Engineering Conferences International

ECI Digital Archives

Bio-Char II: Production, Characterization and Applications

Proceedings

9-19-2019

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

Muhammad T. Afzal

Patrick Godwin

Huining Xiao

Follow this and additional works at: https://dc.engconfintl.org/biochar_ii

Part of the Engineering Commons

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

Patrick M. Godwin[a,b], Muhammad T. Afzal[a*], Huining Xiao[b]

[a*] Department of Mechanical Engineering,
[b] Department of Chemical Engineering,
University of New Brunswick, Canada

Email: *mafzal@unb.ca

Biochar II: Production, Characterization and Applications

September 15-20, 2019, Cetraro (Calabria), Italy

Outlines

UNB

- Background
- Problem Statement, Purpose & Significance
- Literature Reviews
- Research Questions & Hypotheses
- Research Methodology
- Results and Discussion
- Conclusions

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

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

Heavy Metal ions

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

Organic Pollutants

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

Methylene Blue, Methyl Violet, Methyl Orange

Wastewater treatment technologies

UNB

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

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

Types of Adsorbent

Activated Carbon, **Biochar**

Zeolites, Resins, Clay, Silica gel

Most effective in heavy metal ions adsorption from aqueous solution[1]

[1] Ali I 2010 The Quest for Active Carbon Adsorbent Substitutes: Inexpensive Adsorbents for Toxic Metal Ions Removal from Wastewater *Sep. Purif. Rev.* **39** 95–171

Biochar Vs Activated Carbon

UNB

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

	Biochar	Activated Carbon
Energy Demand	6.1 MJ/kg	97 MJ/kg
GHG Emissions	- 0.9 kg CO_2 e/kg	+6.6 kg CO_2 e/kg
Price *	USD $5.00/kg	USD $5.00/kg

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

	Biochar		Activated Carbon	
	Adsorption mg/g	Economic Performance	Adsorption mg/g	Economic Performance
Chromium	3.03 - 123	$40	1.1 - 117	$500
Zinc		$200		$1,240
Cadmium	1.5 - 51.41	$550	1.5 - 8	$1,250
Copper	0.08 - 89	$600	1.8 - 11.4	$600
Lead	0.07 - 256	$300	0.20 - 152	$180

Studied under an equivalent functional unit to adsorb heavy metals.

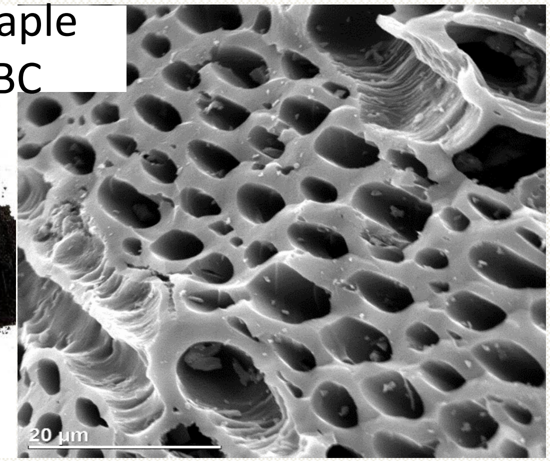
[2] Alhashimi H A and Aktas C B 2017 Life cycle environmental and economic performance of biochar compared with activated carbon: A meta-analysis *Resour. Conserv. Recycl.* **118** 13–26

What is Biochar?

UNB

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

Maple BC



Production Methods

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

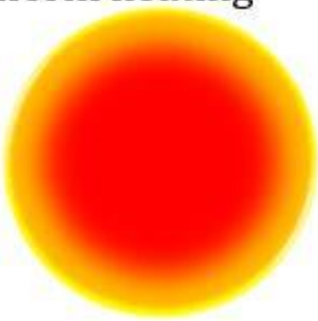
❑ **Microwave-Assisted Pyrolysis**

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

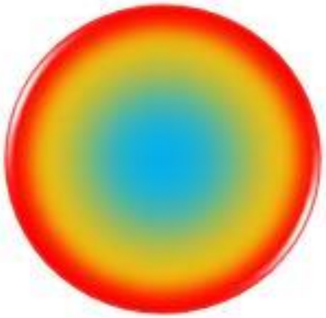
Biochar Production

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

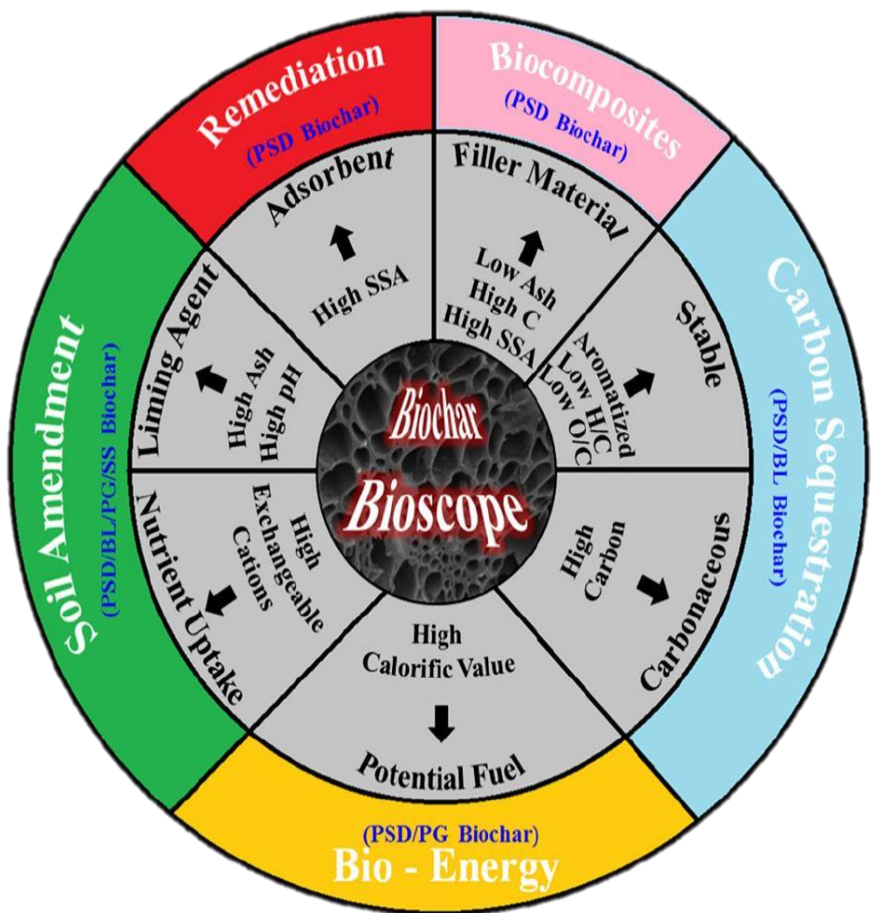


- Conventional:
  - Indirect
  - Reactor is heated through electrical heating
  - Biomass is heated through conduction and convection
- Uneven heating



