Lignocellulosic Hydrolysate Detoxification

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(2)

Motivation

In the past century, Earth's average surface temperature **increased by approximately 2°F** [1]. This adversely effects sea levels, glaciers, flora and fauna, and other environmental elements [2]. Large emissions of carbon dioxide through fossil fuel burning is the primary cause for climate change. As of October 2019, the amount of carbon dioxide in the atmosphere was approximately **412 ppm,** a **42 ppm increase in 19 years** [3].

Alternative sources of energy are essential.

(3)

"We can't save the world by playing by the rules, because the rules have to be changed. **Everything needs to change** – and it has to start today" [4].

-Greta Thunberg

Background

Second Generation Biofuel

Second generation biofuels are fuels produced from an array of low value feedstock such as lignocellulosic biomass, agricultural residues, and industrial waste [5]. Biofuels are not only **renewable** and **cost effective**, but also an **environmentally benign alternative** to fossil fuels [6].

Ethanol, one of the most common types of second-generation biofuel, is typically produced through fermentation. However, before fermentation occurs, the feedstock must be pretreated to the correct physical and chemical properties necessary for fermentation.

Furfural (6)

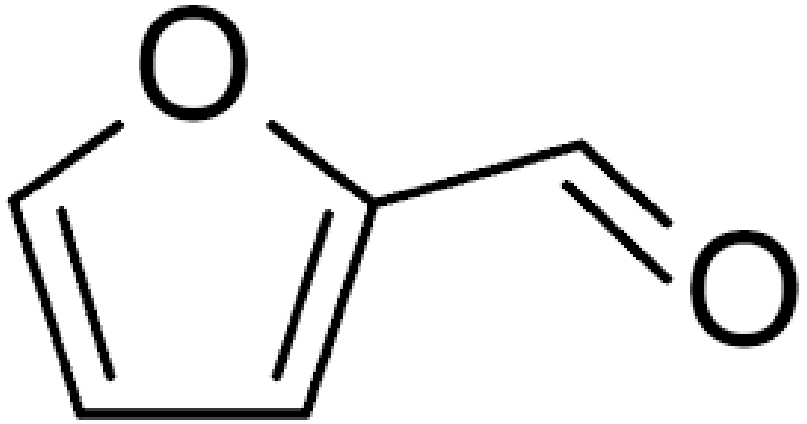


Figure 1. *Structure of furfural.*

5-Hydroxymethylfurfural (7)

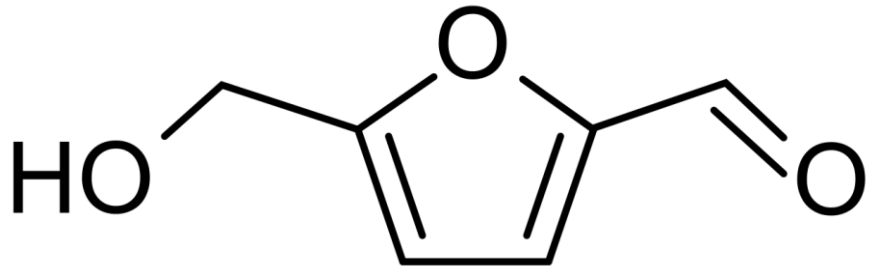


Figure 2. *Structure of 5-HMF.*

Pretreatment

One of the most common method for pretreatment of lignocellulos biomass (plant matter) is through **acid hydrolysis**. Acid hydrolysis breaks down the rigid structure of lignocellulose biomass into its constituent monomers and oligomers [7]. In addition to producing the preferred carbohydrates the degradation of lignocellulose biomass also produces **5-hydroxymethyl furfural** (5-HMF), **furfural,** and other phenolic compounds*. These degradation compounds reduce microorganism activity, inhibiting fermentation.

* 5-HMF and furfural are commonly referred to as furans

Presence of inhibitors and their effect on fermentation by yeast S. cerevisiae

Percent of ethanol produced when varying concentration of 5-HMF are present.

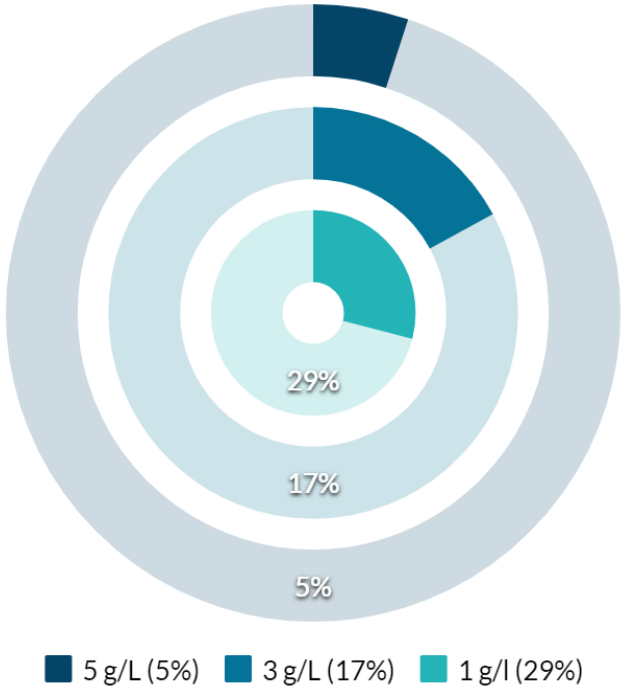


Figure 3. Ethanol produced from S. cerevisia in the presence of 1, 3, and 5 g/L of 5-HMF [8]. Percentages are created by comparing the amount of ethanol produced without inhibitors present to amount of ethanol produced with inhibitors.

