Analysis of Glucose Hydrochars

A Major Qualifying Project Submitted to the faculty of Chemical Engineering Department at
Worcester Polytechnic Institute
In partial fulfillment of the requirements for the Degree of Bachelor of Science

April 27, 2017

Submitted by:

_____

Abhinav Adhikari

_____

Shaelyn Quinn

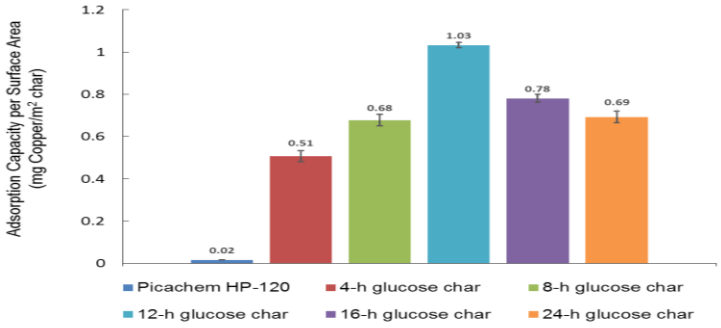
Approved by:

_____

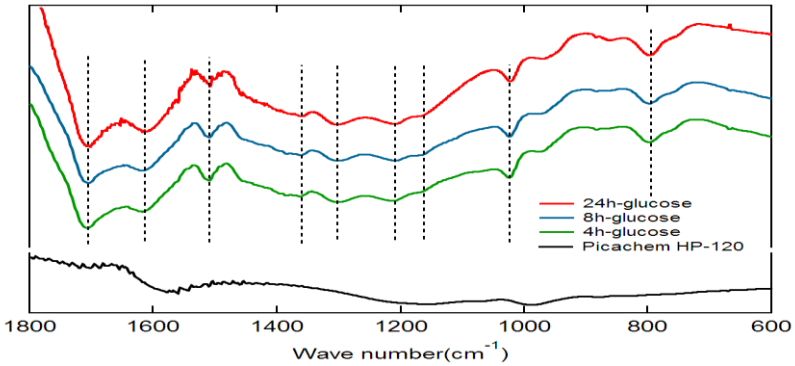
Michael Timko

Abstract

Heavy metals in drinking water is a serious health concern. Activated carbon is a commonly used adsorbent to remove heavy metals from water. Although effective, it is expensive and difficult to manufacture. Our project analyzes glucose hydrochars to determine if they could be a viable alternative for heavy metal adsorption in the future. The structure of the glucose hydrochar is dependent on its reaction time. We compared the adsorption capacity and surface area of different synthesized hydrochars to the activated carbon, Picachem HP-120. The results showed that activated carbon had the largest adsorption capacity by mass, but the hydrochars had a significantly larger capacity by surface area. The results are shown in the figure below.



The surface area of the activated carbon is 100 times larger than the chars, yet it is only able to adsorb 5 times more copper than the chars. The results shown above confirm the structure of the char interacts significantly more with the copper than the activated carbon. We attributed this result to the large number of functional groups on the hydrochar surface.



The IR spectrum above confirms that the chars, signified by the blue, green, and red lines, exhibit many functional groups on its surface. The black line represents the activated carbon which shows a very small number of functional groups.

Table of Contents

List of Figures

List of Tables

Acknowledgements

We would like to thank Professor Timko for advising this project and for his guidance over the past year. We would also like to thank Brendan McKeogh and Avery Brown for supplying the chars, collecting the activated carbon and hydrochar surface areas by gas sorption, giving the IR spectrum, and always being there for us.

Introduction

The basis of life is water. Clean drinking water should be easily available to everyone in the world. Researchers are finding more efficient and affordable ways to ensure that safe drinking water is easily accessible. Our research is focusing on filtering water that has been contaminated by copper. Copper is a naturally occurring metal that can be found in soil, rocks, and water.[1] The body requires low levels of copper to function normally, but at high levels copper can cause very serious health effects. It has been found that any copper levels above 1.3 mg/L can cause nausea, as well as damage to the liver and kidneys.[2] It is clear that copper can be very dangerous if not properly managed.