UNB

BC Application Routes

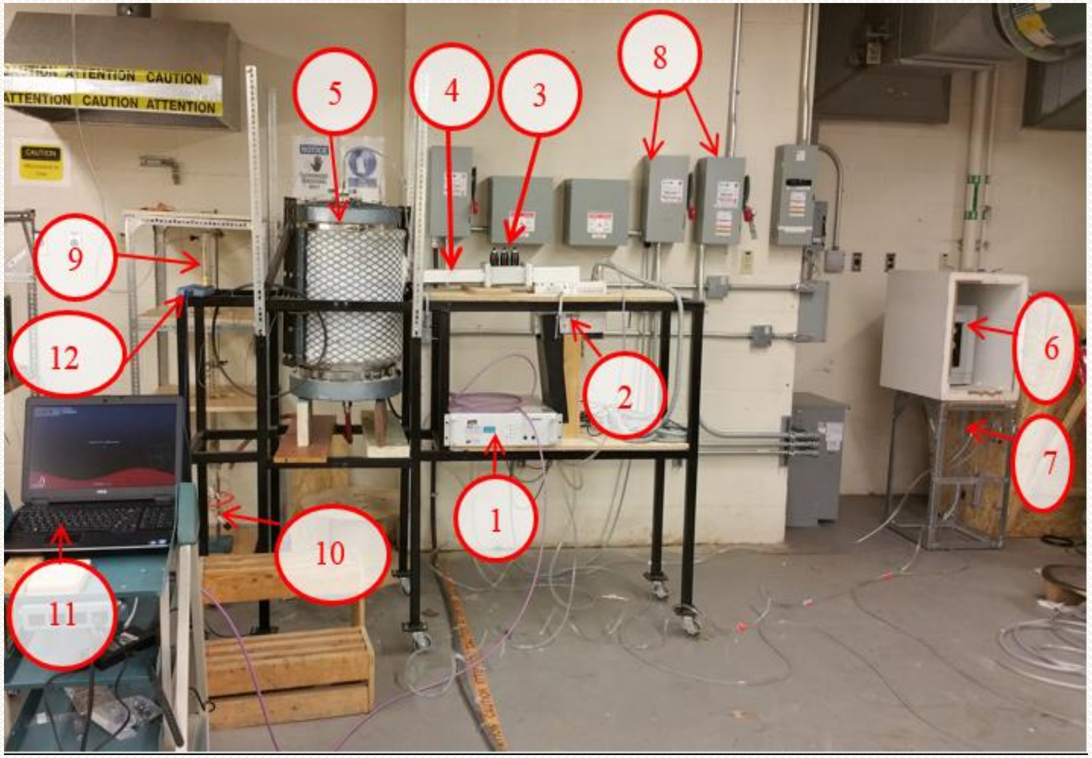


Science of the Total Environment 512-513 (2015) 495-505

- Developed:
  - Contaminant remediation
  - Soil amendment
  - Carbon sequestration
- Biochar filler in composites:
  - Low ash
  - High C
  - High SSA
- Diversified applications:
  - Stable biochar market

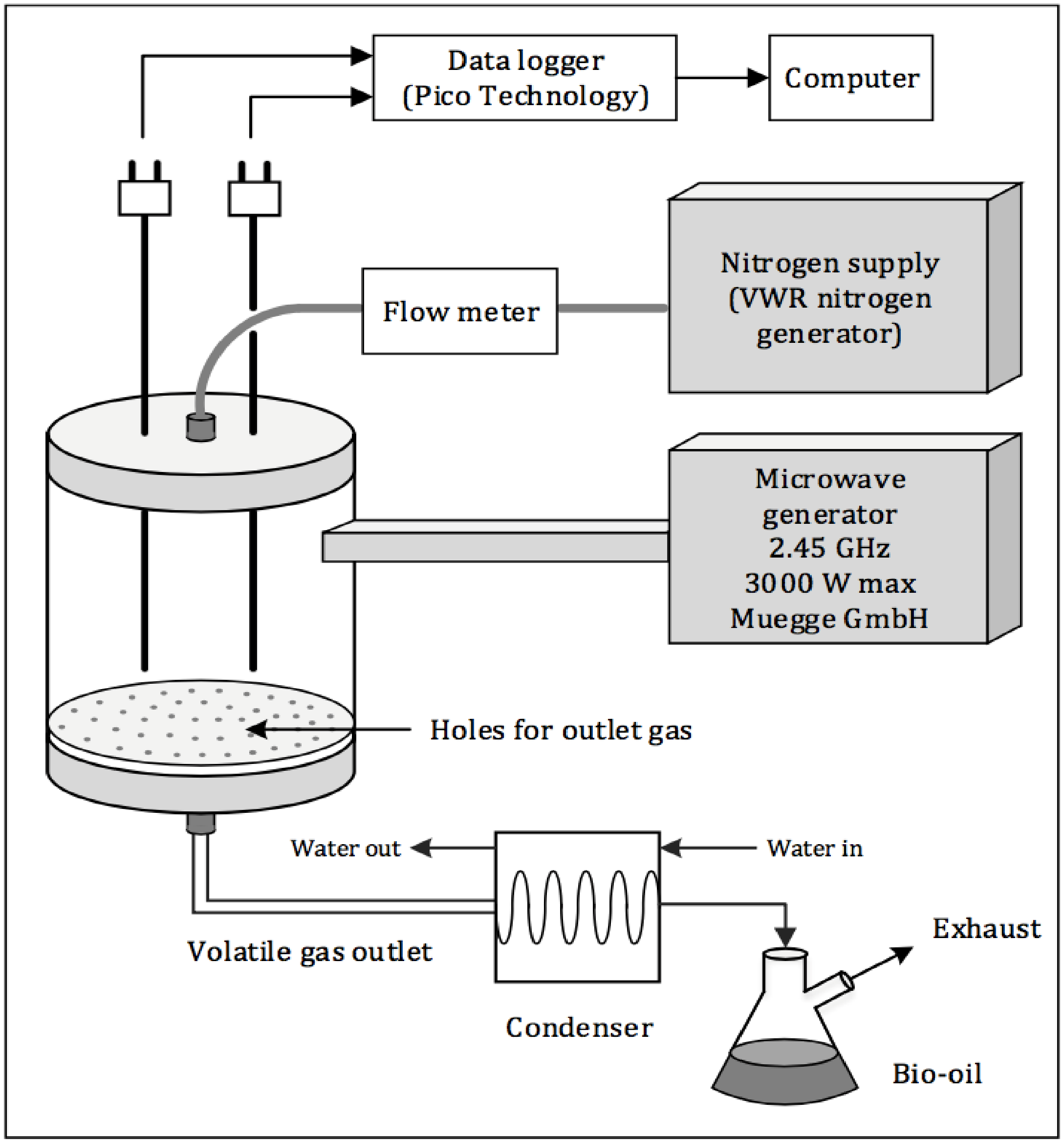
Scaled-up microwave reactor

- 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), 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)

Reactor System PFD



UNB

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

Problem Statement, Purpose & Significance

UNB

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).

Problem Statement, Purpose & Significance

Significance

- Relief on traditional bio-sorbent like activated carbon
- Produce a cost effective and eco-friendlier 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 (CO_2/ammonia mixture)

Impregnation with mineral oxides
- Kaolinite
- Gibbsite

Solves separation problem

Magnetic
- Chemical co-precipitation of Fe^{3+}/Fe^{2+}

UNB

Literature 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**

UNB

UNB

❑ 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

UNB

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.