Percent of ethanol produced when varying concentration of furfural are present.

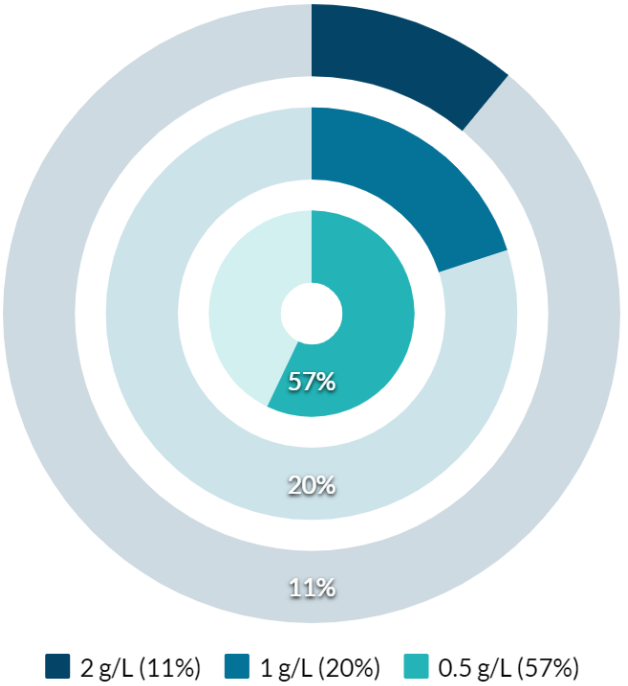


Figure 4. Ethanol produced from S. cerevisia in the presence of 0.5, 1, and 2 g/L of furfural [8]. Percentages are created by comparing the amount of ethanol produced without inhibitors present to amount of ethanol produced with inhibitors.

Detoxification

Detoxification is another step to the ethanol production process; thus a **cheap**, but **efficient**, method is preferred. Additionally, the method should have high selectivity and be environmentally friendly [9].

One method that fits the above criteria is activated carbon adsorption. **Activated carbon adsorption** is an **easy process to operate, requires minimal energy use,** and has **high selectivity** [10]. Additionally, adsorption with a carbon-based sorbent is typically very successful due to the **low price, high surface area,** and **renewability** of the adsorbent [11].

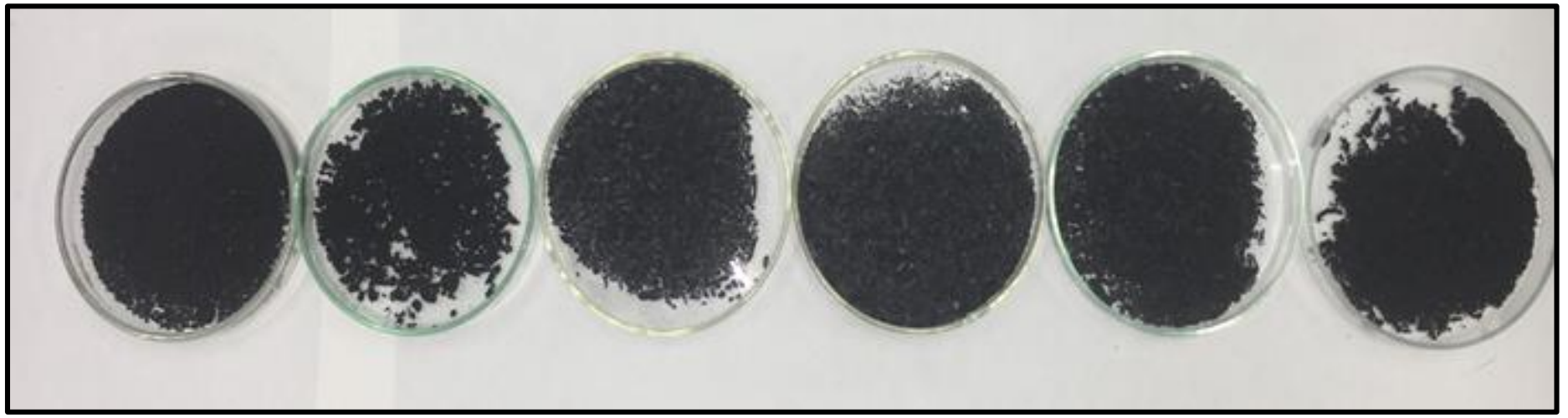
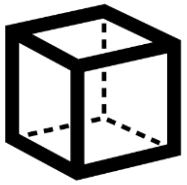


Figure 5. *Six different biochar's were donated by NextChar, an industrial biochar company, to be tested as sorbents.* Picture was taken in Professor Tânia Foster Carneiro's lab



