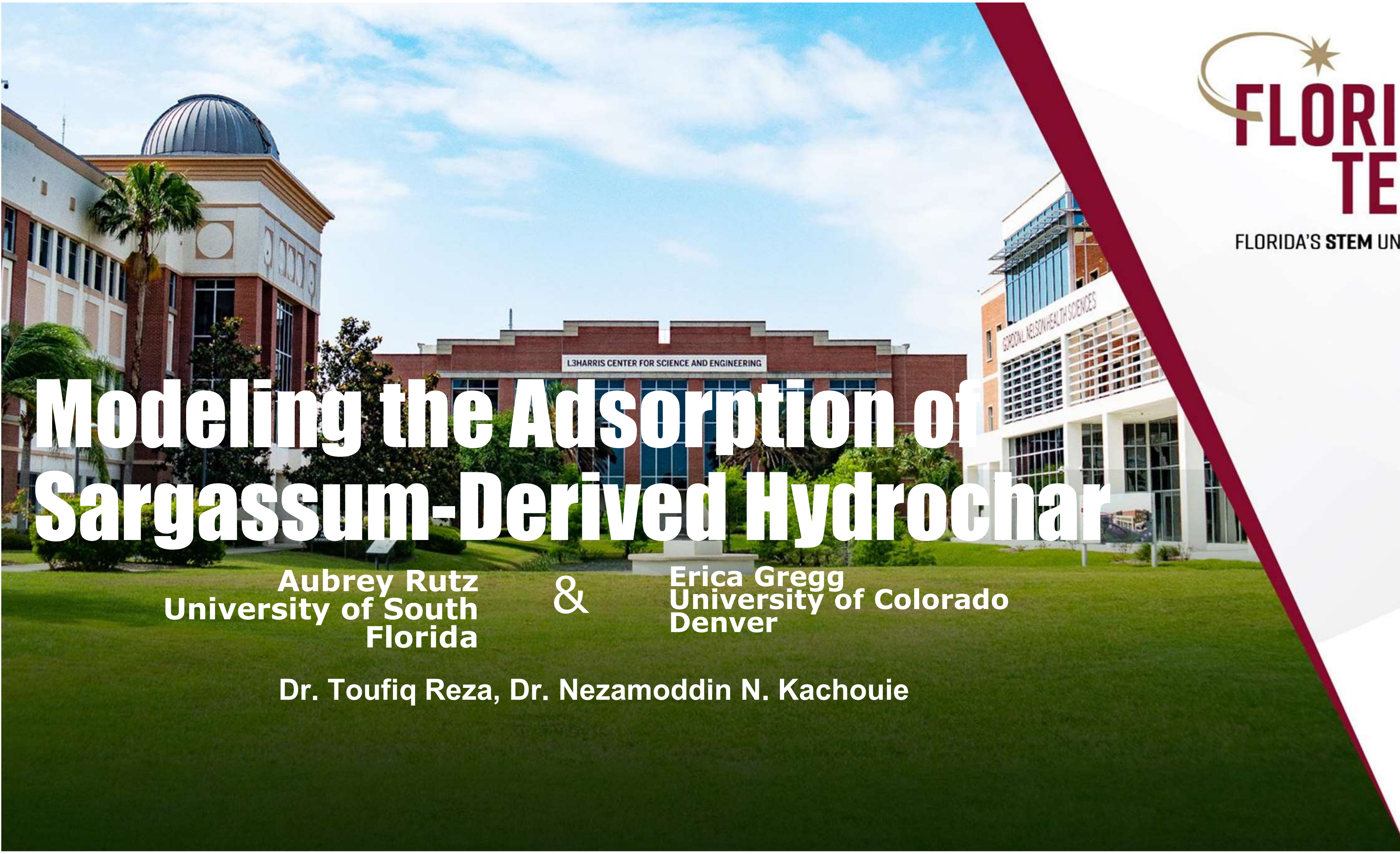

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Modeling the Adsorption of Sargassum-Derived Hydrochar

Aubrey Rutz
University of South Florida

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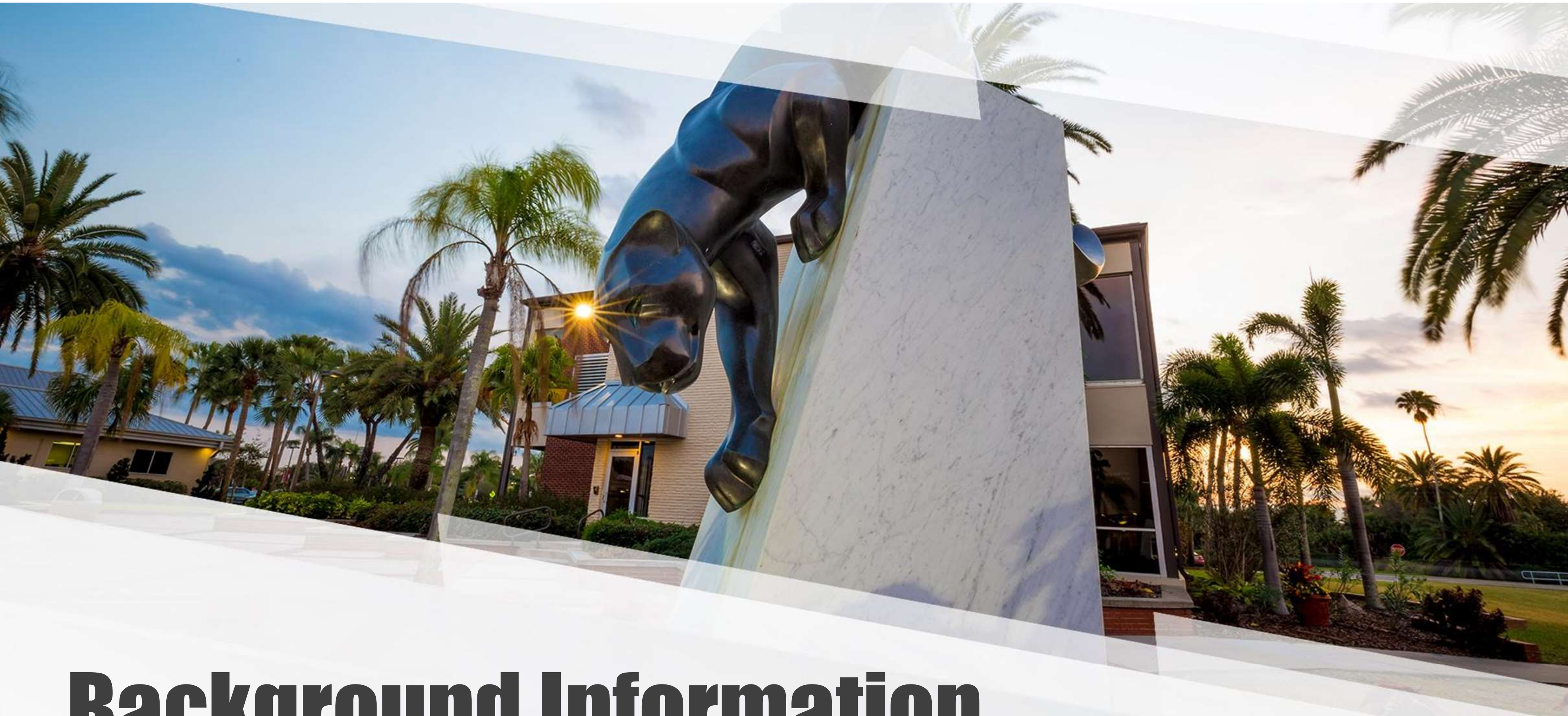
Dr. Toufiq Reza, Dr. Nezamoddin N. Kachouie



Background Information

Algal Blooms

- Overgrowth of algae or cyanobacteria
- Climate change (& human influence)
- Harmful algal blooms are just one type
- Methylene blue dye (MB) as a proxy for toxins

Credits of Image to FAU (1)

Sargassum Seaweed

- Brown algae: FL, Gulf of Mexico, Caribbean
- Natural role of habitat, reducing erosion

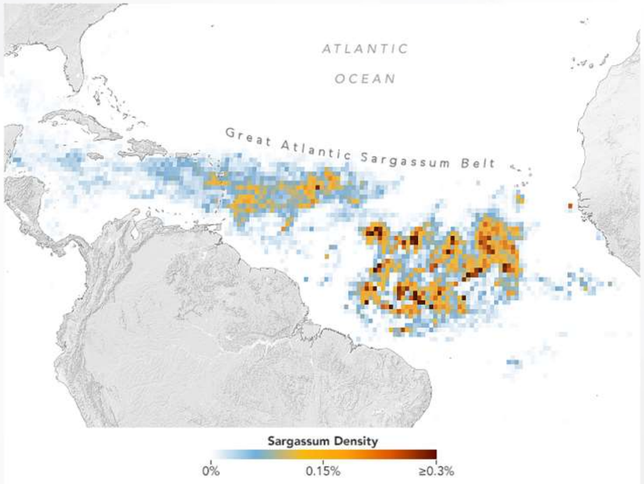

Credits of Image to New York Post (3)


Credits of Image to Franziska Elmer (2)

(NOAA, 2023; “What is Sargassum?” n.d.)

Why Sargassum?