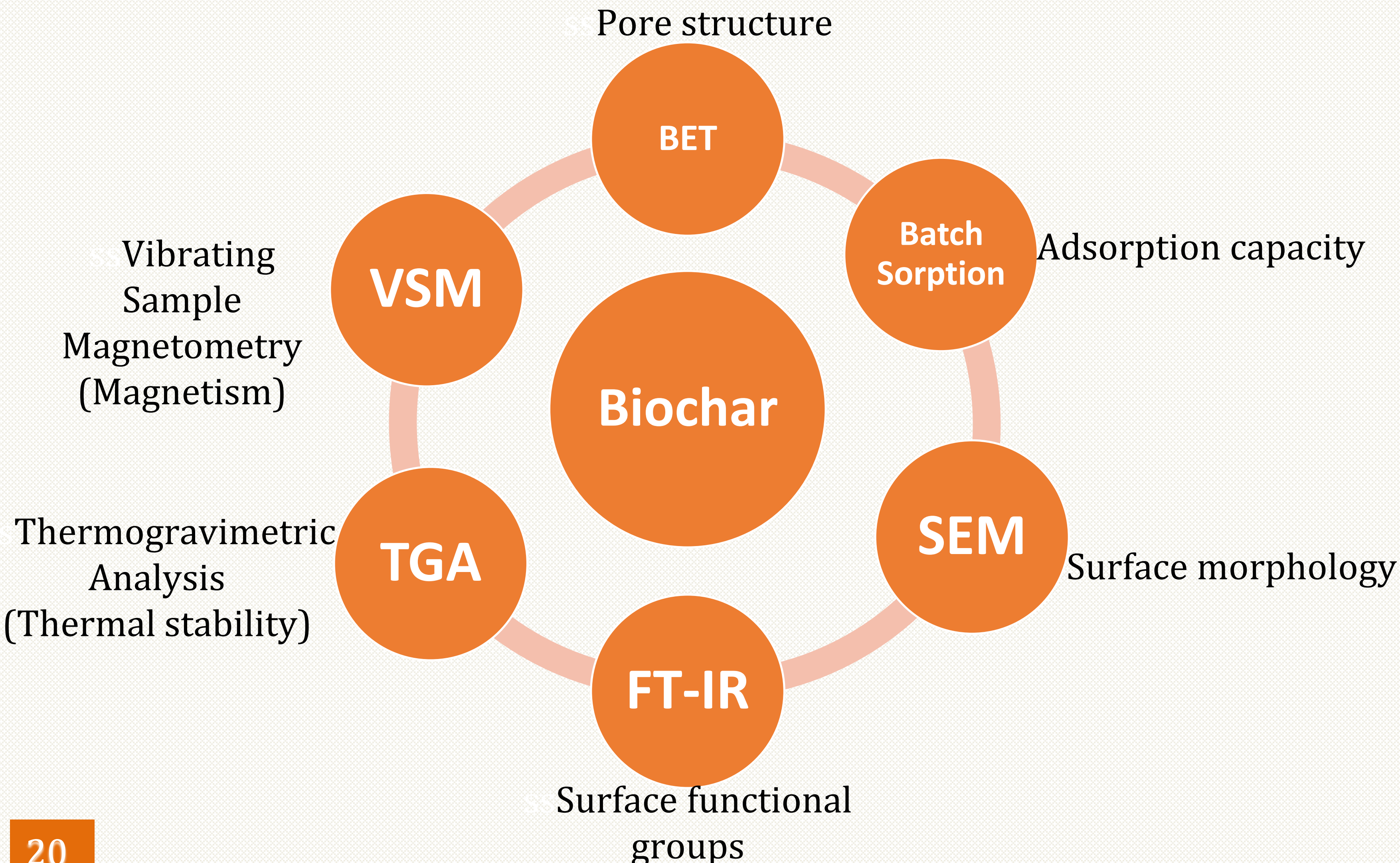
Samples	BET surface areas, m^2/g
Maple BC 300µm 2.7kW, 1.5kg, 1.5 h	107.78
Hemp BC 300µm 2.7kW, 1.5kg, 1.5h	78.51

Research Methodology

UNB

Adsorbent preparation	• BC production • BC modification
Biochar characterisation	• FT-IR, SEM, EDX, TGA, VSM & BET
Adsorption Characterisation	• Single metal system • Batch mode