Large Surface Area

Renewable

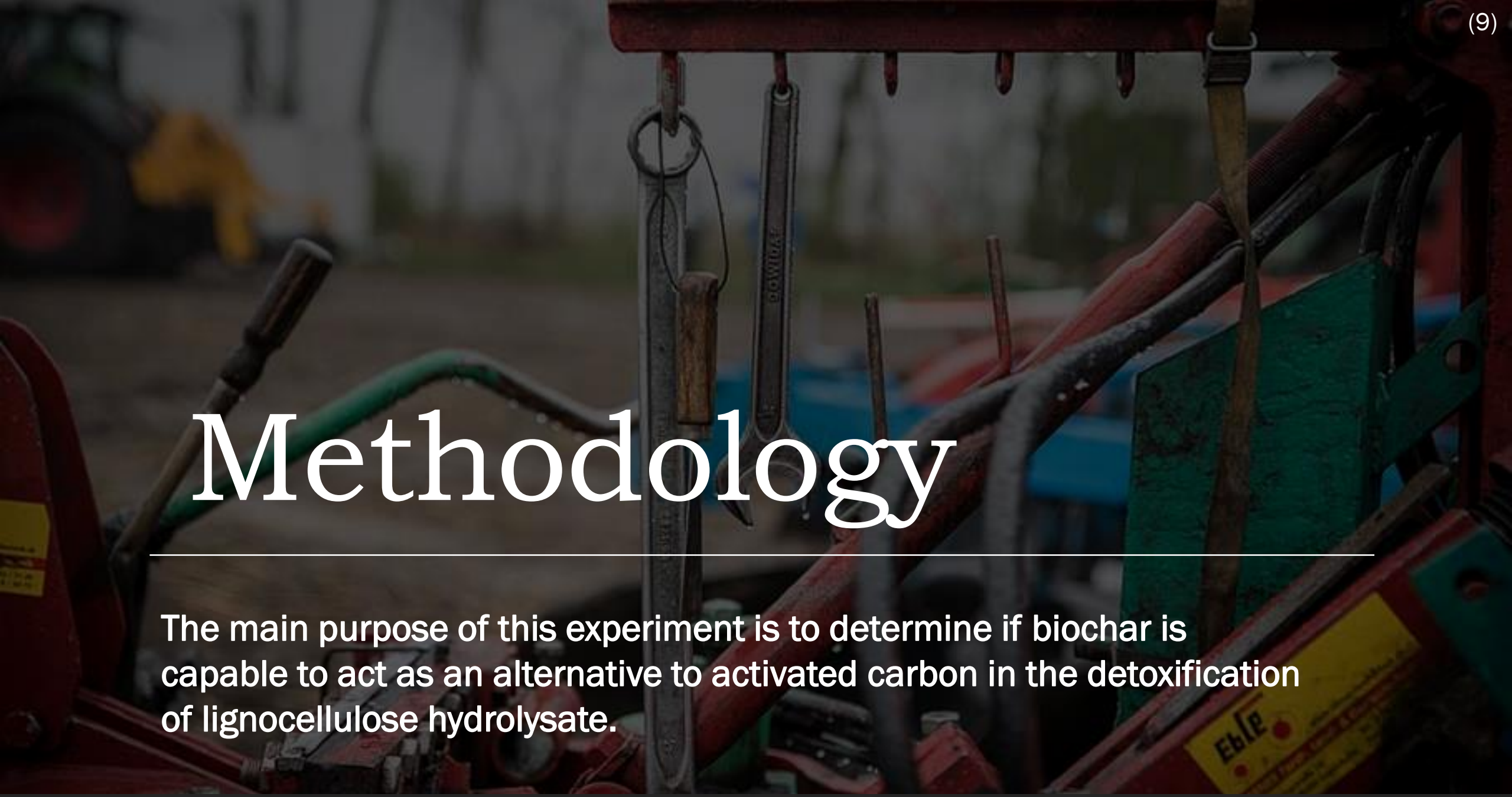
High Organic Content

Fine Grained Texture

High pH

Biochar

Biochar, known for its porous structure, high organic carbon content, fine grained texture, and high pH, is a pyrogenic carbon rich substance produced by the thermal degradation of biomass [12].



Methodology

The main purpose of this experiment is to determine if biochar is capable to act as an alternative to activated carbon in the detoxification of lignocellulose hydrolysate.

Adsorbents

Eight different adsorbents were studied in this experiment. Of the adsorbents studied, seven were a type of biochar and the eigth adsorbent was activated carbon.

Table 1. *List of the eight different adsorbents tested.* Biochar 1-6 were donated by NextChar and came with a name. Biochar 4 was activated in the lab using NaOH.

Adsorbent	Name
Activated Carbon	Activated Carbon
Biochar 1	Cool Terra
Biochar 2	Blak I
Biochar 3	Rogue
Biochar 4	Gold Standard
Biochar 5	Art I
Biochar 6	Wakefield
Activated Biochar 4	Activated Gold Standard

Experimental

To test the capacities of the sorbents, a synthetic lignocellulosic hydrolysate solution was made and pumped through a column.

Effluents were collected at increments of five for the first 30 mL, then ten for the next 40 mL.

Two different experimental set-ups were used. A switch was made to the CO_2 Peltier pump because the positive displacement pump was unable to hold a consistent flow rate.