There are two methods in which copper can be exposed to drinking water. Well water can be directly contaminated by mining, farming manufacturing, which can release copper into the environment.[3] The other method, which we are more concerned about, is caused by corrosive copper pipes. The pipes will release copper into the water if it is at all acidic.[4] The large amount of copper can cause serious health effects. It has been found that any copper levels above 1.3 mg/L can cause nausea, as well as damage to the liver and kidneys.[5]

Copper is currently filtered out of water using methods such as reverse osmosis, ultra-filtration, distillation, and ion exchange.[6] In addition to these treatments, methods also utilize adsorbents like activated carbons, adsorbent resins, metal oxides and synthetic zeolites to remove contaminants. Among them, granular activated carbons and powdered activated carbons, produced from a variety of carbon-containing raw materials like wood, wood charcoal, peat, sawdust, coconut shells, are the most widely applied adsorbents.[7] Although activated carbon is a very efficient method of removing heavy metals such as carbon, it is very difficult and expensive to produce.[8]

A cheaper and more environmentally friendly alternative exists in biochars.[9] On average, biochars cost $350−$1,200 per tonne[10] compared to $1,100− $1,700 per tonne for powdered

activated carbons.[11] Hydrothermal carbonization (HTC) of biomass further reduces the cost and environmental footprint of production, and its product, hydrothermal chars, are a promising alternative to be used in the treatment of heavy metal contamination of water. Hydrothermal carbonization (HTC) is a technology developed in the early twentieth century for converting biomass to coal-like materials.[12] HTC is a thermochemical conversion process in which the biomass feed gets converted, in a batch process, to a carbonaceous solid—hydrothermal char—by the action of water at moderate temperatures (180–230 °C) and autogenic pressure.[13]

Our project was analyzing the capacity and surface hours of different synthesized glucose chars. We ran experiments on chars that were synthesized from 4 hours to 24 hours. The capacity and surface area of each glucose char was then compared to the activated carbon, Picachem HP-120. The goal of our research was to determine a glucose char that could be a viable solution for heavy metal adsorption, and substitute activated carbon in the future. Our objectives included creating a procedure to collect data that would produce optimal results, analyzing the chars and Picachem HP-120 by their capacity to adsorb copper, and identify the functional groups formed on each synthesized char that could directly relate to its ability to adsorb copper. Through our research, we hoped to provide data that will further the understanding of these chars, and the relationship between its reaction time and structure. In the future, this data could be used to formulate a procedure to obtain the char that adsorbs the optimal amount of char.

Background

Biomass is an important source of renewable energy. Currently, bioenergy accounts for roughly 10% of the world's total primary energy supply.[14] However, much of the biomass is used as fuel by direct combustion, resulting in low energy recovery and emission of greenhouse gases.[15] The prospect of processing waste biomass into valuable carbonaceous materials is attractive primarily because the resulting materials have a higher heating value and carbon content, and they also release less greenhouse gases.[16] One example of this material is biochar, a solid formed by gasification, pyrolysis, flash carbonization, or hydrothermal carbonization (HTC)* of biomass.[17] There are distinct differences in each of these technologies. During the gasification processes, the biomass is partially oxidized at a temperature of about 800 °C at atmospheric or elevated pressure to mostly yield gas and small amounts of char and liquid.[18] Pyrolysis, unlike gasification, does not use oxygen in the conversion process, and is generally carried out between 400-500 °C.[19] Flash carbonization is a process that yields mainly gaseous and solid product. A flash fire is ignited at elevated pressure (1-2 MPa) at the bottom of a packed bed of biomass, and the fire moves upward through the carbonization bed creating temperatures in the reactor to reach 300-600 °C.[20] Hydrothermal carbonization (HTC) is a thermochemical conversion technique that uses water to convert carbon present in biomass to more carbonaceous materials.[21] Temperatures between 180-220 °C and elevated pressure (usually autogenic with the vapor pressure of subcritical-water corresponding to the reaction temperature[22]) work together with water to yield solid, liquid and gaseous products.[23]

Among these processes, hydrothermal carbonization is one of the least studied, whereas pyrolysis is a well-developed technology.[24] The HTC process, however, has several advantages over pyrolysis. In addition to having a higher carbon recovery and more surface

* Biochar formed by HTC process is often referred to as a hydrochar or hydrothermal char

oxygen-containing groups[25], the HTC process uses a much lower operating temperature[26] (higher energy efficiency), pre-drying is not necessary (saving energy costs), and gases such as carbon dioxide, nitrogen oxides and sulfur oxides are dissolved in water, reducing the possibility of air pollution.[27] Moreover, the porosity, surface chemistry and electrical properties of the resulting char can be better tuned by additional activation procedures or thermal treatments.[28] Another advantage of the hydrothermal process is that the resulting char particles have oxygenated (polar) groups on the surface, which can be utilized in post-functionalization strategies.[29]

Although the exact reactions involved in the HTC process are not confirmed, several mechanisms have been proposed.[30,31,32,33,34,35] Because it is not easy to elucidate the complex molecular structure of biomass, simple carbohydrates are generally used as model precursors in order to study their mechanism of formation into hydrothermal chars.[36] Among them, glucose is the most promising material as it is the most abundant and inexpensive carbohydrate available.[37] In this MQP, glucose was used as the starting material for the hydrothermal chars.