Biochar Characterization



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

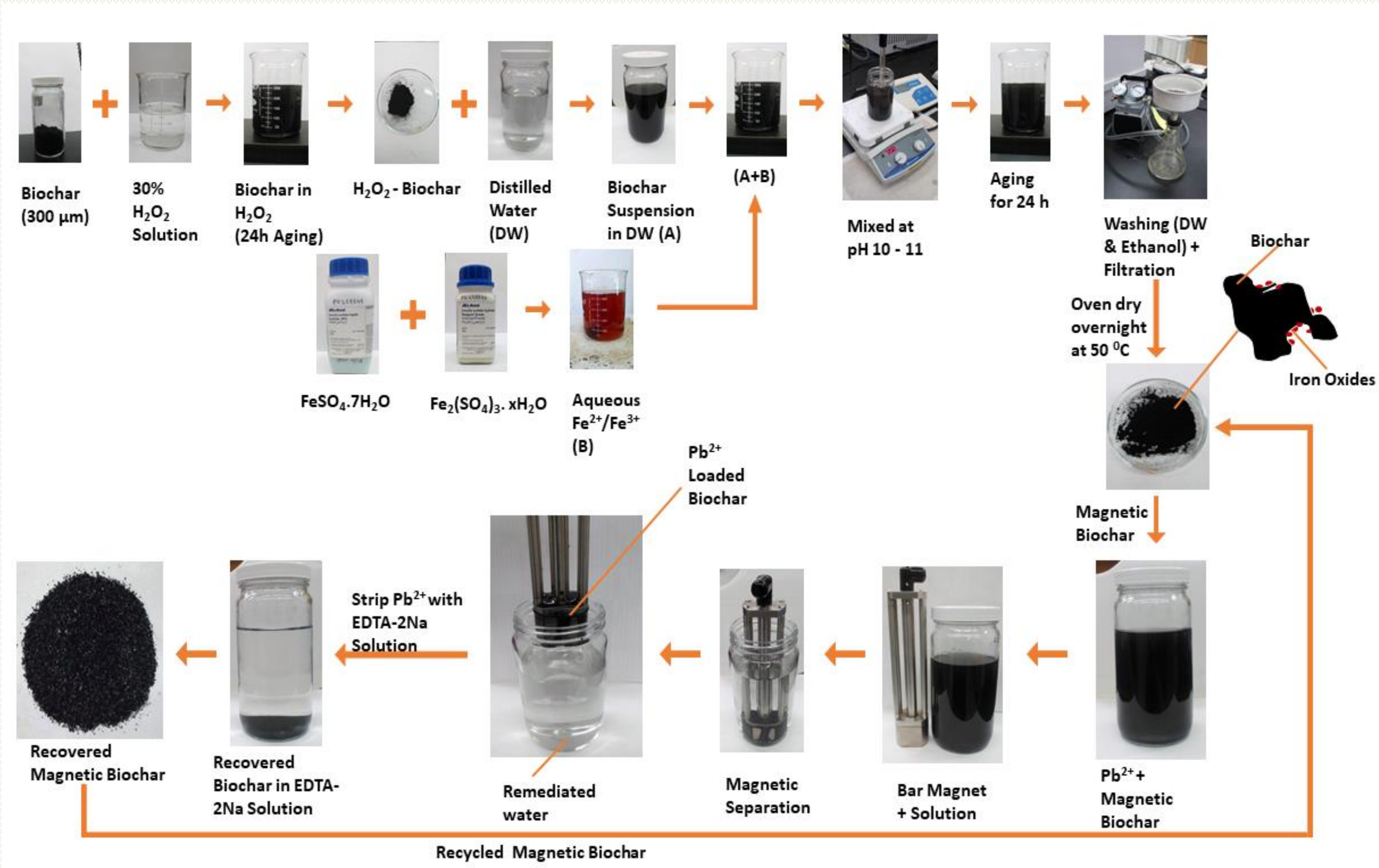
H_2O_2 Impregnation

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

Magnetic modification

- Introduces Fe oxides
- Enhances ease of separation

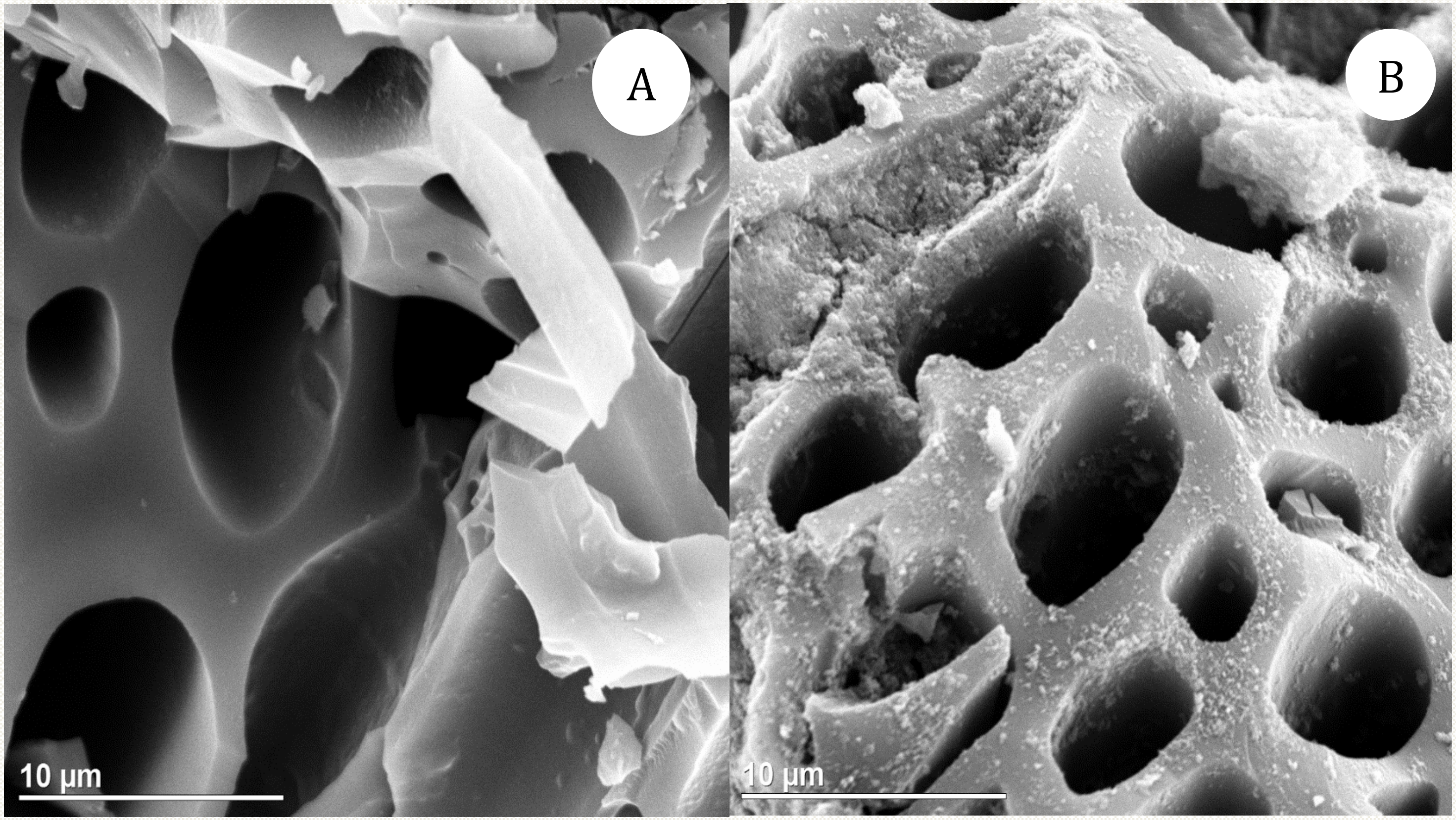
Biochar Modification



[3] Mohan D, Kumar H, Sarswat A, Alexandre-Franco M, Pittman CU. Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars. Chem Eng J. 2014;

Results and Discussion

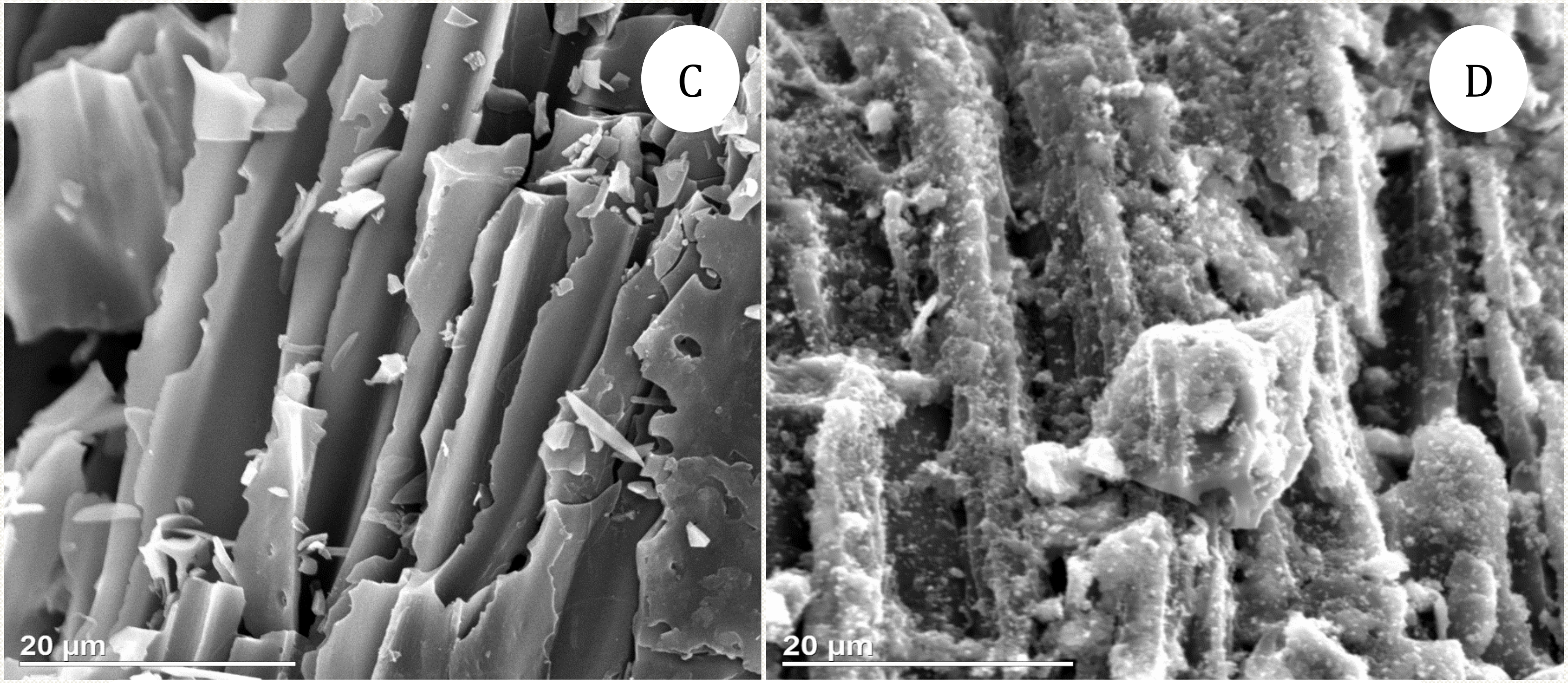
Characterizations SEM



Unmodified maple BC (A), Magnetically modified maple BC (B)