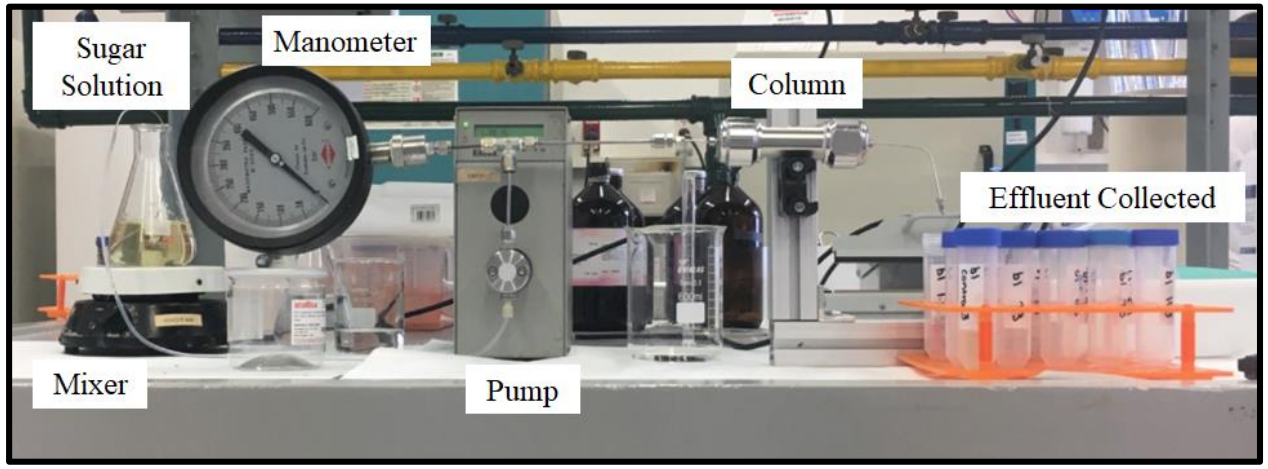


Figure 6. *Experimental set up with the positive displacement pump.* In this set up there was a manometer attached to the pump to record the pressure.

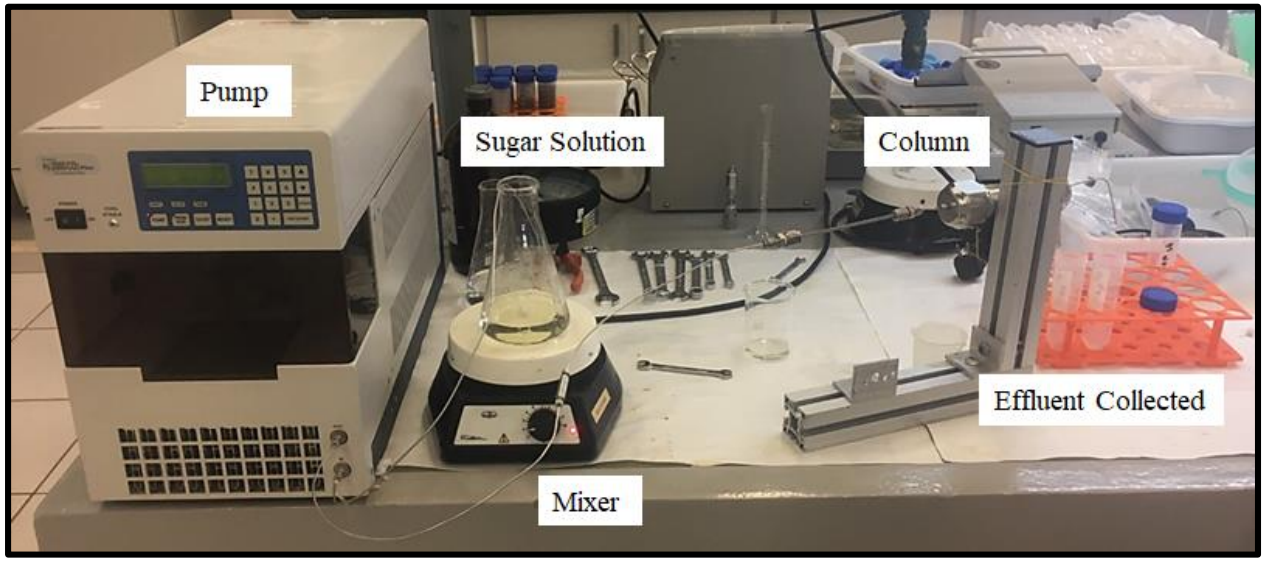


Figure 7. *Experimental set up with the CO_2 Peltier pump.* In this set up there was no need for the manometer, because the pump measured the pressure.

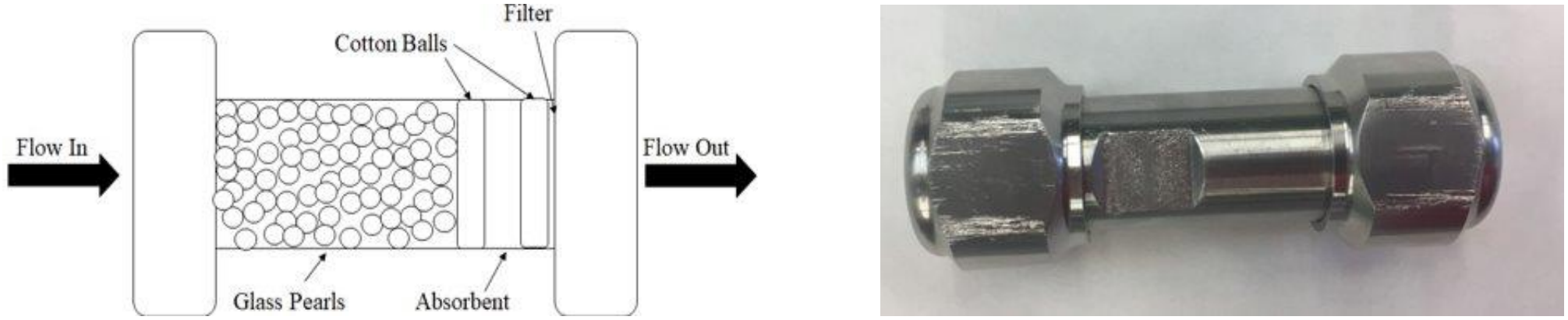


Figure 8. *Illustration of the inside of the column is on the left. On the right, is a picture of the column used for experimentation.* Picture was taken in Professor Tânia Foster Carneiro's lab