- Readily available
- Essentially untouched as a resource
- Potential as an adsorbent in water treatment



Credits of Image to NASA (4)

(NASA, 2023)

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Sargassum-Derived Hydrochar

Hydrochar (HC)

- A cooked biomass that has undergone hydrothermal carbonization (HTC)
- Ground into a fine powder

Hydrochar Adsorption

Hydrochar (HC)

- **Adsorption** = particles stick to surface
- **Absorption** = substance absorbs (enters) another

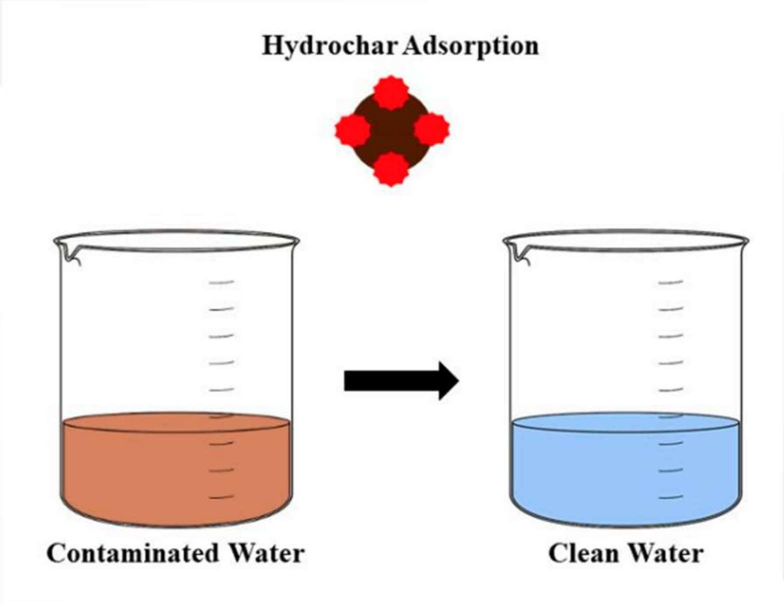
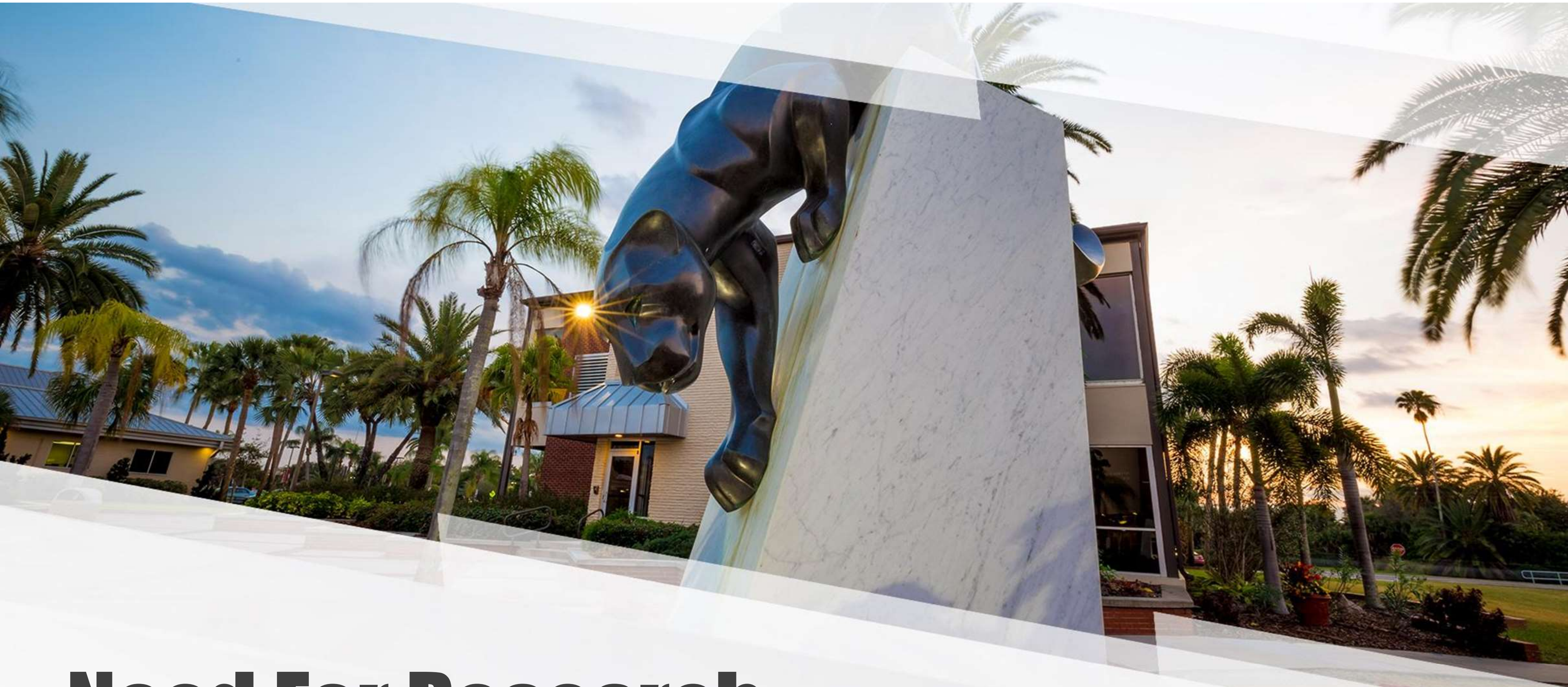


Image Credit to Tahmid Islam (5)



Need For Research

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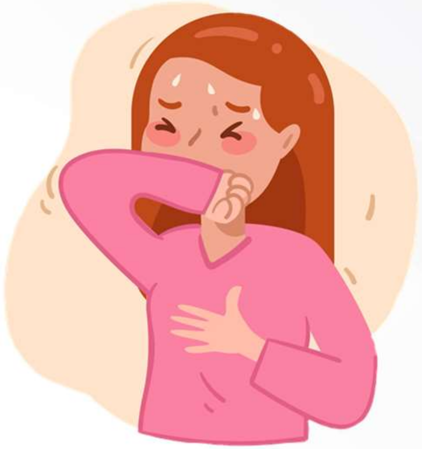
Algal Blooms

Harmful Algal Blooms (HABs) pose a threat to three main categories:

Human Health



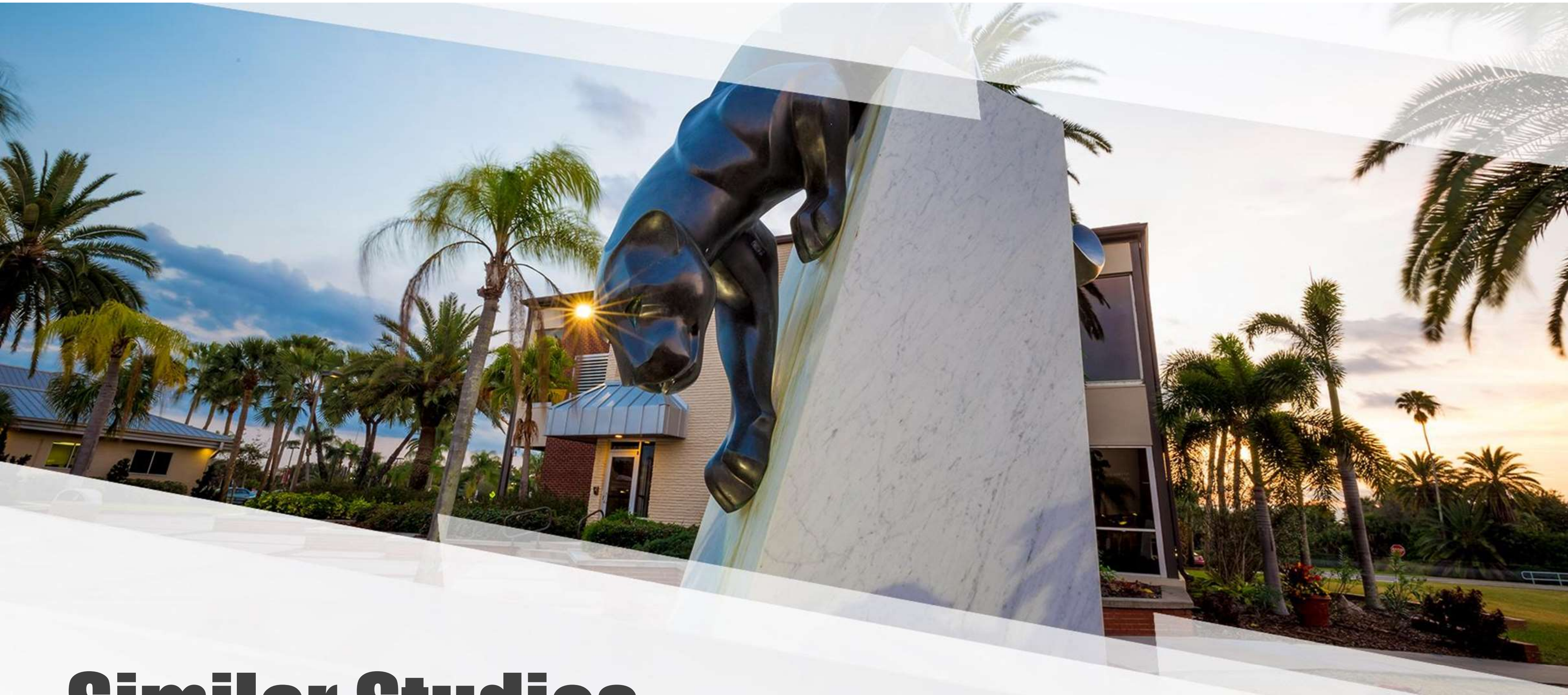
Environmental Health

Image Credit to Ben Depp (6)

Economic Health

Image Credit to Fox 13 (7)

(Heil & Muni-Morgan, 2021)



Similar Studies

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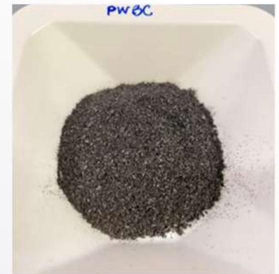
Similar Studies

- 2016 study on pig manure, pine wood, and cardboard-derived adsorbents with MB dye
- 2023 study on sargassum-derived superactivated hydrochar with MB dye



Pine wood adsorbent

Image Credit to Marta Rossi (8)

Image Credit to Cadianne Chambers (9)

(Lonappan et al., 2016; Chambers, 2023)

Gap In Academia

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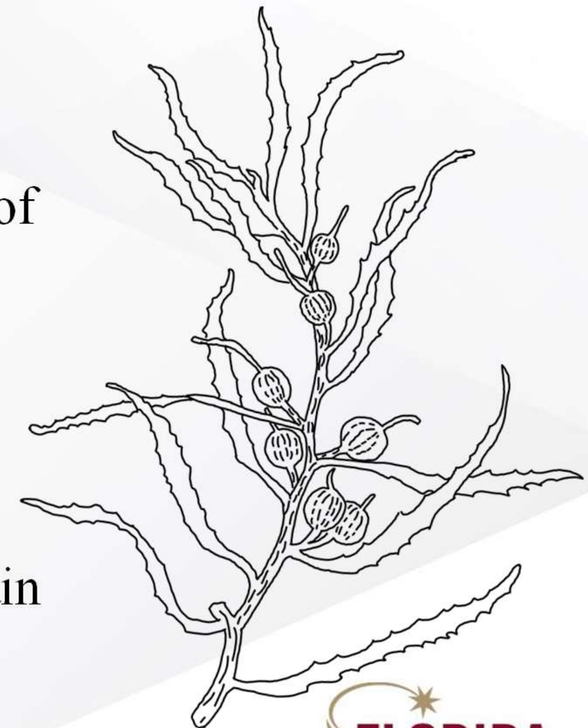
Gap In Academia

- Sargassum by itself not fully explored
- Lack of study about the singular potentiality of sargassum itself
    - Increased production efficiency
- Circle of renewability and environmental chain



Focal Of This Study

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Focus Of The Study

1: Determine the adsorption capability of sargassum-derived hydrochar on methylene blue (MB) dye.