Results and Discussion

Characterizations SEM

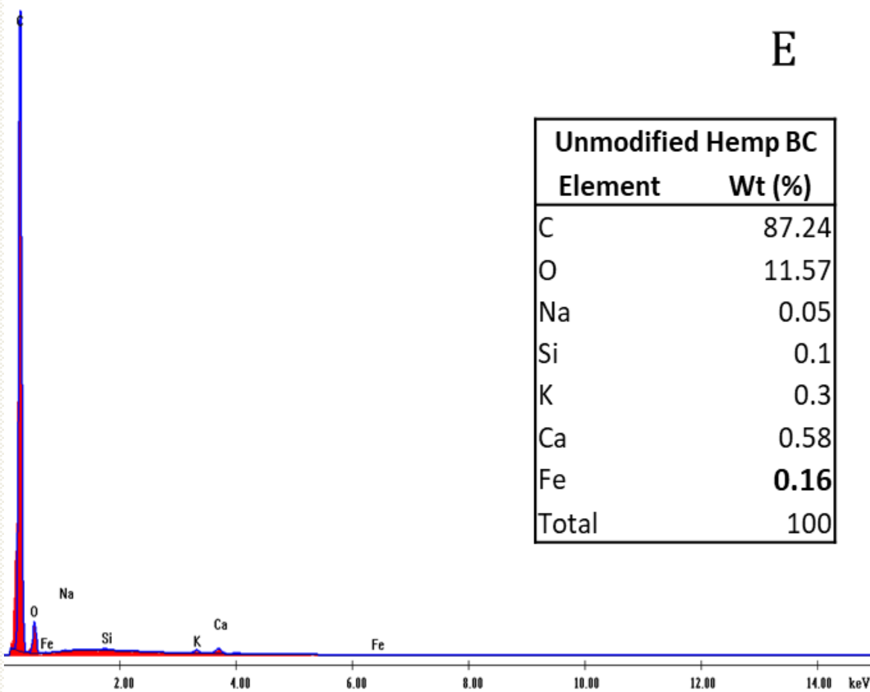


Unmodified Hemp BC (C), Magnetically modified Hemp BC (D)

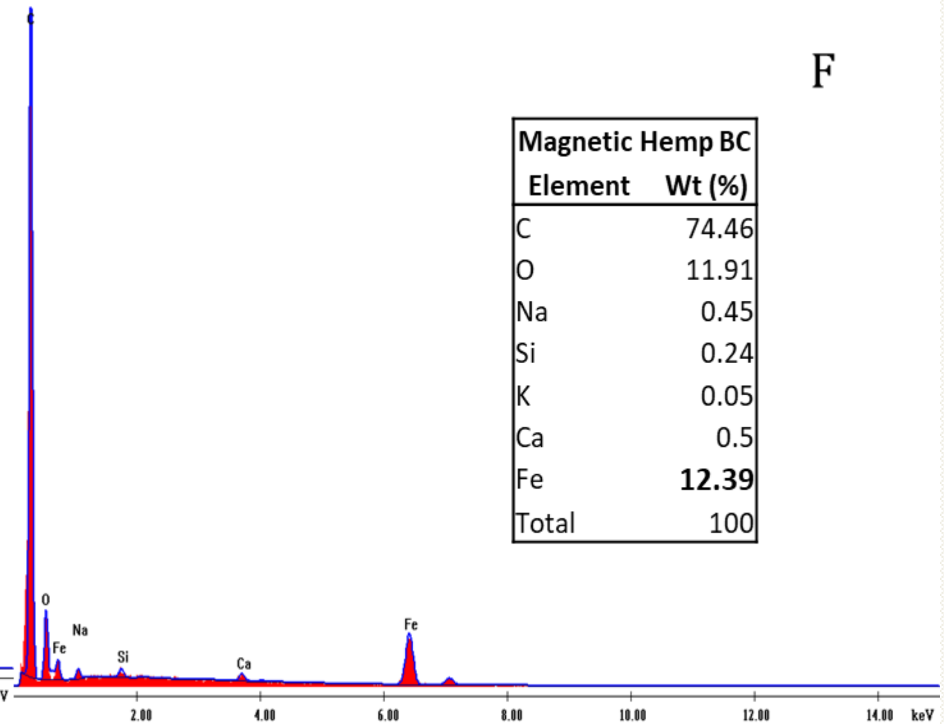
- Hairy like particles on BC surfaces physically confirms successful Fe loading

Results and Discussion

Characterizations EDX



Unmodified Hemp BC	
Element	**Wt (%)**
C	87.24
O	11.57
Na	0.05
Si	0.1
K	0.3
Ca	0.58
Fe	**0.16**
Total	100

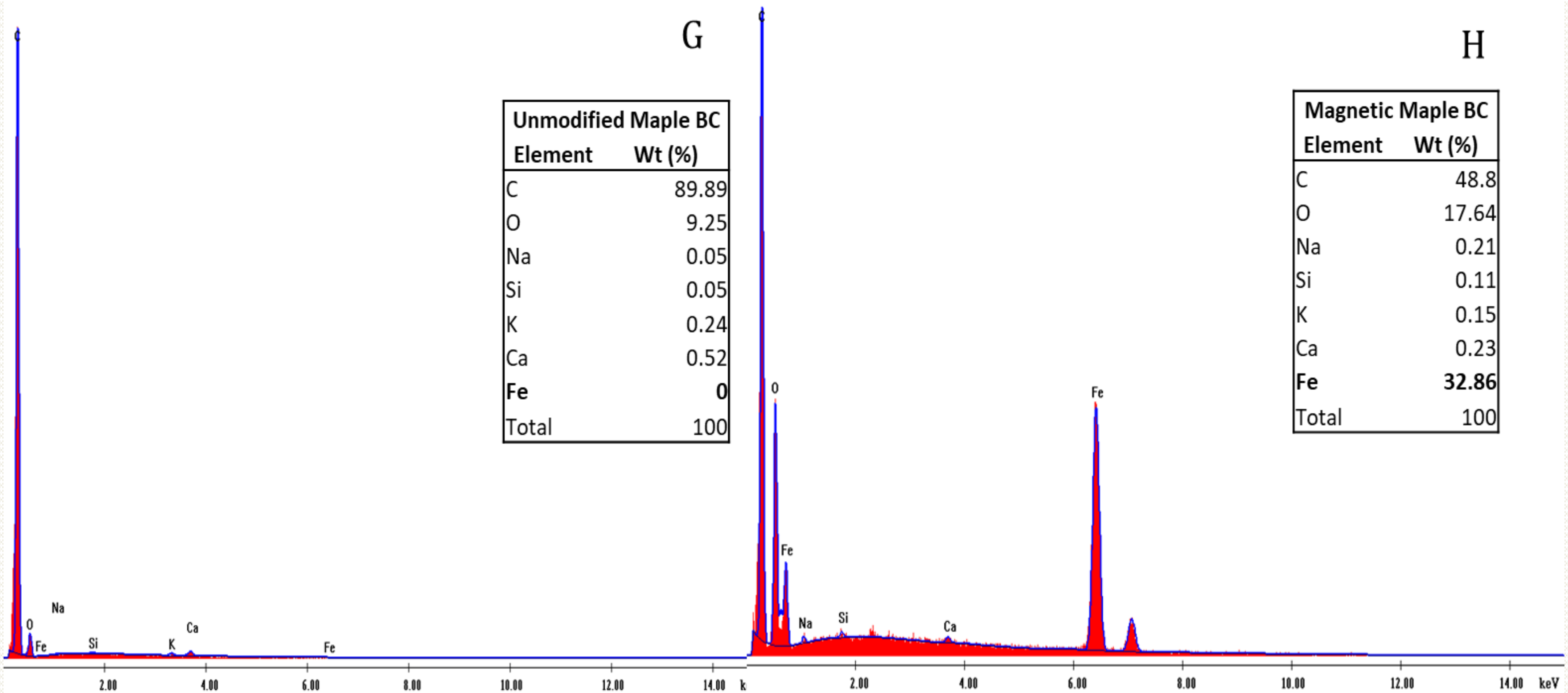


Magnetic Hemp BC	
Element	**Wt (%)**
C	74.46
O	11.91
Na	0.45
Si	0.24
K	0.05
Ca	0.5
Fe	**12.39**
Total	100

- Percent weight of Fe on Hemp BC increased from 0.16 to 12.39. Fe loading confirmed.

