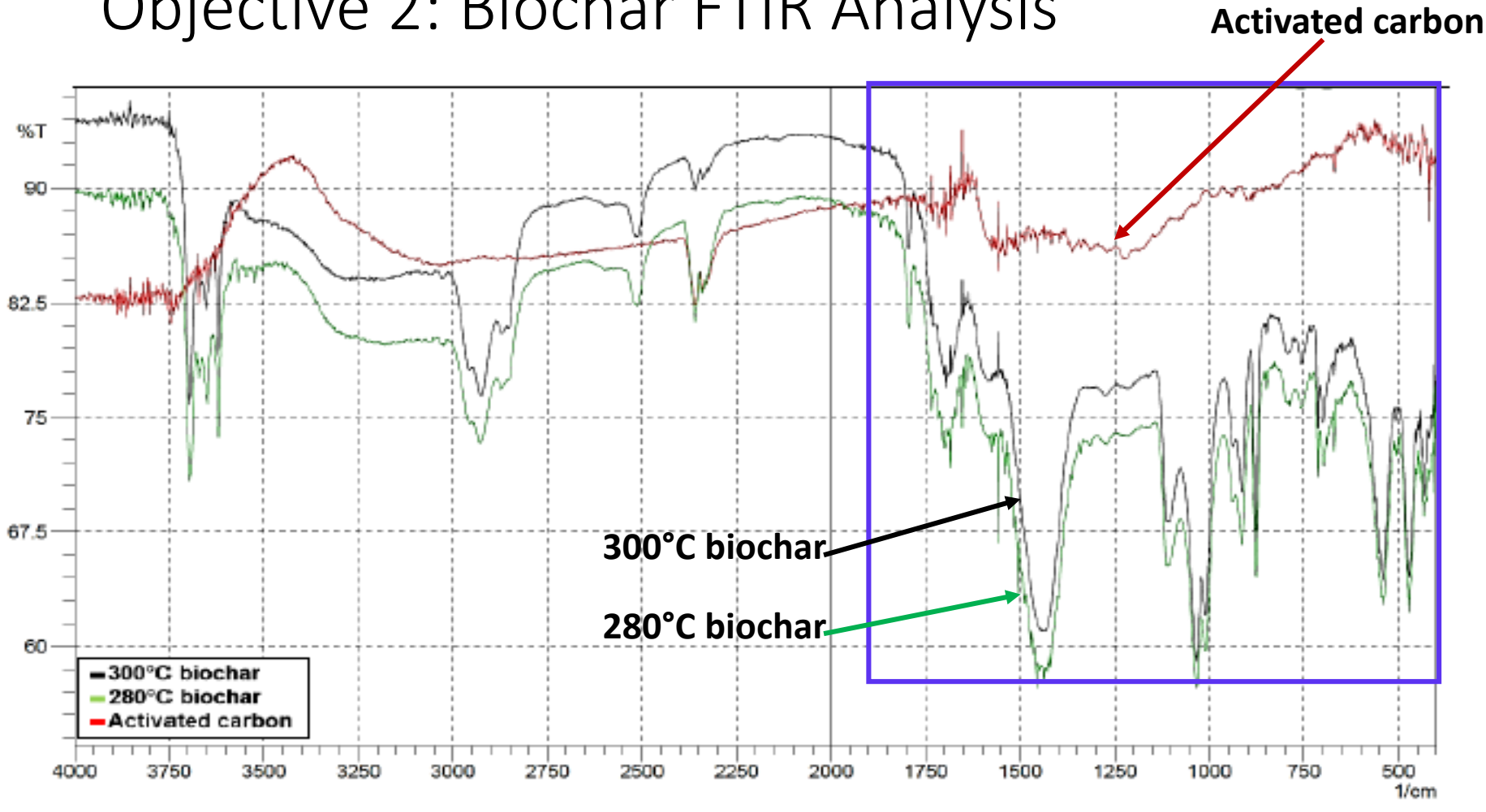


After splitting

Objective 2: Biochar Characterisation

Analysis type	Purpose of analysis	Progress
FTIR analysis	Surface functional groups	Done
Proximate analysis	Moisture, volatile and ash content as well as the fixed carbon	In progress
Calorific analysis	Higher heating value	Done
SEM analysis	Physical morphology	Done
Particle size analysis	Particle size distribution	Done
BET analysis	Surface area, average pore size distribution, average pore size and average porosity	To be done
Elemental analysis	C, H, N, S, O content	To be done

Objective 2: Biochar FTIR Analysis



Objective 3 – 5: Planning

- Adsorption experiments to start after characterisation
  - Maximum adsorption capacity will be determined
    - Heavy metal environment
    - Organic contaminant environment
- The manipulated variables include:
  - pH
  - Adsorbent dosage
  - Contact time
  - Rotary speed
  - Initial adsorbate concentration
- Temperature will be kept constant

Any questions?