Hydrothermal chars have many potential applications spanning many industries. They can be used in energy production because the HTC process increases the higher heating value by increasing the carbon to oxygen ratio.[38] The HTC process also reduces ash, alkali and alkaline metal content from raw biomass, improving its combustion properties.[39] Another use of chars is in carbon sequestration, potentially helping create a carbon-negative environment.[40] Hydrothermal chars can also benefit agriculture, especially because of its structural (high surface area and porosity) and chemical properties (hydroxyl, ketone, ester, aldehyde, amino, nitro, phenolic and carboxyl groups) that allow it to enhance the cation exchange capacity (CEC), nutrient retention capacity (NRT) and water holding capacity (WHC) of soil, dramatically improving soil health and increasing crop productivity.[41] The subject of this MQP, however, is another important application of the hydrochars: adsorbents for water remediation.

Hydrochars as Adsorbents

Biochars have been shown to have high surface areas and oxygen-containing groups that enable them to function as adsorbents for soil and water remediation.[42] Hydrochars, on the other hand, typically have lower surface areas than biochars but due to the presence of more oxygen-containing groups on their surface that enable them to have more electrostatic interactions, they can potentially function as good adsorbents especially for treatment of water contaminated with heavy metals.[43]

Currently, the water treatment methods for heavy metals, apart from adsorption, include chemical precipitation, ion exchange, reverse osmosis, and coagulation-flocculation.[44] However, each of these have severe limitations. Chemical precipitation, for example, is slow and requires a large amount of chemicals to reduce metals to an acceptable level for discharge.[45] In addition, it produces excessive sludge, demanding further treatment to avoid long-term environmental impacts of disposal.[46] Sludge formation is a problem for the coagulation-flocculation method as well, which also requires high operational costs in the first place due to high chemical consumption.[47] Ion exchange has its own disadvantages in that it cannot handle concentrated metal solutions, is nonselective and is highly sensitive to the solution pH.[48] The main limitation of reverse osmosis is high energy requirement due to high pressure requirements (20-100 bar).[49]

Water remediation by the use of carbon adsorbents have the potential to overcome many of these limitations. Activated carbons are the most common adsorbents currently applied for water treatment. Their internal surface areas, which are primarily responsible for their adsorption properties, range from 800-1000 m^{-2}/g. Hydrochars, although have less available surface areas, have a large number of functional groups on their surface.[50] They also cost much less than the price of $1,100− $1,700 per tonne for powdered activated carbons.[51] In addition, because they are much easier to synthesize, hydrochars may prove to be a very attractive adsorbent, especially for the developing world.

The purpose of this project was to examine the heavy metal adsorption capabilities of glucose hydrochars synthesized in the laboratory for varied reaction times and to try to relate the surface functional groups present in them to their adsorption performance. For this project, copper nitrate solution was used as a source of Cu^{2+} ions.

Procedure

Calibration Curve

A calibration curve was required to convert the absorption units given in the UV spectroscopy to concentration of copper nitrate. The concentration of copper nitrate in molar units was needed for future calculation. The calibration curve was created by using 8 solutions of known concentrations ranging from 0.01M to 0.08M. An initial 180 mL of 0.08M copper nitrate solution was made and stirred for 20 minutes. The initial solution was then added to DI water to get the desired 20 mL of the copper concentration, which Table 1 outlines.

Copper Concentration (M)	Initial Solution (mL)	DI water (mL)
0.08	0	0
0.07	17.5	2.5
0.06	15	5
0.05	12.5	7.5
0.04	10	10
0.03	7.5	12.5
0.02	5	15
0.01	2.5	17.5

Table 1: Calibration Curve Solutions

The solutions were then analyzed using UV spectroscopy, which gives a reading in adsorption units. A graph of copper concentration (M) vs. adsorption data was then generated from the collected data. The resultant trend line is the calibration curve that would allow conversion between adsorption units and molar concentration.