2: Discover the significance of sargassum-derived hydrochar’s synthesis parameters.

HTC Temperature

HTC Time

HTC Sargassum:Water Ratio

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Research Questions

1. Which tested HTC treatment variation of sargassum-derived hydrochar has the highest adsorbance capability of methylene blue dye?
2. What is the significance of the different parameters in the HTC treatment against methylene blue dye removal?

Methodology

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Schematics

Experimental Design → Conduct Experiments → Data Collection → Data Analysis & Modeling

Taguchi Method

1. Prep seaweed
2. HTC (Cook) seaweed
3. Process hydrochar
4. Hydrochar + MB

5. Absorbance Reading

Timeline

1. Prep seaweed
2. HTC (Cook) seaweed
3. Process hydrochar
4. Hydrochar + MB
5. Absorbance reading

2-4 hrs Prep Seaweed for HTC — 1-2 hrs HTC (Cook) — 24 hrs Oven Drying

1 hr Grind HC Into Fine Powder — 24 hrs Oven Drying — 24 hrs Allow for Adsorption

Total Duration: ~75 hours per data point

Experimental Design

Experimental Parameters

In hydrochar creation:

HTC Temperature – 180°C, 220°C, 260°C

HTC Time – 15 min, 30 min, 60 min

HTC Sargassum:Water **Ratio** – 1:10, 1:15, 1:20

Parr reactor

Experimental Design

Taguchi Method

- Taguchi method is used for product experimentation
- It's focus lies in optimization of the product and experimentation
  - Cut down 27 experiments to 9
- Allows for experimentation of a variety of different degrees of parameters

(Krishnaiah, 2012; Karna & Sahai, 2012)

Taguchi Method

Experimental Design

Experiment #	HTC Temp (C)	HTC Time (Minutes)	Water Ratio
1	180°	15	1:10
2	180°	30	1:20
3	180°	60	1:15
4	220°	15	1:20
5	220°	30	1:15
6	220°	60	1:10
7	260°	15	1:15
8	260°	30	1:10
9	260°	60	1:20

Experiments

Materials

<u>Machines:</u>

- Parr Reactor
- Tube Revolver
- Spectrophotometer

<u>Substances:</u>

- Sargassum Seaweed
- Sargassum-derived Hydrochar
- Methylene Blue

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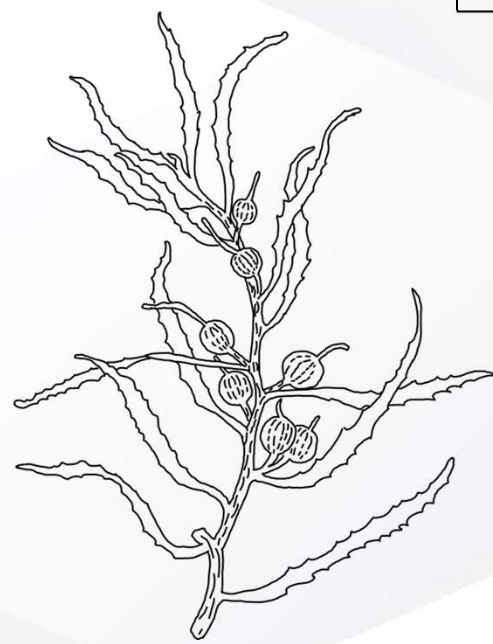
Seaweed Preparation

Conduct Experiments

1. Prep seaweed
2. HTC (Cook) seaweed
3. Process hydrochar
4. Hydrochar + MB
5. Absorbance reading

- Collected from beach
- Washed with water
- Frozen
- Thawed
- Chopped for Parr reactor suitability



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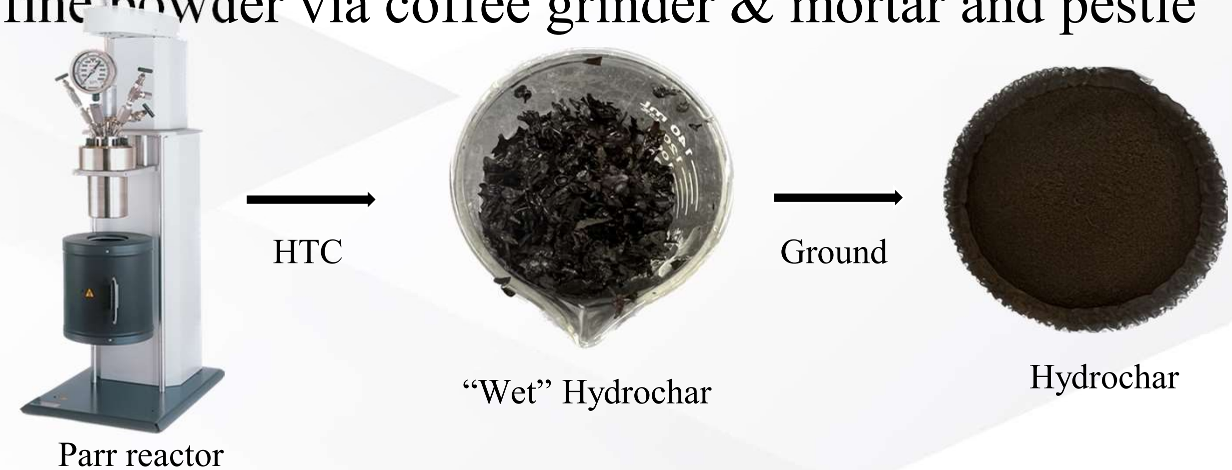
Conduct Experiments

1. Prep seaweed
2. HTC (Cook) seaweed
3. Process hydrochar
4. Hydrochar + MB
5. Absorbance reading

HTC

Hydrochar (HC)

- A cooked biomass that has undergone hydrothermal carbonization (HTC)
- Ground into a fine powder via coffee grinder & mortar and pestle



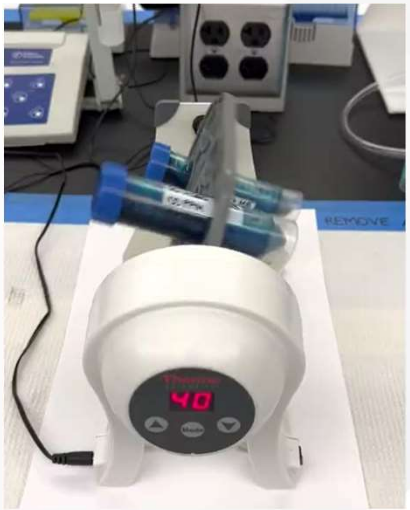
Conduct Experiments

1. Prep seaweed
2. HTC (Cook) seaweed
3. Process hydrochar
4. Hydrochar + MB
5. Absorbance reading

Treatment

- Taking chosen hydrochar variation and mixing it with 100 ppm dye
- Left to adsorb for 24 hrs (in revolver for even mixing)
- Hydrochar filtered out

Before
(30 mg Hydrochar + 30mL dye)



24 hours

(H260 t30 1:10)

Absorbance Reading

Conduct Experiments

1. Prep seaweed
2. HTC (Cook) seaweed
3. Process hydrochar
4. Hydrochar + MB
5. Absorbance reading

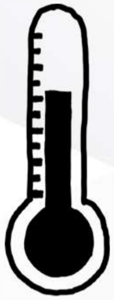
After HC has had 24 hours to adsorb the MB dye,

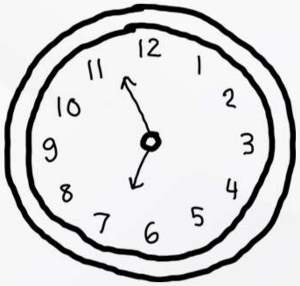
we read final absorbance to obtain percentage removal of the MB.

Varying & Increased Concentration

<u>Varying Concentration:</u>

- Testing the highest performing HC against higher MB concentrations– 150, 200, 250, and 300 ppm.
- A higher concentration is picked for further experimentation





<u>Increased Concentration:</u>

- The 300 ppm MB tested against all HCs
- Same experimental design as 100 ppm

Results

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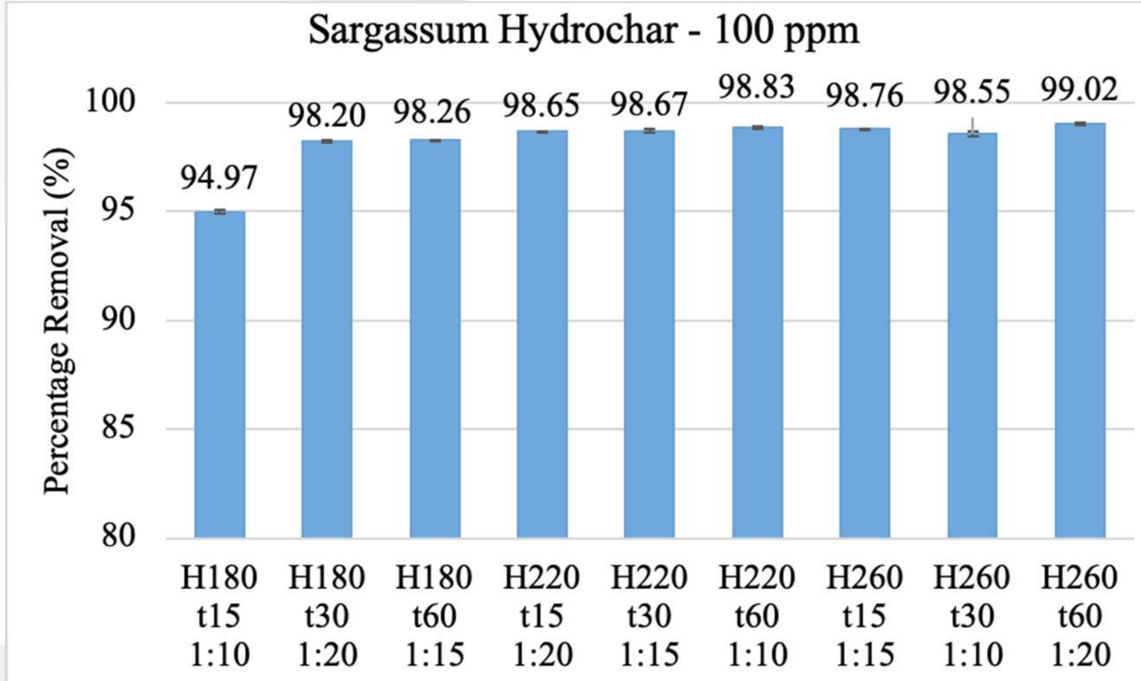
100 PPM