Results and Discussion

Characterizations EDX



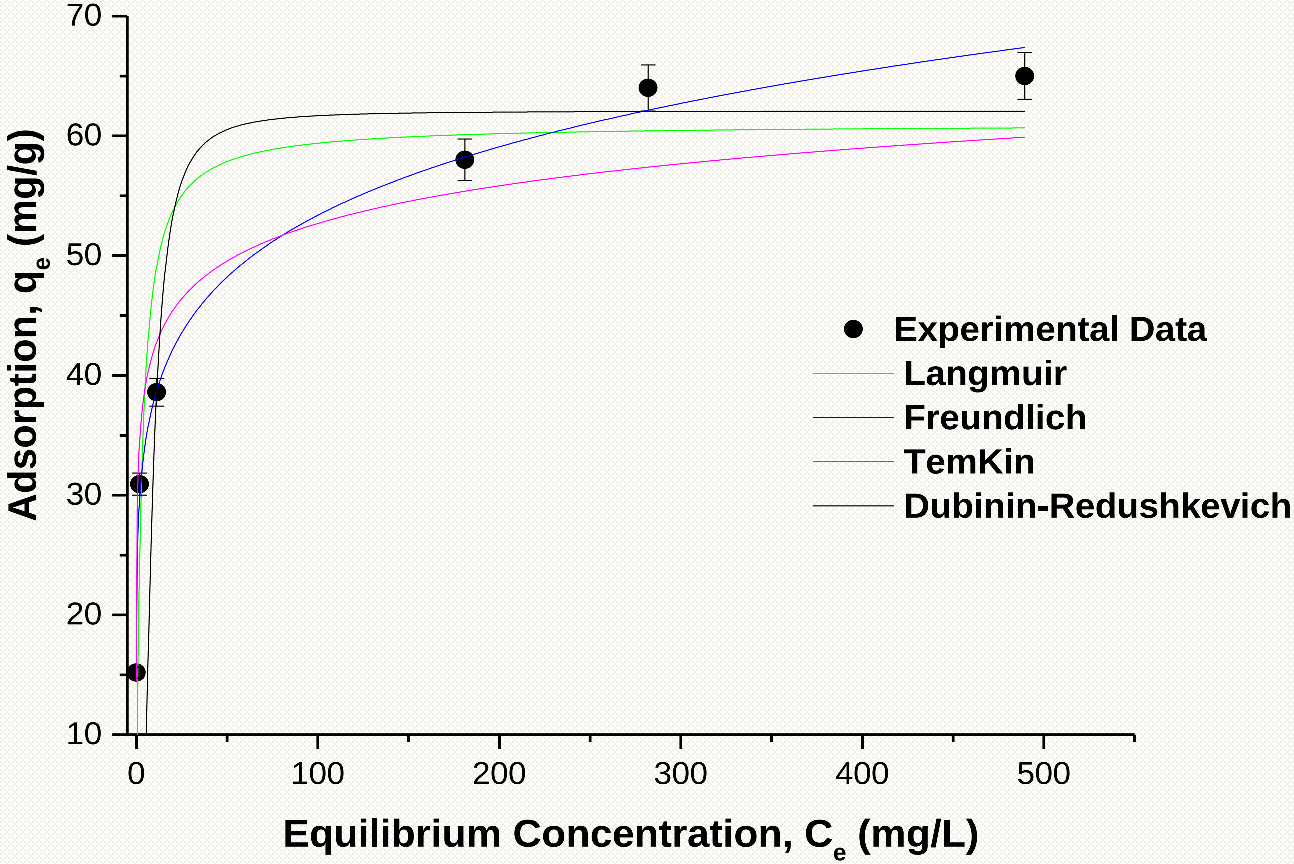
Unmodified Maple BC	
Element	Wt (%)
C	89.89
O	9.25
Na	0.05
Si	0.05
K	0.24
Ca	0.52
Fe	**0**
Total	100

Magnetic Maple BC	
Element	Wt (%)
C	48.8
O	17.64
Na	0.21
Si	0.11
K	0.15
Ca	0.23
Fe	**32.86**
Total	100

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

Results and Discussion

Adsorption Isotherm – Magnetic Hemp Biochar

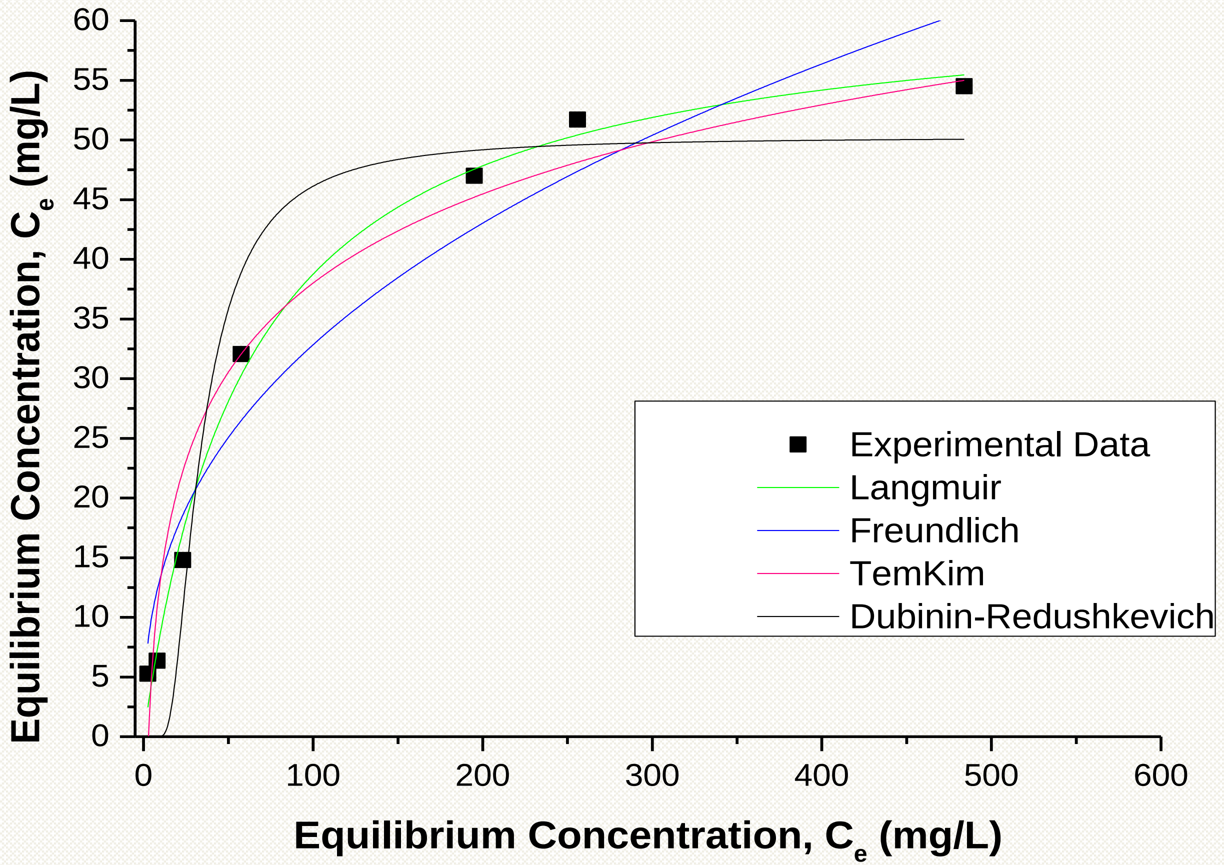


- Freundlich model has the best fit
- $R^2 = 0.997$
- Heterogeneous adsorption surface and active sites of biochar