Preliminary Experiments

Before we could determine a final procedure, there were several tests we ran to determine several factors in our experiments. These factors included the mass of char to be used in each experiment, the initial concentration of copper nitrate in each sample, the type of vial used, and the method of filtration. The experiments completed to determine these factors are explained in this section.

Amount of char used in experiment

The amount of char we analyzed was 0.06, 0.2, 0.4, and 0.6 grams. 8-hour glucose in 0.06M copper nitrate solution was used to run experiments in which we would shake the samples between the hours of 4 and 24 hours. The samples were then analyzed using UV spectroscopy, and the concentration was obtained using the calibration curve. The percent of copper nitrate absorbed was then calculated. The mass that absorbed the most copper nitrate was used in further experiments.

Plastic vs. glass vials

This experiment was carried out to see if there was any variability in results when using plastic or glass vials. Two samples with char and an initial solution were each made for the plastic and glass vials. The glass and plastic vial were then put into the shaker for the same exact amount of time, which was about 19 hours. The vials were then taken out of the shaker and filtered using the centrifuge for filtration. The samples were then tested using the UV. The results were analyzed, and the best results determined which vial type was chosen.

Centrifuge vs. Vacuum Filtration

This experiment was conducted to see if there was any variability in results when using the centrifugation or vacuum filtration method to separate the copper nitrate solution from the char after the adsorption experiments. Four vials were used in total- two each for the centrifugation method and the vacuum filtration method. In addition, an initial vial each was also subjected to the two processes to serve as control. 0.4 grams of Picachem HP-120 was used with a 0.06M copper nitrate solution and the solution shaken for 19 hours. Then the resulting solutions were either centrifuged at 4000RPM for 5 minutes or vacuum filtered, and the UV absorptions measured.

Final Procedure for experiments

After our preliminary experiments, we were able to write a standard procedure that would be used for the remainder of our data collection. The data collected with this procedure was further analyzed in this report to determine the relationship between the char's capacity and surface area. The following outlines the standard procedure (full detailed procedure is in Appendix I).

Preparing the samples

1. The 0.06M copper nitrate was first prepared. The appropriate amount of copper nitrate was measured using a balance and then transferred to a flask. Distilled water was then added to the copper nitrate. The amount prepared depended on the number of vials being used. Each vial required 20 mL of copper nitrate solution. The copper nitrate solution was then stirred for approximately 10 minutes using a magnetic stirrer with parafilm over the opening to ensure no vapor escaped.
2. While the copper nitrate solution was being prepared, 0.4 grams of char was measured in a glass vial. For each experiment, two samples (A and B) were prepared.

3. Using a pipette, 20 mL of the copper nitrate solution was transferred to the two vials containing the char, and then 20 mL of the solution was also transferred to an empty glass vial which would be the “initial” sample.
4. The vials were then placed in the shaker and shaken at 385 oscillations per minute in Burrell Scientific Wrist Action Shaker model 75 for the desired amount of time.

Analyzing the Samples

1. After the vials were shaken, they were taken out of the shaker and their contents poured from the glass vial to plastic vials. The plastic vials were then placed in the centrifuge which ran for 5 minutes at 4000 rpm.
2. The supernatant was then pipetted out of the plastic vials into small glass vials as prep for the UV readings. 0.45μm syringe filter was used to further filter the solution before its analysis in the UV-Vis spectrophotometer to ensure no char particles were present.
3. UV-Vis spectroscopy was used to analyze the solutions from each sample. Before the samples could be tested, DI water was used as a blank in the UV. Once the UV-Vis spectrophotometer was calibrated, each sample was read three times and the absorption reading was recorded.

Determining the equilibrium time

A capacity vs. time curve for several chars was plotted to identify the equilibrium time. 8-, 16-, and 24-hour glucose chars were used to model the equilibrium time. This experiment was carried out over a time range of 0 to 30 hours (up to 80 hours for some samples), and each char was analyzed using the UV spectroscopy in regular intervals. The capacity at each time point was graphed.

The equilibrium time was determined as the point when the curve begins to level off. This would be chosen as the time to be used for all the following adsorption experiments.

Results and Discussion

Calibration Curve

In order to quantify the amount of copper adsorbed by the char, the UV-Vis Spectrophotometer was used taking advantage of the dependence of the color intensity of the copper nitrate solution on its concentration. A calibration curve is required to convert the 'Absorption Units' reading of the instrument to the corresponding concentration value of the solution.