X-Axis Labeling Key:
H : Temperature (°C)
t : duration (minutes)
sargassum:water



- All perform sufficiently
- Best Performing:
  - H260 t60 1:20
- Worst Performing:
  - H180 t15 1:10
- Green hue by leaching

100 ppm Dye

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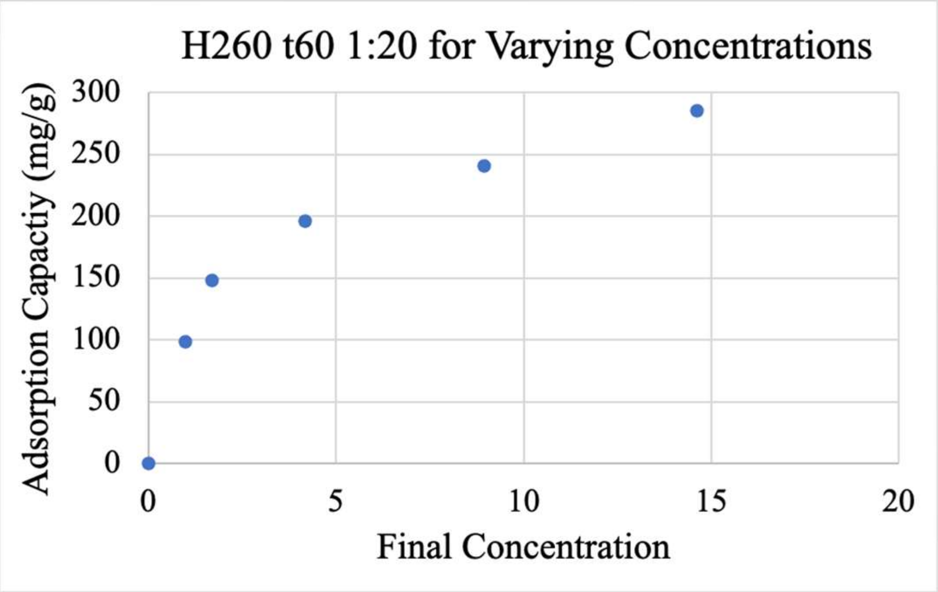
Varying Concentration Test

Concentration (ppm)	Percentage Removal (%)
100	99.02 ± 0.05
150	98.86
200	97.92
250	96.43
300	95.13



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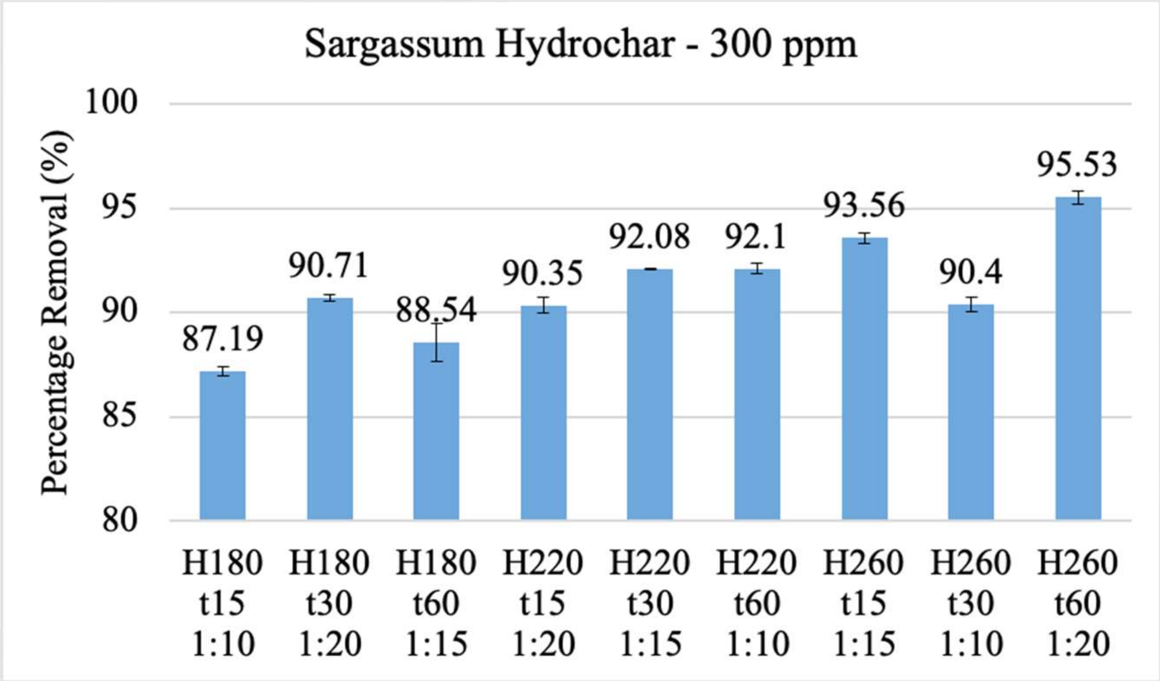
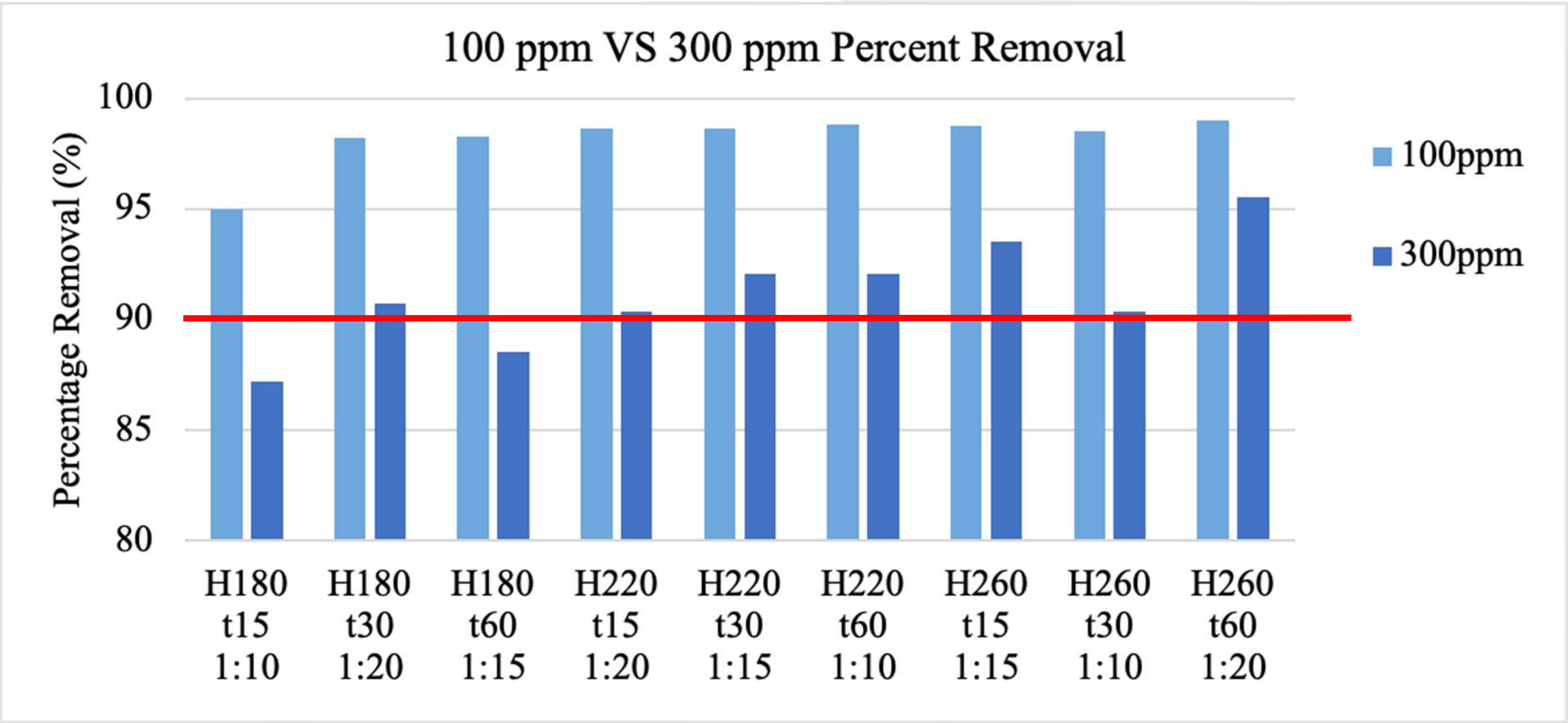
300 PPM