The Column

As the hydrolysate was pumped through the column, it interacted with four different components: glass pearls, cotton balls, an adsorbent, and a filter. The glass pearls, occupied empty space in the column to help diffusion begin. Next, the cotton balls ensured the adsorbent was secure and did not clog the filter. Mass transfer between the liquid phase adsorbate and solid phase adsorbent occurred through the third phase, the absorbent. Finally, the filter stopped any large particles from exiting the column with the effluent.

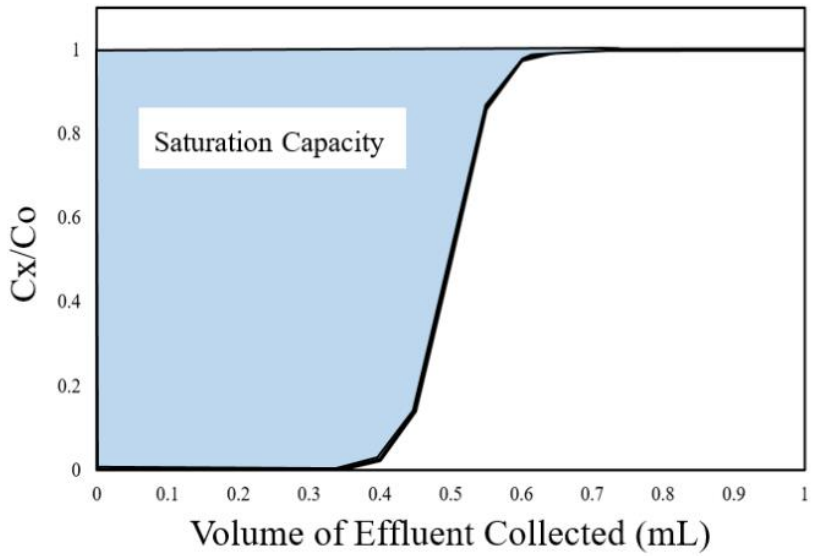


Figure 9. *Illustration of the area of a graph that applies to saturation capacity on a breakthrough curve.* Cx/Co stands for the concentration in the effluent over the initial concentration. All concentration were found by analyzing the results from a high-performance liquid chromatography unit.

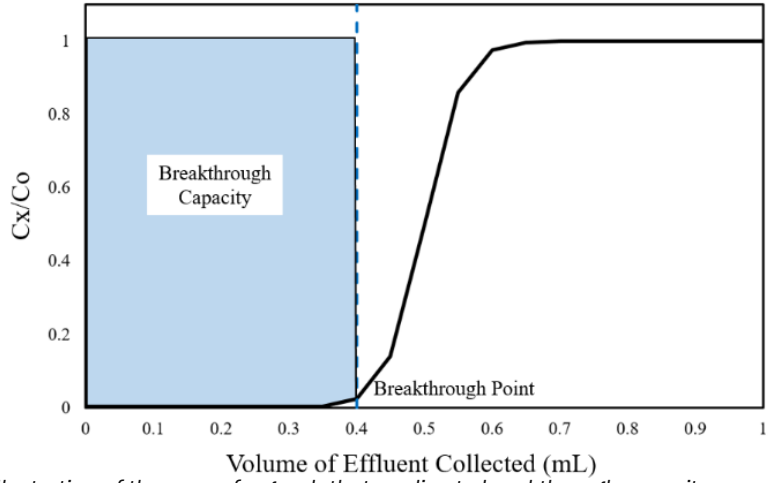


Figure 10. *Illustration of the area of a graph that applies to breakthrough capacity on a breakthrough curve.*

Adsorption Characterization

Saturation and breakthrough capacity of each solvent was calculated to quantify the adsorption ability of each sorbent .The saturation capacity, seen in Figure 9, illustrates the maximum capacity of the sorbent. The breakthrough capacity (Figure 10) shows the sorbent absorption maximum prior to the breakthrough point.

Results and Discussion

Activated Charcoal

Activated charcoal is known for its high selectivity.

- Adsorption of inhibitors: high
- Adsorption of sugars: low
- Over 97% adsorption of inhibitors
- In literature activated carbon adsorbed 38.7%, 57% and 46.8% of furans, phenolics, and acetic acid respectively, while having less than a 10% impact on the concentration of sugar [13].