In order to do that, UV-Vis readings of concentrations of the copper nitrate solution in the range of 0.01M to 0.08M were measured in 0.01 M increments in duplicates. A scatter plot of the Absorption Units versus concentration was made, shown in Figure 1, and a line of best fit drawn through the 8 data points. The equation obtained was

$$y = 11.334x + 0.0119 \qquad (1)$$

where x and y signify the copper nitrate concentration (M) and Absorption Units, respectively. The R^2 value of the regression line was determined to be 0.9998, showing a good linear fit.

All the subsequent adsorption experiments were carried out within the limits of the calibration curve. Raw data and sample calculations can be found in Appendix II.

In order to convert the Absorption Units to the copper nitrate solution concentration, the following form of the equation was used:

$$\mathrm{x} = \frac{\mathrm{y} - 0.0119}{11.334} \qquad (2)$$

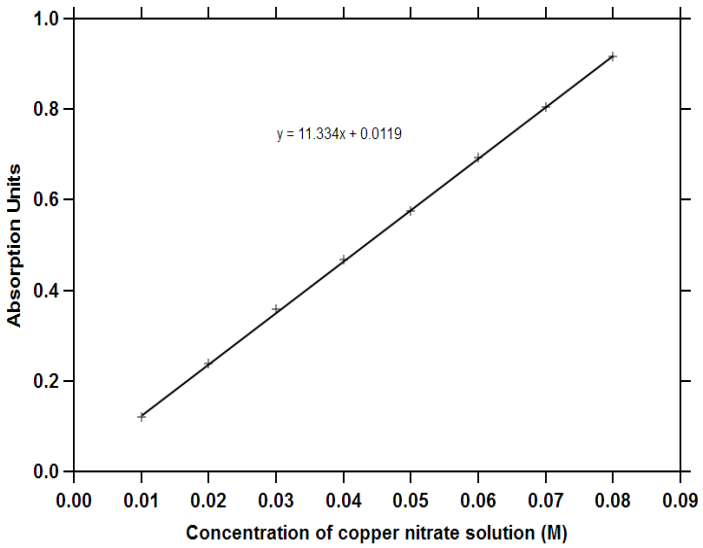


Figure 1: UV-Vis Calibration Curve

Conversion of UV-Vis reading to adsorption capacity

In order to calculate adsorption capacity per mass or per surface area basis of char, equation 2 was used for both the control copper nitrate solution (without the chars) and the solution containing chars to calculate the solution concentration. This concentration value was used to calculate the mass of copper present in the solution. In order to determine the mass of copper adsorbed onto the char, the difference between the mass of copper in the control solution and that in the solution containing chars was calculated. Finally, this value was divided by the total mass or total surface area of the chars used to determine the capacity per mass or surface area basis respectively.

Preliminary Results

Before carrying out the experiments to compare the adsorption capacities of the different chars, it was necessary to determine the mass of the char used, concentration of the copper nitrate

solution, and the experimental procedure used. This section looks at these factors.

Mass of char used in experiment

In order to determine the mass of char to be used in the experiments, various adsorption experiments were carried out with both the activated carbon and the glucose hydrochar. The mass used ranged from 0.06 grams to 0.6 grams. 8-hour glucose char was used for these experiments because of its abundance. Table 2 below shows the results of these experiments.

Mass of Char used (g) (char type, adsorption hours)	Adsorption capacity (mg Copper/g char)	% Copper adsorbed
0.06 grams (8h-glucose, 4 hours)	-3.53 ± 0.53[†]	-0.28
0.06 grams (Picachem, 4 hours)	27.1 ± 0.36	2.39
0.2 grams (8h-glucose, 8 hours)	2.11 ± 0.23	0.56
0.4 grams (8h-glucose, 12 hours)	7.38 ± 1.09	4.04
0.4 grams (Picachem, 12 hours)	19.2 ± 1.02	10.5
0.6 grams (8hg, 12 hours)	2.33 ± 0.32	1.86
0.6 grams (Picachem, 12 hours)	20.40 ± 1.04	16.3

Table 2: Mass of Char Used Experimental Results

The results of the table suggest that the highest percent copper adsorbed as well as the capacity are the highest for 0.4 grams mass used. Maximizing the percent adsorbed was important because it would allow a more accurate reading difference in the UV-Vis spectrum,

[†] negative values resulted from the noise of the UV-Vis reading because the amount adsorbed was negligible

therefore maximizing accuracy. Because this MQP compared the capacities of the glucose chars, the results of the glucose chars in the above table, rather than that of Picachem, were used in determining the mass used.