X-Axis Labeling Key:
H : Temperature (°C)
t : Duration (minutes)
Sargassum:Water

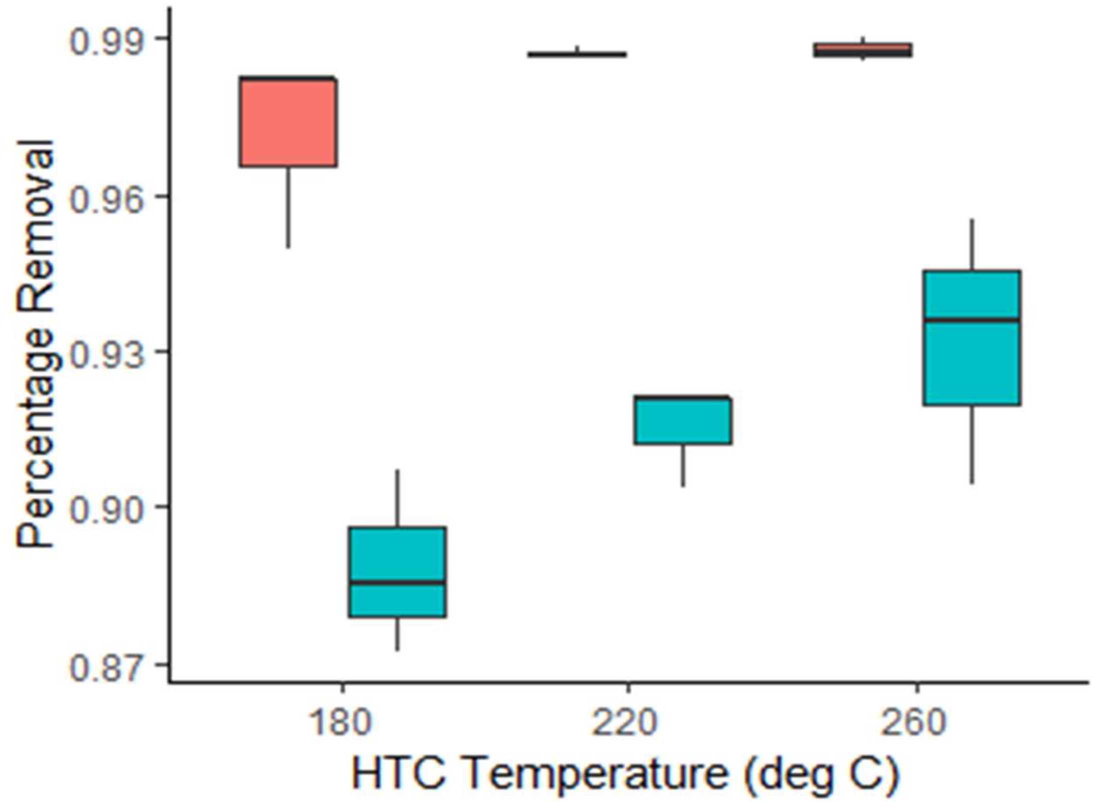
- Best Performing:
    - H260 t60 1:20
- Worst Performing:
    - H180 t15 1:10
- Similar trends as 100 ppm



100 ppm Vs. 300 ppm



Box Plot: HTC Temperature



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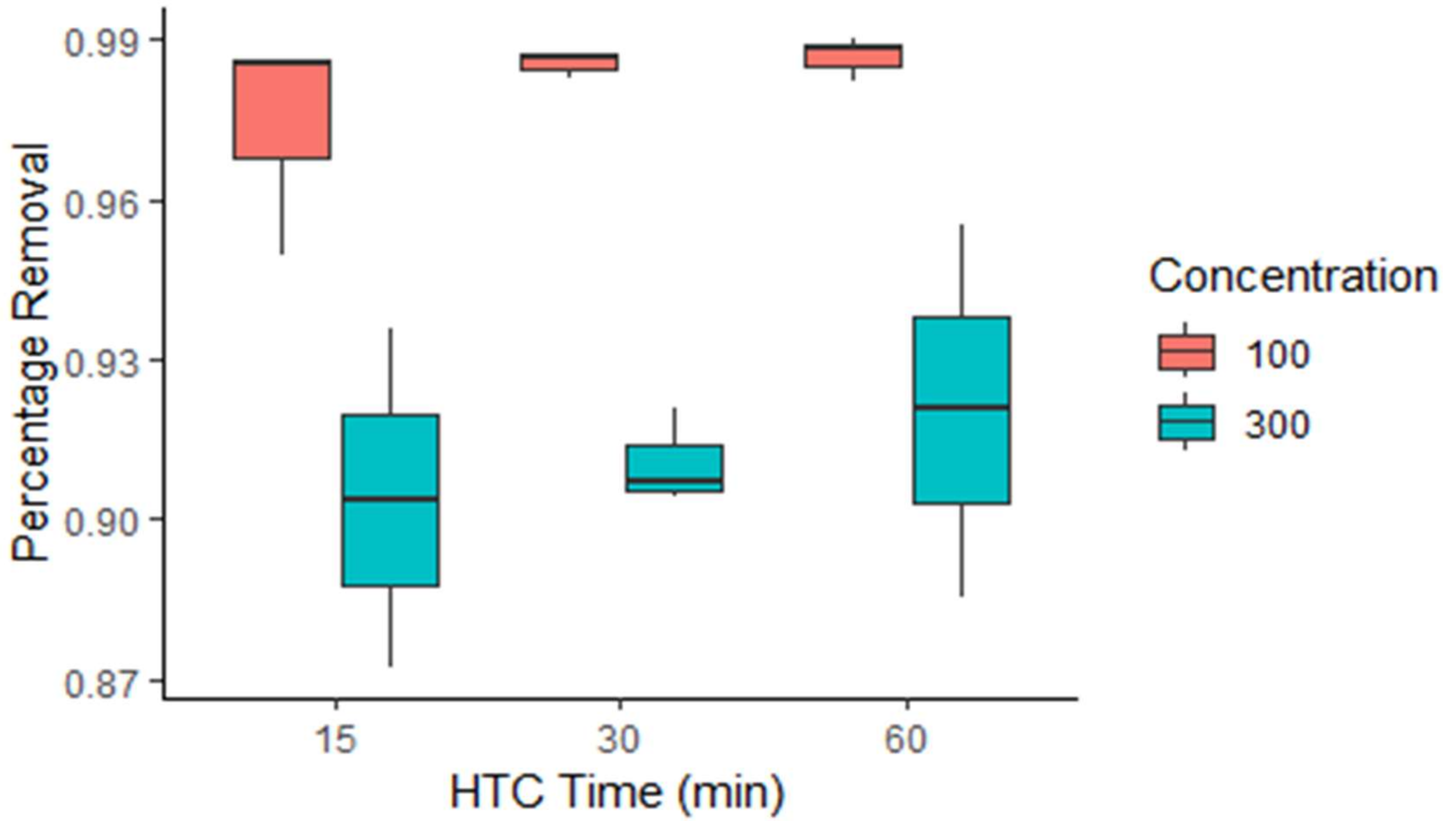
Box Plot: HTC Time



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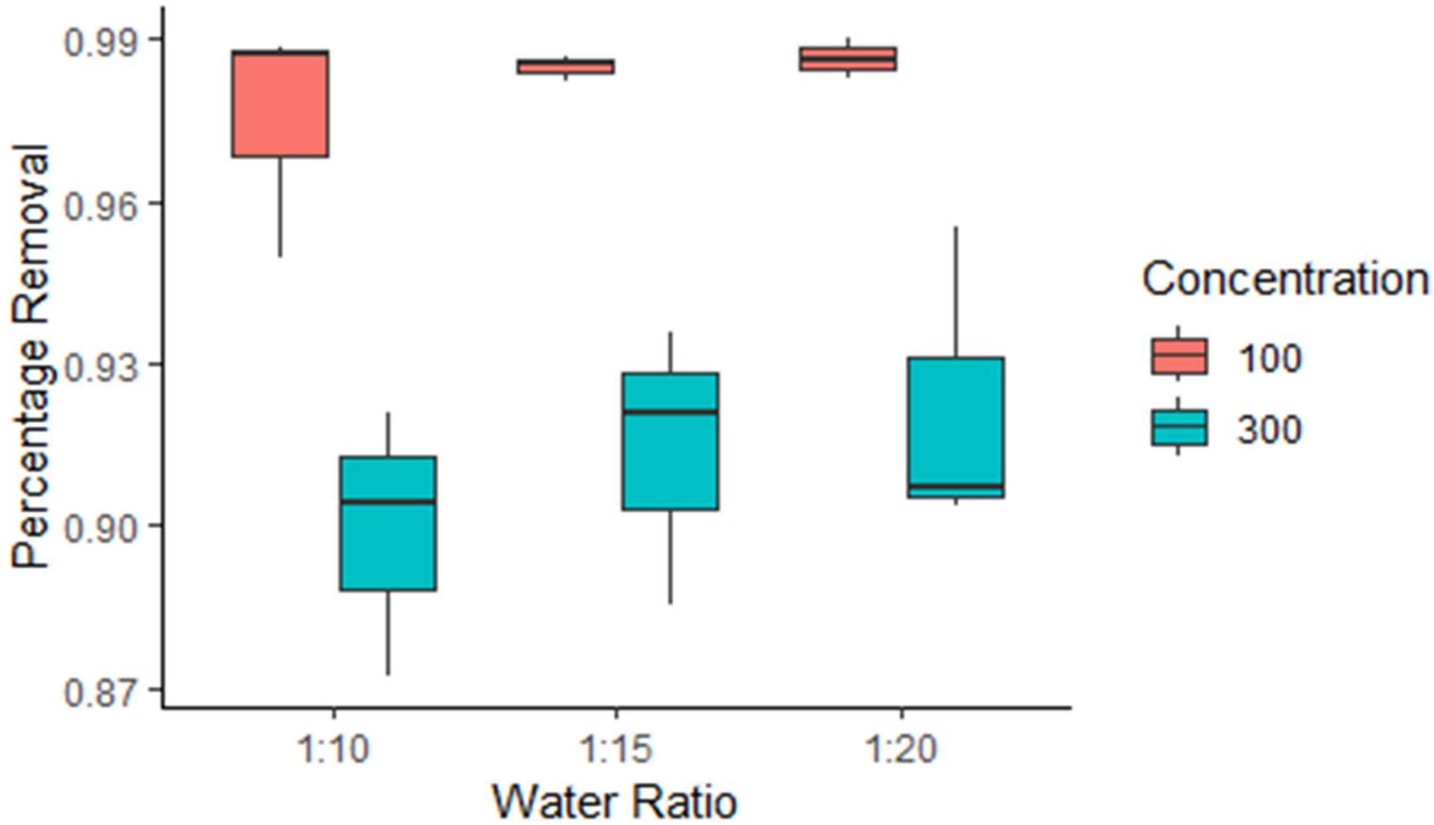
Box Plot: Sargassum-to-Water Ratio