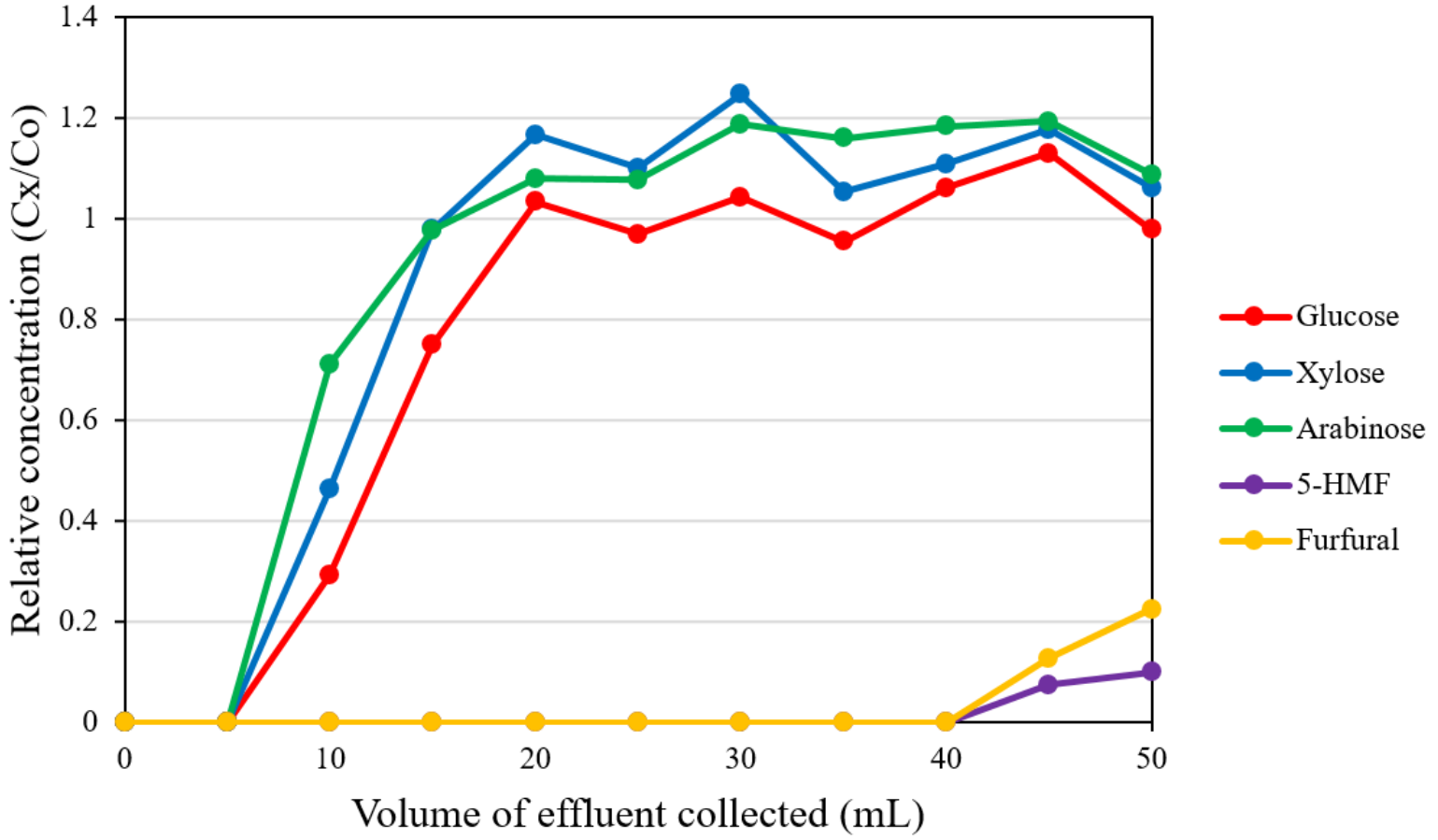


Figure 11. *Breakthrough curves for glucose, xylose, arabinose, 5-HMF, and furfural.* This specific trial occurred while using activated charcoal as the adsorbent in the positive displacement pump. The y-axis shows the concentration found in the effluent divided by the concentration found in the control. The x-axis shows the volumes of effluent collected to be tested by the HPLC.

Biochar 2: Blak I

Biochar 2 had the worst selectivity of all adsorbents tested.

- Adsorption of inhibitors: low
- Adsorption of sugars: low
- Larger adsorption of sugar molecules than inhibitors