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

Results and Discussion

Adsorption Isotherm – Magnetic Maple Biochar

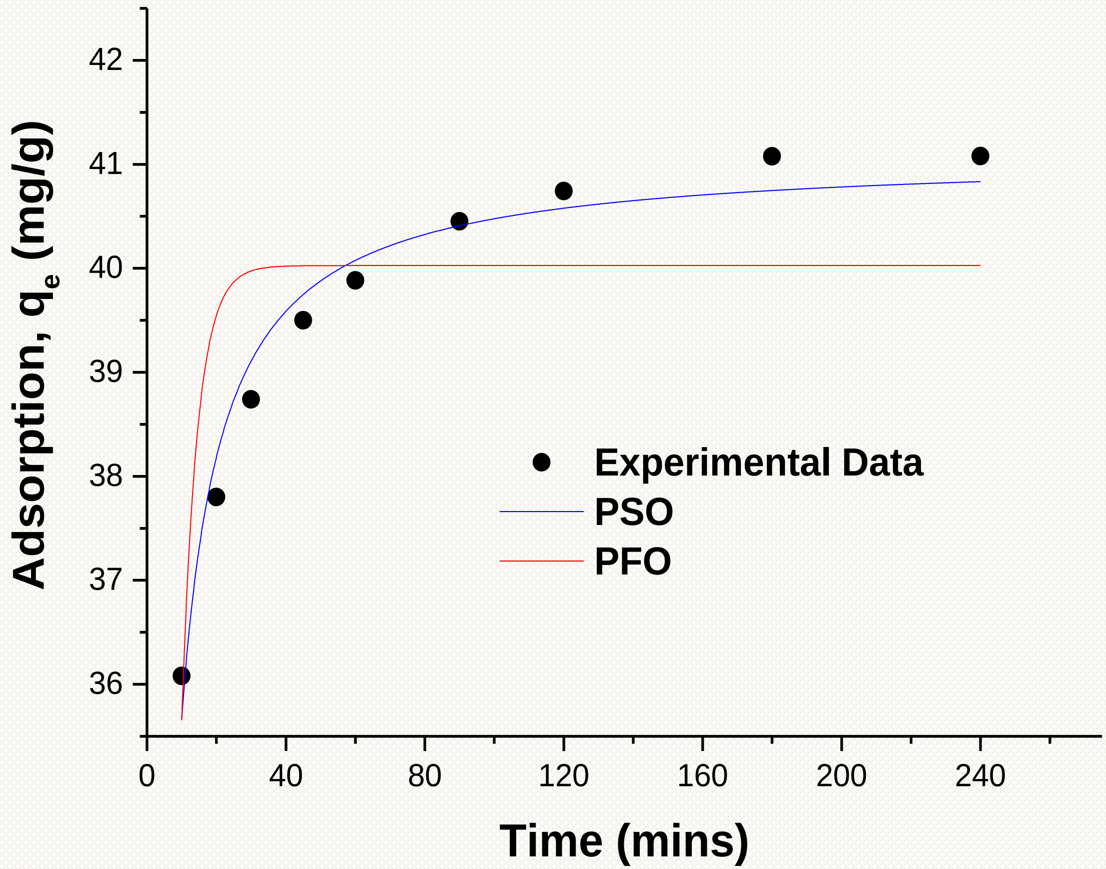


- **Langmuir model has the best fit**
- **$R^2 = 0.993$**
- **Sorption occur at active sites uniformly distributed on biochar surface**

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

Results and Discussion

Adsorption Kinetics – Magnetic Hemp Biochar

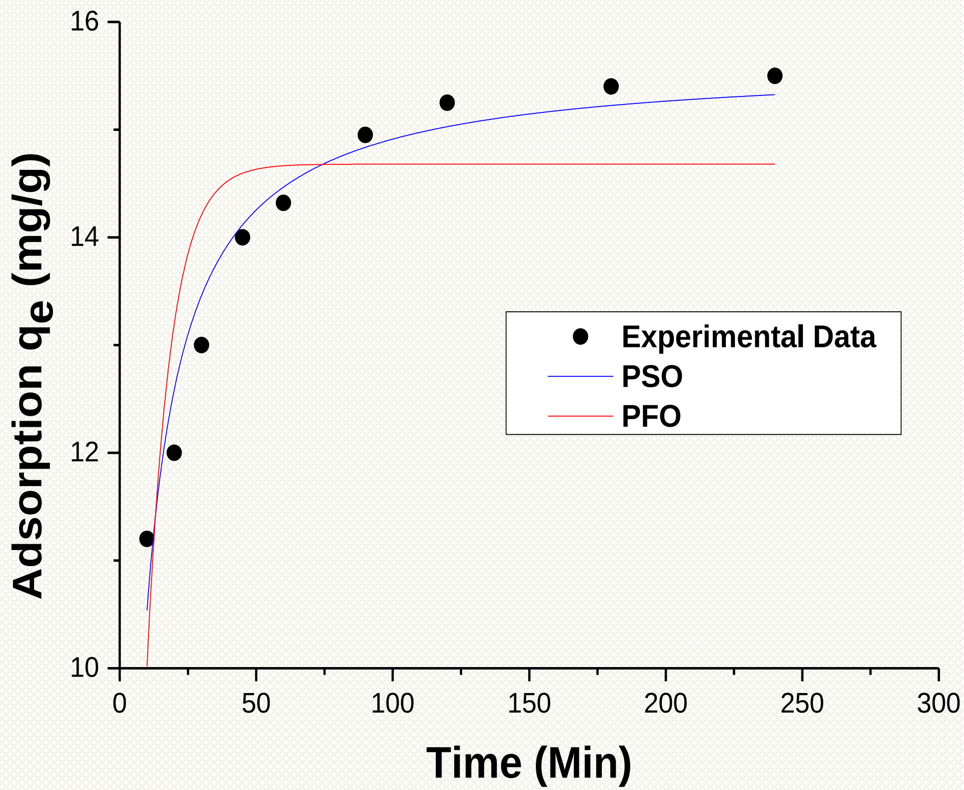


- Pseudo-second order model fits better
- $R^2 = 0.962$
- Pb^{2+} ions removed by chemisorption