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Modeling

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Modeling

Cauchit Link Function

$$g(u) = tan(\pi(u - \frac{1}{2}))$$

- Beta regression
  - Discover if and how the parameters affect percentage r
  - Utilized for bounded response variables between 0 and 1
  - Link functions: $[0,1] \rightarrow \mathbb{R}$
  - Pseudo R-squared & AIC measure fit of the model to the data
- Modeling three datasets:
  - 100 ppm, 300 ppm, Combined dataset

Goal:
Higher R-squared & Lower AIC

(Ferrari & Cribari-Neto, 2004)

Predictors: HTC Temperature | HTC Time | Sargassum:Water Ratio

Beta Regression Model:

Model:

$$g(\mu_i) = \beta_0 + \beta_1(temperature) + \beta_2(time) + \beta_2(ratio)$$

Response: $\mu_i =$ Percentage Removal

100 ppm *All Variables*

P Value < 0.05 = **Significant**

3 Variable ***Continuous*** Model:

Variable	Coef. Estimate	P-Value
Intercept	-32.59148	8.17e-16
Temperature	0.19762	< 2e-16
Time	0.22226	1.72e-08
Water Ratio 1:15	2.60562	0.117
Water Ratio 1:20	8.24170	8.86e-09
Pseudo R-Squared: 0.8615 AIC: -79.2611		

3 Variable ***Categorical*** Model:

Variable	Coef. Estimate	P-Value
Intercept	6.28999	< 2e-16
Temperature 220	10.89503	< 2e-16
Temperature 260	13.30246	< 2e-16
Time 30	5.67935	< 2e-16
Time 60	9.28842	< 2e-16
Water Ratio 1:15	1.95730	1.38e-05
Water Ratio 1:20	6.07861	< 2e-16
Pseudo R-Squared: 0.9867 & AIC: -99.4049		

P Value < 0.05 = **Significant**

300 ppm *All Variables*

3 Variable ***Continuous*** Model:

Variable	Coef. Estimate	P-Value
Intercept	-2.023726	0.0824
Temperature	0.022521	7.75e-05
Time	0.011621	0.2327
Water Ratio 1:15	0.272150	0.5199
Water Ratio 1:20	0.788053	0.0610
Pseudo R-Squared: 0.7473 & AIC: -41.4058		

3 Variable ***Categorical*** Model:

Variable	Coef. Estimate	P-Value
Intercept	2.21749	1.11e-15
Temperature 220	0.91227	0.02274
Temperature 260	1.79495	0.00024
Time 30	0.02853	0.94873
Time 60	0.49532	0.26701
Water Ratio 1:15	0.32417	0.44974
Water Ratio 1:20	0.87185	0.05646
Pseudo R-Squared: 0.7628 & AIC: -37.5023		

Full Data *Categorical* Model

- Utilizing full data set with categorical factors
  - 18 data points and added 'Concentration' variable

Goal:
Higher R-squared & Lower AIC

P Value < 0.05 = **Significant**

Variable	Coef. Estimate	P-Value
Intercept	1.80668	< 2e-16
Temperature 220	0.18645	2.97e-05
Temperature 260	0.28887	4.57e-10
Time 30	0.06982	0.123625
Time 60	0.14314	0.002028
Water Ratio 1:15	0.09620	0.033797
Water Ratio 1:20	0.16104	0.000499
Concentration 300	-0.75597	< 2e-16
Pseudo R-Squared: 0.9661 & AIC: -110.6173		

Conclusions

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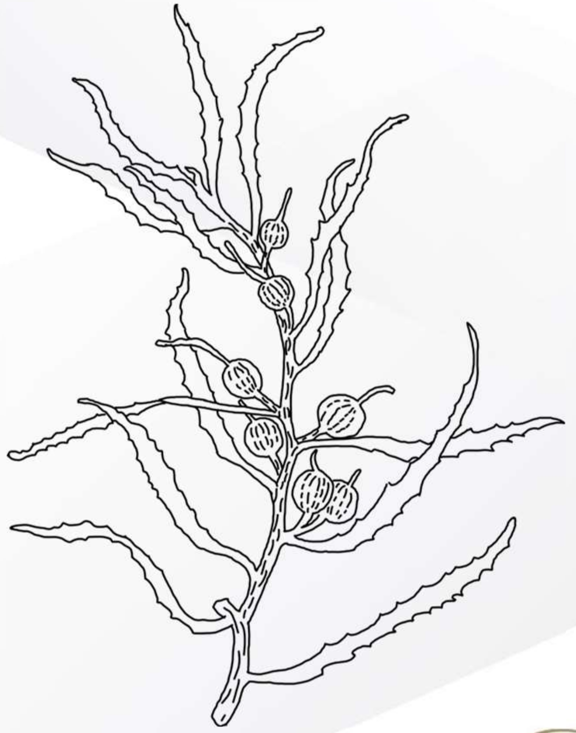
Conclusions

1. Highest level of parameters = Highest performing
   a. HTC Temperature 260°C, HTC Time 60 minutes, Ratio 1:20
2. HTC Temperature is a significant factor and has a positive impact on a hydrochar's percentage removal of MB



Discussion

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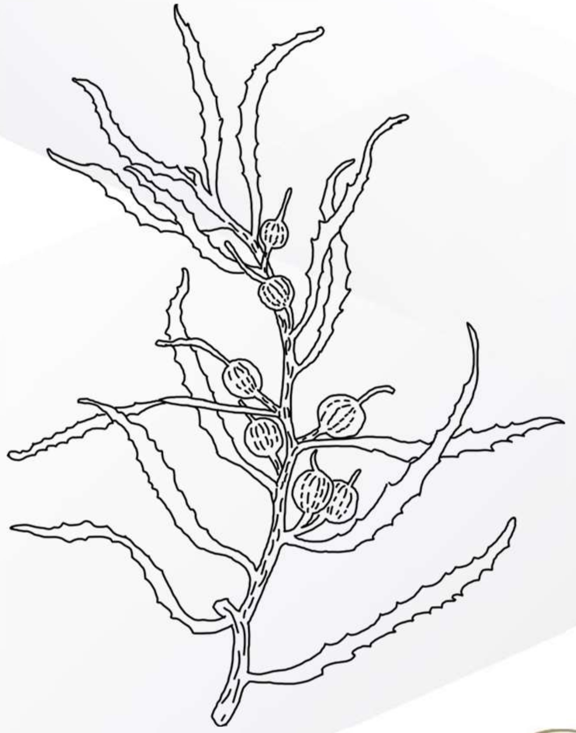
Limitations

- Constraints in data collection
- Limited amount of data
- Taguchi method does not take into account interactions between parameters

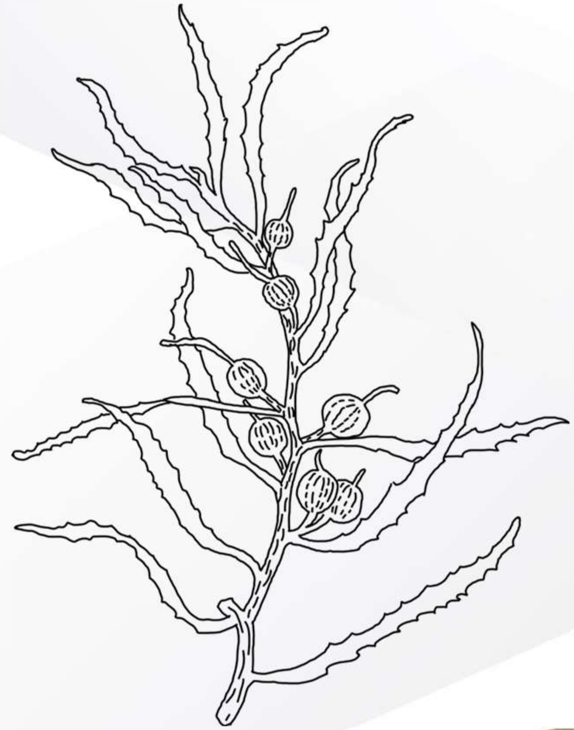


Contributions & Future Work

- Sargassum is supported as a resource for creating a sufficient adsorbent
- Singular sufficiency

Future work:

  - Hydrochar with actual toxin
  - Implementation of hydrochar
  - Algal bloom prediction



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Thank You!

Questions?

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Supplementary

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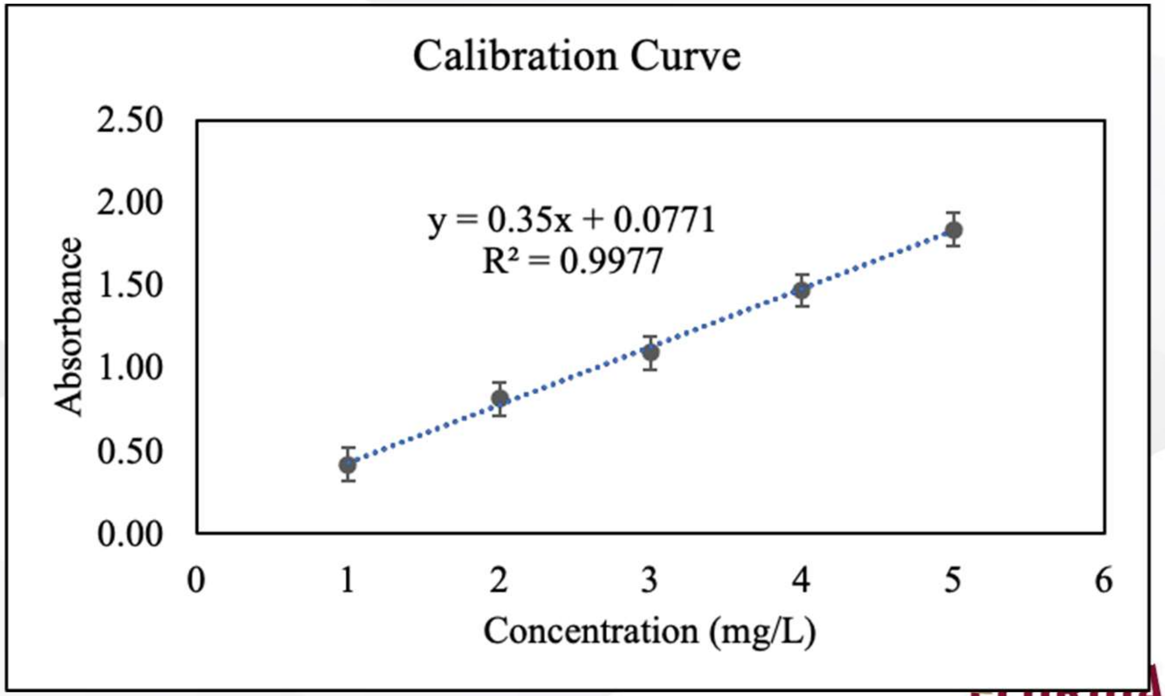
Experimental Design