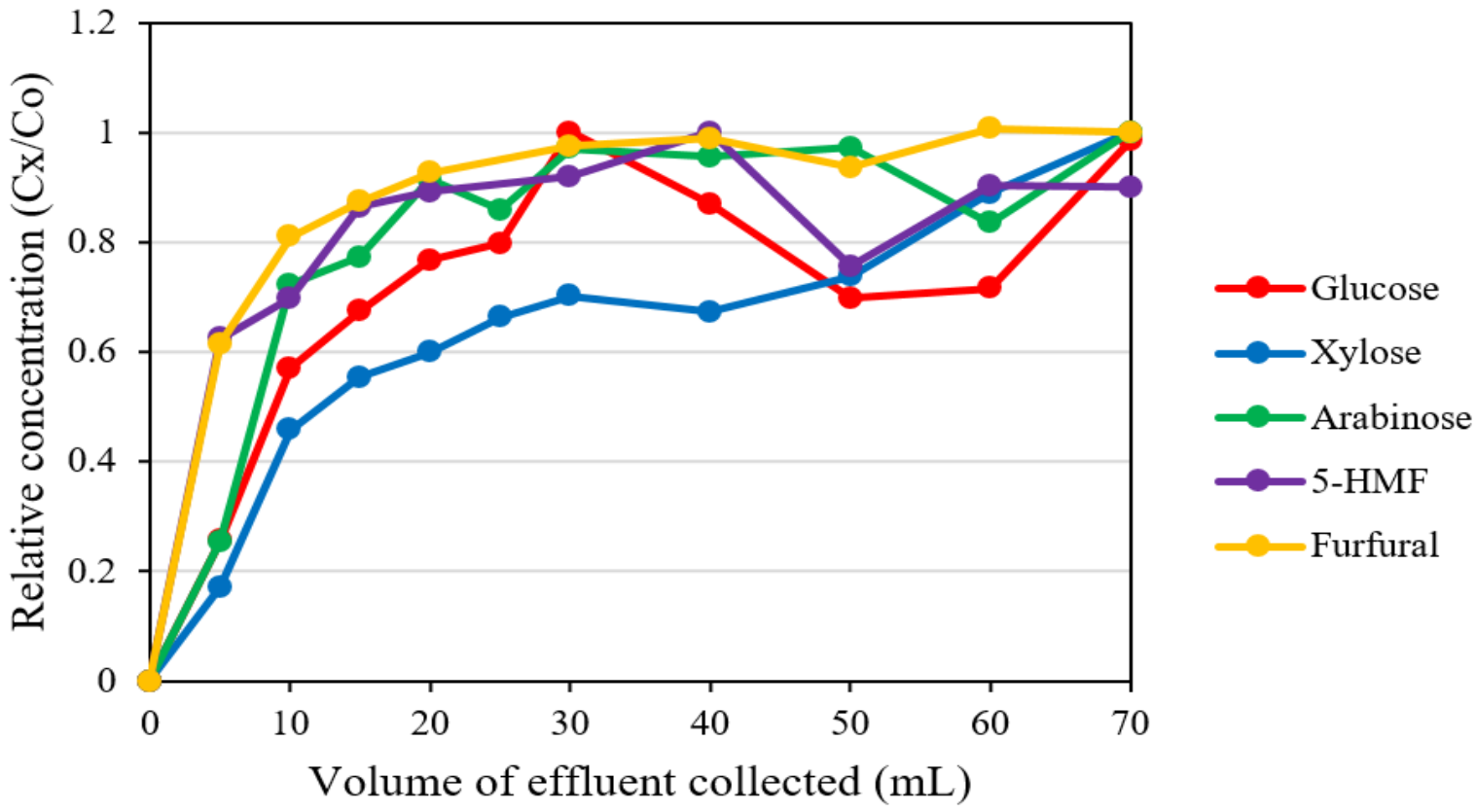


Figure 12. *Breakthrough curve for glucose, xylose, arabinose, 5-HMF, and furfural.* This trials occurred while using biochar 2 as the adsorbent in the CO_2 Peltier pump. All curves were normalized to disallow the relative concentration from exceeding one..

Biochar 4

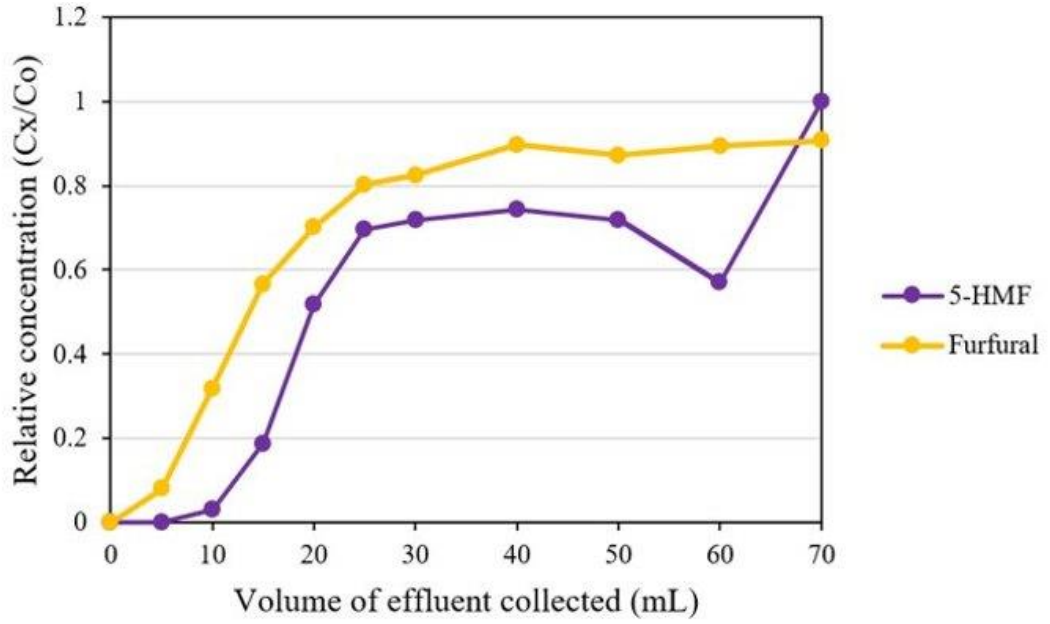


Figure 13. *Breakthrough curves for 5-HMF and furfural.* This trials occurred while using biochar 4 as the adsorbent in the CO_2 Peltier pump.