Thank you

References

[1] Earthwatch Institute 2018. Planet Earth is seemingly awash with water - we call it 'the Blue Planet'. https://freshwaterwatch.thewaterhub.org/content/water-limited-resource Date of access: 10 May 2018.

[2] De Gisi, S., Lofrano, G., Grassi, M., & Notarnicola, M. 2016. Characteristics and adsorption capacities of low-cost sorbents for wastewater treatment: A review. *Sustain. Mater. Technol.* 9:10–40.

[3] Wong, S., Ngadi, N., Inuwa, I.M., & Hassan, O. 2018. Recent advances in applications of activated carbon from biowaste for wastewater treatment: A short review. *J. Clean. Prod.* 175.

[4] Huang, Y., Zeng, X., Guo, L., Lan, J., Zhang, L., & Cao, D. 2018. Heavy metal ion removal of wastewater by zeolite-imidazolate frameworks. *Sep. Purif. Technol.* 194(September 2017):462–469.

[5] Zhou, N., Chen, H., Xi, J., Yao, D., Zhou, Z., Tian, Y., & Lu, X. 2017. Biochars with excellent Pb(II) adsorption property produced from fresh and dehydrated banana peels via hydrothermal carbonization. *Bioresour. Technol.* 232:204–210.

[6] Aziz, H.A., Adlan, M.N., & Ariffin, K.S. 2008. Heavy metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) removal from water in Malaysia: Post treatment by high quality limestone. *Bioresour. Technol.* 99(6):1578–1583.

[7] Ariffin, N., Abdullah, M.M.A.B., Mohd Arif Zainol, M.R.R., Murshed, M.F., Hariz-Zain, Faris, M.A., & Bayuaji, R. 2017. Review on Adsorption of Heavy Metal in Wastewater by Using Geopolymer. *MATEC Web Conf.* 97:01023.

[8] Barakat, M.A. 2011. New trends in removing heavy metals from industrial wastewater. *Arab. J. Chem.* 4(4):361–377.

[9] Kong, J., Gu, R., Yuan, J., Liu, W., Wu, J., & Fei, Z. 2018. Ecotoxicology and Environmental Safety Adsorption behavior of Ni (II) onto activated carbons from hide waste and high-pressure steaming hide waste. 156(December 2017):294–300.

[10] Gratuito, M.K.B., Panyathanmaporn, T., Chumnanklang, R.A., Sirinuntawittaya, N., & Dutta, A. 2008. Production of activated carbon from coconut shell: Optimization using response surface methodology. *Bioresour. Technol.* 99(11):4887–4895.

References

[11] Tan, X., Liu, Y., Zeng, G., Wang, X., Hu, X., Gu, Y., & Yang, Z. 2015. Application of biochar for the removal of pollutants from aqueous solutions. *Chemosphere*. 125:70–85.
[12] Burakov, A.E., Galunin, E. V., Burakova, I. V., Kucherova, A.E., Agarwal, S., Tkachev, A.G., & Gupta, V.K. 2018. Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review. *Ecotoxicol. Environ. Saf.* 148(August 2017):702–712.
[13] Gollakota, A.R.K., Kishore, N., & Gu, S. 2018. A review on hydrothermal liquefaction of biomass. *Renew. Sustain. Energy Rev.* 81(August 2016):1378–1392.
[14] Liu, Z., Quek, A., Kent Hoekman, S., & Balasubramanian, R. 2013. Production of solid biochar fuel from waste biomass by hydrothermal carbonization. Fuel. Elsevier Ltd. 103:943–949.
[15] He, X., Wu, S., Fu, D., & Ni, J. 2009. Preparation of sodium carboxymethyl cellulose from paper sludge. *J. Chem. Technol. Biotechnol.* 84(3):427–434.
[16] Boshoff, S., Gottumukkala, L.D., van Rensburg, E., & Görgens, J. 2016. Paper sludge (PS) to bioethanol: Evaluation of virgin and recycle mill sludge for low enzyme, high-solids fermentation. *Bioresour. Technol. Elsevier Ltd*. 203:103–111.
[17] Hojamberdiev, M., Kameshima, Y., Nakajima, A., Okada, K., & Kadirova, Z. 2008. Preparation and sorption properties of materials from paper sludge. *J. Hazard. Mater.* 151(2–3):710–719.