Calibration Curve

Concentration (ppm)	Average Absorbance
1	0.356
2	0.721
3	1.09
4	1.418
5	1.7065



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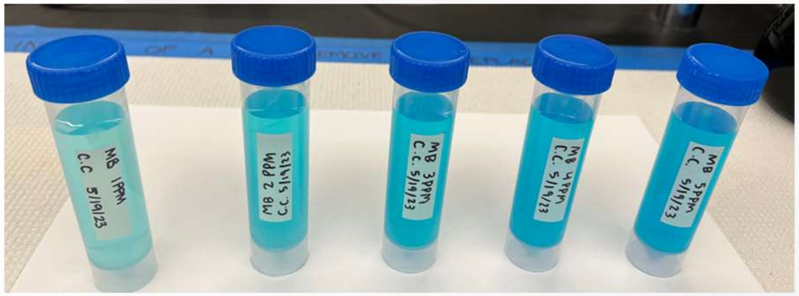
Calibration Curve

Absorbance: The amount of light absorbed by a substance

Range for Spectrophotometer Readings: 0.356 → 1.702



Full 100 ppm Results

Type of Hydrochar	Percentage Removal (%)
H180 t15 1:10	94.97 ± 0.07
H180 t60 1:15	98.26 ± 0.03
H180 t30 1:20	98.20 ± 0.04
H220 t15 1:20	98.65 ± 0.03
H220 t30 1:15	98.67 ± 0.08
H220 t60 1:10	98.83 ± 0.08
H260 t15 1:15	98.76 ± 0.01
H260 t30 1:10	98.55 ± 0.12
H260 t60 1:20	99.02 ± 0.05

Full 300 ppm Results

Type of Hydrochar	Percentage Removal (%)
H180 t15 1:10	87.19 ± 0.23
H180 t60 1:15	90.71 ± 0.18
H180 t30 1:20	88.54 ± 1.03
H220 t15 1:20	90.35 ± 0.38
H220 t30 1:15	92.08 ± 0.07
H220 t60 1:10	92.10 ± 0.29
H260 t15 1:15	93.56 ± 0.30
H260 t30 1:10	90.40 ± 0.26
H260 t60 1:20	95.53 ± 0.32

Experimental Design

The Taguchi Method:

Experiment #	Parameter: A	Parameter: B	Parameter: C
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

Experiment #	HTC Temp (C)	HTC Time (Minutes)	Water Ratio
1	180°	15	1:10
2	180°	30	1:20
3	180°	60	1:15
4	220°	15	1:20
5	220°	30	1:15
6	220°	60	1:10
7	260°	15	1:15
8	260°	30	1:10
9	260°	60	1:20

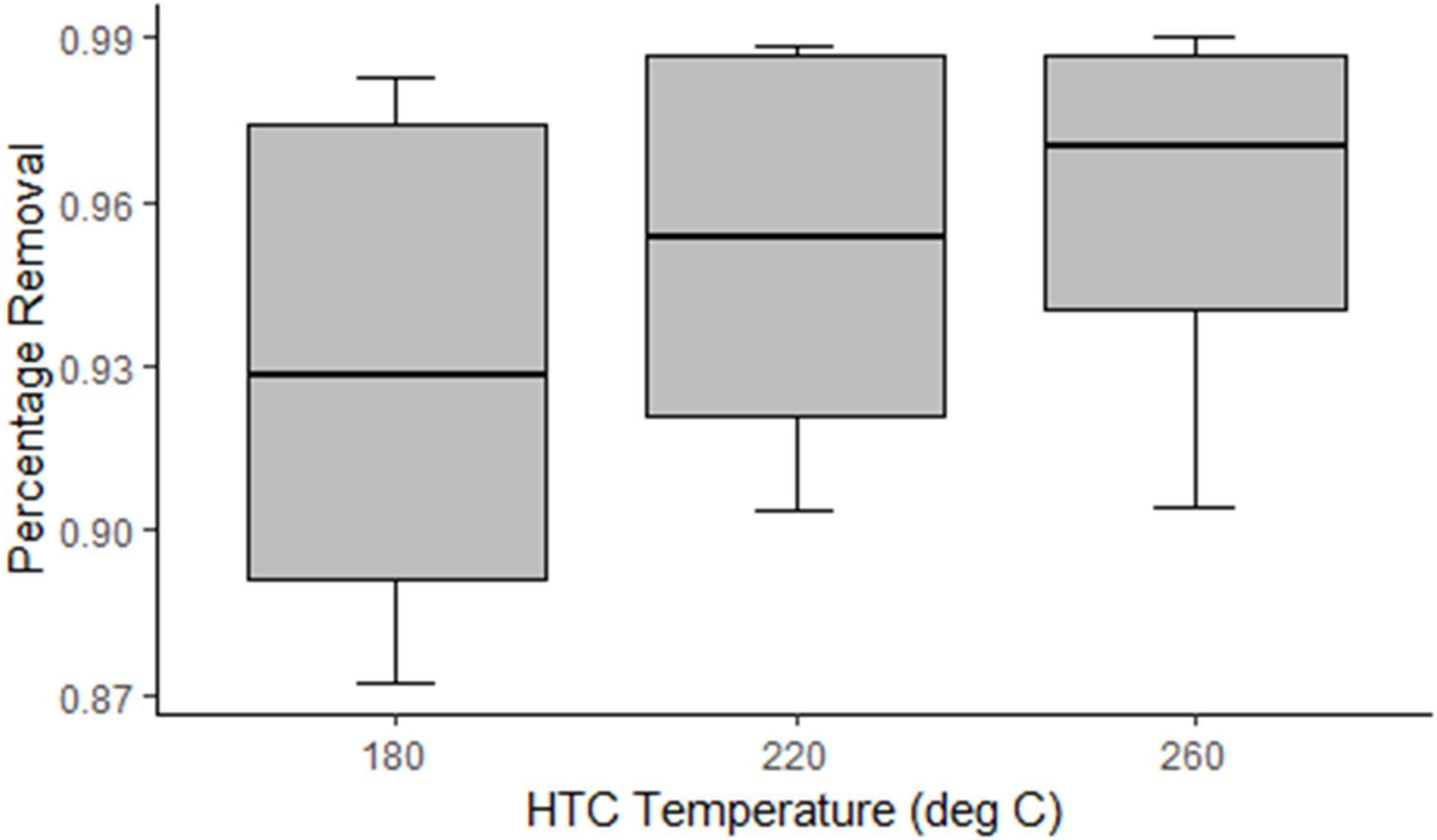
Carbon Offset

"Cooking" biomasses via HTC commonly produces gases as byproducts (CO_2, …)

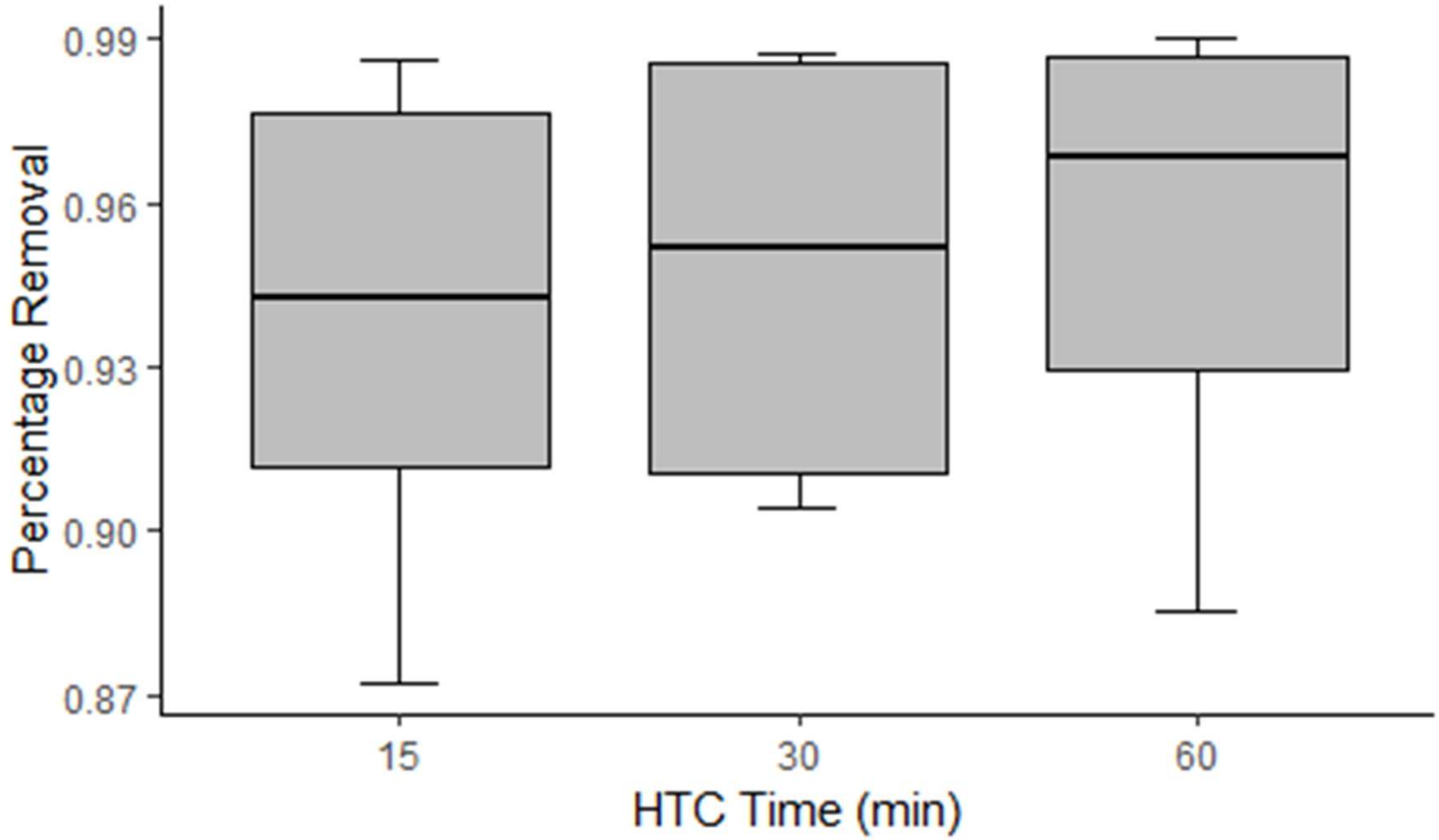
HTC (for hydrochar) not as energy intensive as pyrolysis (for biochar)