Activated Biochar 4

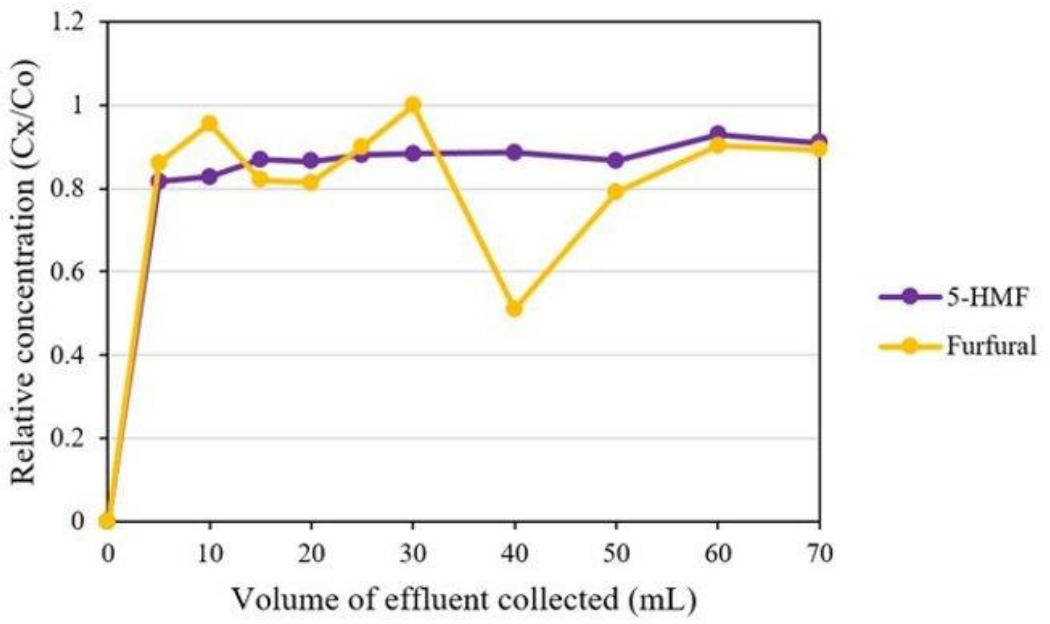


Figure 14. *Breakthrough curves for 5-HMF and furfural.* This trials occurred while using activated biochar 4 as the adsorbent in the CO_2 Peltier pump. The curve for furfural was normalized.

Biochar 4 had one of the largest capacities for inhibitors, however, when activated, the adsorption capacity of the biochar completely diminished. Indicating activation collapsed the pores on the surface of the biochar.

Biochar 4 vs. Activated Biochar 4

Saturation Capacity

A large capacity for inhibitors while a small capacity for sugars is preferred. Biochar 1, 2, 5, and activated biochar 4 all have little to no affinity for any compounds as seen in Table 2. Biochar 4 and 6 had the largest affinity for inhibitors. In literature the saturation capacity of actiavted carbon is found to be 75 g/g for both 5-HMF and furfural [14].

Table 2. *Saturation capacity of eight different adsorbents.* All capacities are recorded in mg/g and are the average of two trials from the CO_2 Peltier pump. (Dashed lines indicate unavailable data)

Adsorbent	Glucose	Xylose	Arabinose	5-HMF	Furfural
Activated Carbon	23.5	23.5	21.6	-	-
Biochar 1	16.3	10.9	14.6	-	-
Biochar 2	15.9	18.1	11.3	10.5	6.3
Biochar 3	-	-	-	-	-
Biochar 4	-	-	-	31.4	20.8
Biochar 5	-	-	-	20.9	10.4
Biochar 6	-	-	-	32.6	19
Activated Biochar 4	-	-	-	10	14.1

Table 3. *Breakthrough capacity of eight different adsorbents.* All capacities are recorded in mg/g and are the average of two trials from the CO_2 Peltier pump. For some of the capacities the amount is lower than the value listed in the table below (dashed lines indicate unavailable data).

Adsorbent	Glucose	Xylose	Arabinose	5-HMF	Furfural
Activated Carbon	14.4	14.3	9.9	-	-
Biochar 1	< 2.9	< 2.9	< 3.1	-	-
Biochar 2	< 4.3	< 4.4	< 4.2	< 4.2	< 4.2
Biochar 3	-	-	-	-	-
Biochar 4	-	-	-	7.5	4.8
Biochar 5	-	-	-	< 4.0	< 3.3
Biochar 6	-	-	-	9.6	4.5
Activated Biochar 4	-	-	-	< 2.9	< 2.9

Breakthrough Capacity

In industry, breakthrough capacity is normally more important than saturation capacity. At the breakthrough point the sorbent is typically replaced to allow regeneration. Therefore, the largest breakthrough capacity is indicative of the most successful adsorbent. As before, a larger capacity of inhibitors is still preferred.

Conclusion & Recommendations

Conclusion

Any research into sustainable energy alternatives, whether successful or unsuccessful is beneficial, because it could lead to a cleaner and less polluted world.

Upon comparison, the saturation capacity and breakthrough capacity of all six biochars were insignificant when compared to the adsorption capacity of activated carbon.

Recommendations

01

Perform tests on the surface properties of all adsorbents to understand why activated carbon is more successful than biochar at adsorption.

02

Perform tests with biochars prepared under known methods, allowing correlation between production method and adsorption capacity to be made.

03

Enhance the surface properties of the biochar, by performing other activation methods.

04

Perform tests with varying concentration of adsorbent to understand the optimal ratio between adsorbate and adsorbent.

Acknowledgments

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Image References

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