Results and Discussion

UNB

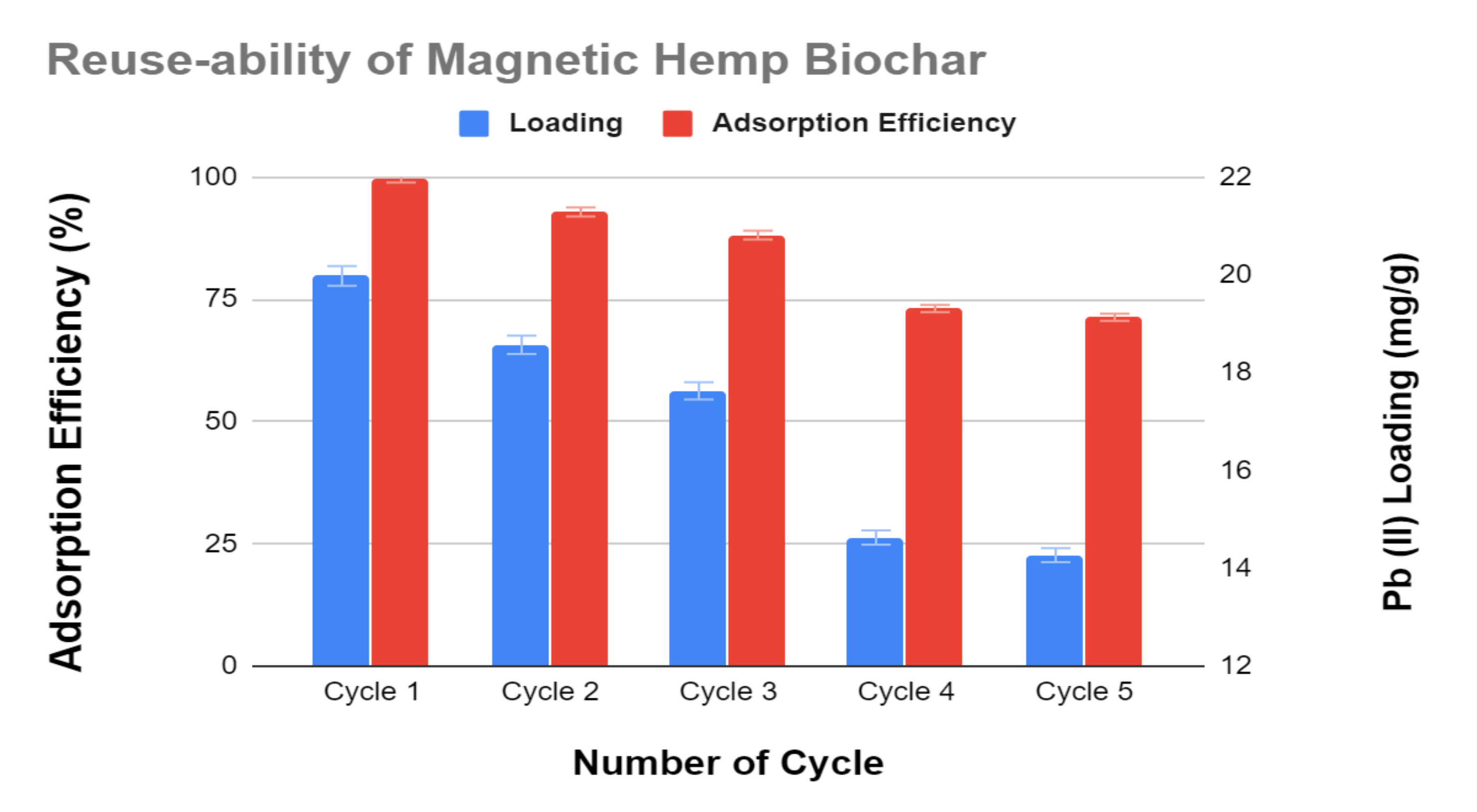
Adsorption Kinetics – Magnetic Maple Biochar



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

Results and Discussion

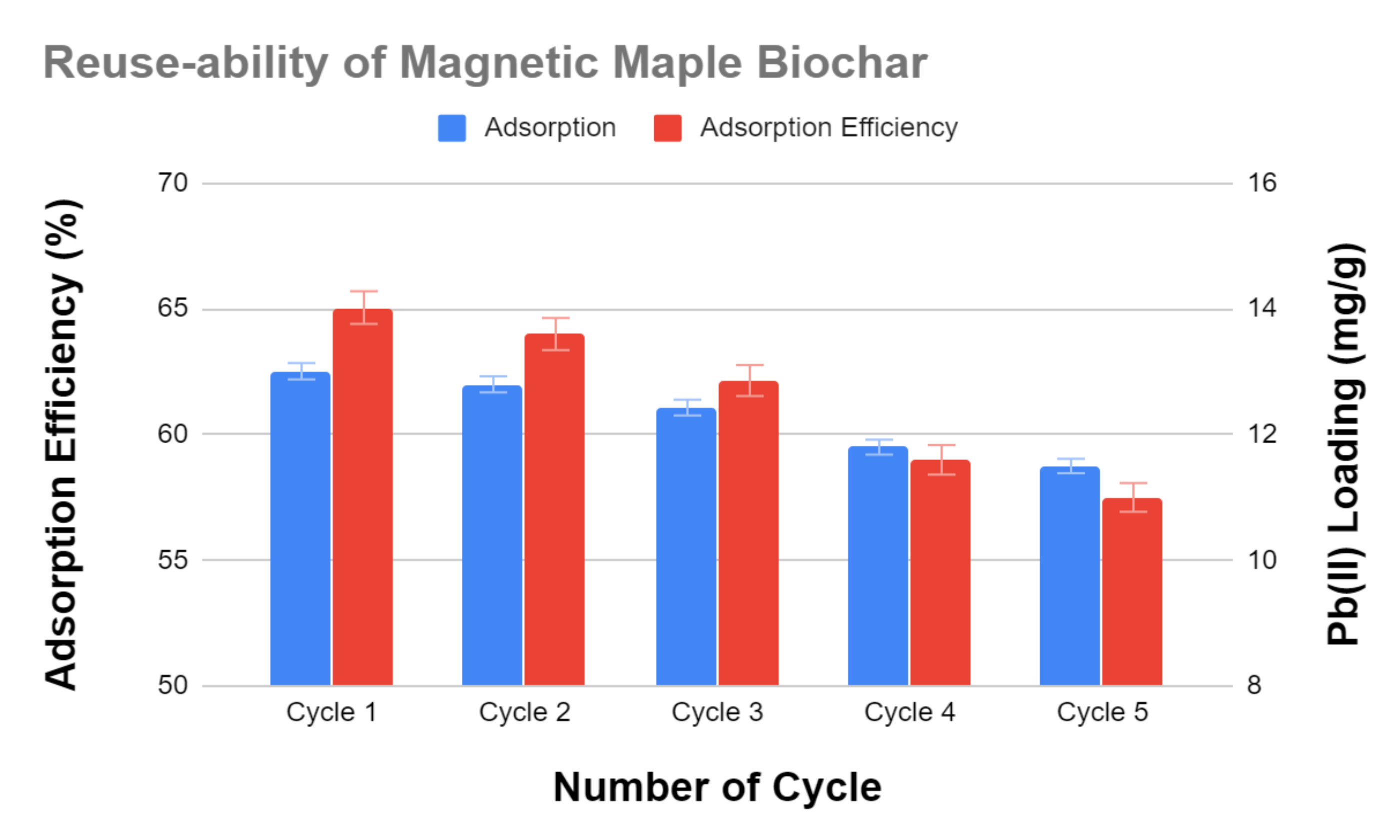
Desorption Study – Magnetic Hemp Biochar



- 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

UNB

- 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 adsorpttion

↓

Clean water

Acknowledgements

THANK YOU!

mafzal@unb.ca