Emissions depend on the biomass & cooking conditions; therefore, to know for sargassum specifically, additional data would be needed

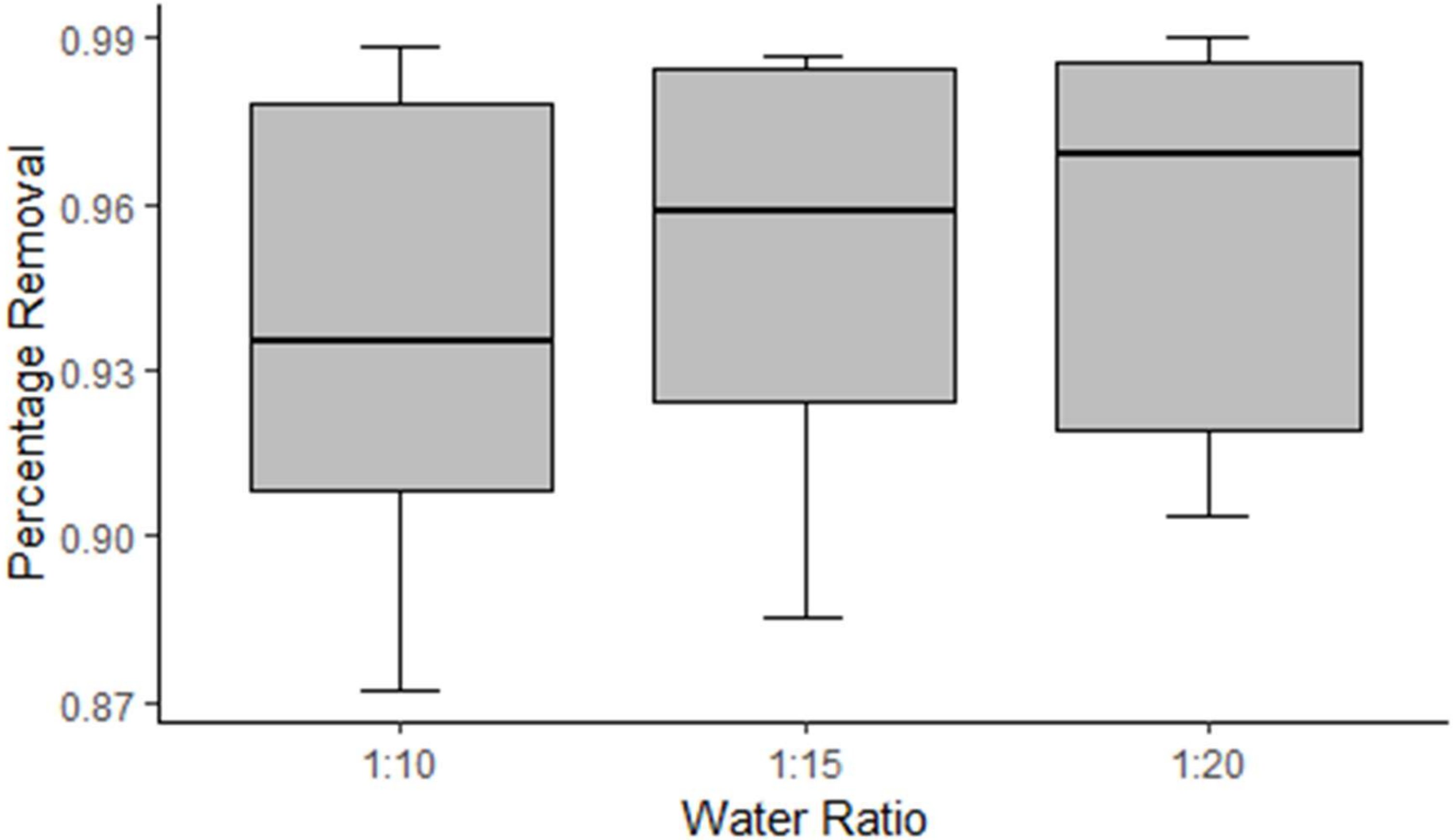
Box Plots


0.99
0.96
0.93
0.90
0.87
Percentage Removal
180
220
260
HTC Temperature (deg C)

Box Plots



Box Plots


Percentage Removal
0.99
0.96
0.93
0.90
0.87
1:10
1:15
1:20
Water Ratio

Preliminary Results


Dried Sargassum


Hydrochar
H180°C 30 min.1:10 ratio


Hydrochar
H220°C 30 min. 1:10 ratio

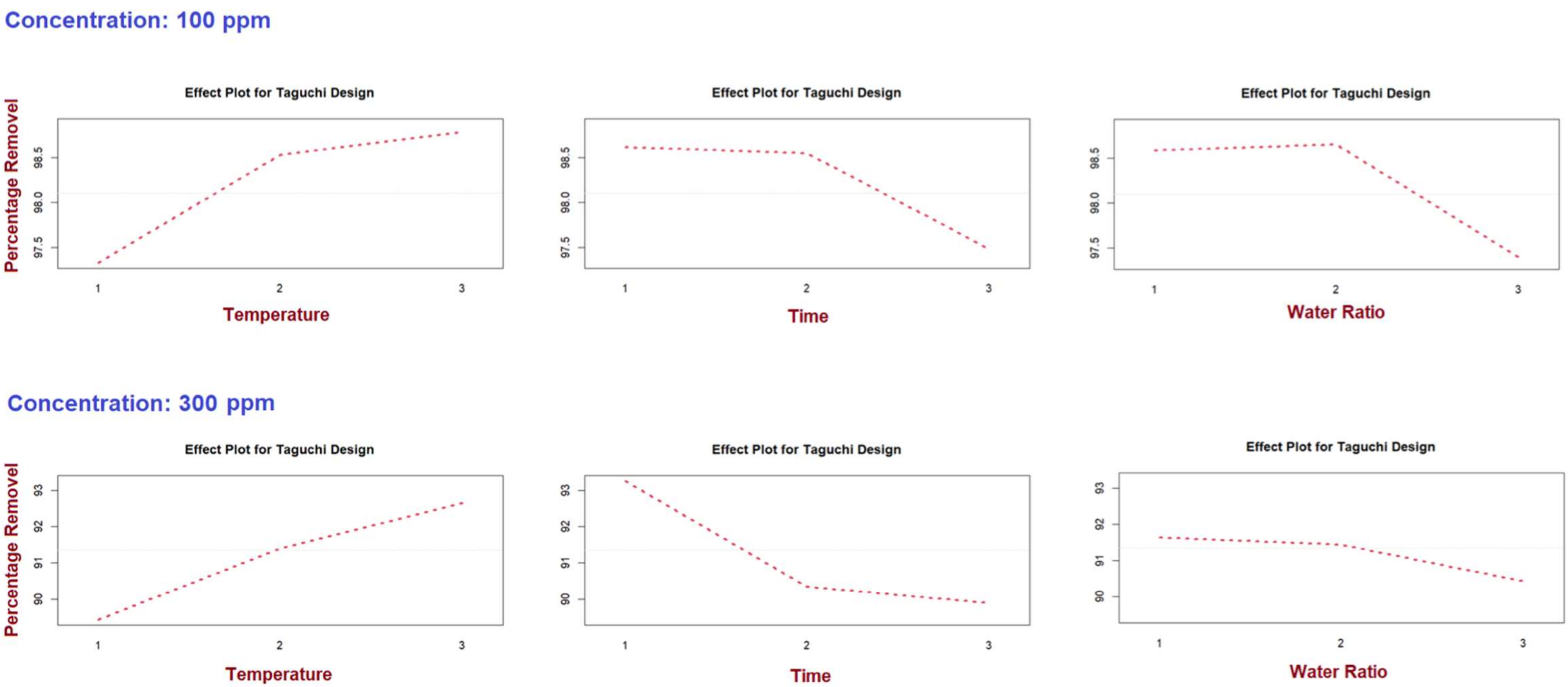

Hydrochar
H260°C 30 min.
1:10 ratio


Biochar
H180°C P400 t15


Biochar
H180°C P600 t30

100 ppm Sargassum-Derived Adsorbent Results:

Type of Biomass	% Removal
SG Raw	98.46%
Hydrochar 180°C	98.01%
Hydrochar 220°C	97.90%
Hydrochar 260°C	98.54%
Biochar H180°C P400 t15	93.24%
Biochar H180°C P600 t30	32.39%


Concentration: 100 ppm
Effect Plot for Taguchi Design
Effect Plot for Taguchi Design
Effect Plot for Taguchi Design
Percentage Removel
97.5
98.0
98.5
1
2
3
Temperature
Time
Water Ratio
Concentration: 300 ppm
Effect Plot for Taguchi Design
Effect Plot for Taguchi Design
Effect Plot for Taguchi Design
Percentage Removel
90
91
92
93
1
2
3
Temperature
Time
Water Ratio

Taguchi Method

- Taguchi method is used for product experimentation
- It's focus lies in optimization of the product and experimentation
- Allows for experimentation of a variety of different degrees of parameters

a = number of rows

b = number of levels

c = number of columns

Degrees of freedom

$$L_a(b^c)$$

Run #	A	B	C
1	1	1	1
2	1	2	2
3	2	1	2
4	2	2	1

(Krishnaiah, 2012; Karna & Sahai, 2012)