Determining the Concentration of the Copper Nitrate Solution

Another parameter to determine was the concentration of copper nitrate solution to be used. It was important that, in order to reduce errors in the calibration curve use, the concentration range to be investigated be in the mid-range of the curve. Two concentrations were tested: 0.06M and 0.04M. Using a 0.4 g mass of 12-hour glucose, the adsorption capacity was determined for these two concentrations. The raw data and sample calculations can be found in Appendix III. The results are summarized in the Table 3 below.

Concentration used (char type, adsorption hours)	**Adsorption capacity (mg Copper/g char)**
0.04M (12h-glucose, 24 hours)	1.71 ± 0.14
0.06M (12h-glucose, 24 hours)	2.87 ± 0.46

Table 3: Concentration of Copper Nitrate Experimental Results

The table shows that 0.06M solution gives a better adsorption capacity. A higher value of the capacity would also enable a better resolution, therefore more accurate results, while comparing the capacities of different chars. As a result, 0.06M was chosen as the standard concentration to be used.

Plastic vs. glass vials

There were two choices for the vials to be used in the wrist-action shaker: glass or plastic. An experiment was run to determine if the capacity and/or error bars differed due to the type of vial. 0.4 grams of Picachem was used in a 0.06M solution of copper nitrate in both vials and shaken

for 19 hours. The difference in adsorption capacity between the two types of vials was just 1.84%, and showed that either option could be used. The glass vials were chosen because they were easier to use and had higher availability in the lab. The raw data and sample calculations can be found in Appendix IV.

Centrifuge vs. Vacuum Filtration

After the solution of copper nitrate was shaken with the chars, it had to be separated from the chars in order to be used in the UV-Vis spectrophotometer. There were two different methods to be used for the process: vacuum filtration or centrifugation.

In order to determine which method was better, 0.06M copper nitrate solution was shaken with 0.4 grams of Picachem for an arbitrary time of 20 hours. Then the solution was either vacuum filtered or centrifuged at 4000 RPM for 5 minutes and then analyzed in the UV-Vis spectrophotometer. The raw data and sample calculations can be found in Appendix V. The results are summarized in the Table 4 below.

Procedure Used	**Adsorption capacity (mg Copper/g char)**
Vacuum Filtration	23.6 ± 0.55
Centrifugation at 4000 RPM for 5 minutes	23.6 ± 0.11

Table 4: Filtration Method Experimental Results

The results show that the adsorption capacity were very similar. However, the major difference was the presence of a larger error for the vacuum filtration method, which was probably due to the increased chances of experimental errors while performing the filtration, or the interaction of the solution with the filter paper. On the other hand, the centrifugation process was a quicker process to separate the solution from the char, and many vials could be run in the centrifuge at

once. Because centrifugation saved time and gave better error bars, it was chosen as the preferred method.

Equilibrium Curves

In order to compare the performance of different glucose hydrochars, a common adsorption time was used to ensure consistency. The first step in determining this time was to plot the adsorption capacity as a function of adsorption time for each char and the activated carbon, Picachem HP-120. Because of time and material constraints, these plots, also known as Equilibrium Curves, were made for the 8-, 16- and 24-hour glucose chars, and for Picachem. The raw data can be found in Appendix VI. As seen in Figure 2, the adsorption capacity for the 8- and 16-hour glucose chars both peaked at 8 hours, while the 24-hour glucose peaked at 12 hours. After each curve peaks, the lines slowly decline until they reach a constant value referred to as the equilibrium value. This behavior, however, was not observed for Picachem. Although the true equilibration time for the hydrochars was much longer, we chose 24 hours as the pseudo-equilibration time because the capacities at this time were close to the equilibrium values, allowing us to carry out the experiments much quicker. All the experiments comparing the performance of different chars were thus carried out at 24 hours. The raw data for the 24 hour experiments can be found in Appendix VII.

A closer look at the equilibrium curve for the glucose chars shows that the peak capacity falls by ca. 30% before it reaches equilibrium. A plausible explanation to this large change is that its structure breaks down in water during the course of the experiment, specifically after 8 hours. In order to test this hypothesis, the pH of the copper nitrate solution containing the 8-hour glucose char was measured at regular intervals to probe into the changing chemistry. The table below includes the results of the pH test. The highest change in pH value was within the first 4 hours

of the start of the experiment, possibly suggesting some change in functional groups. After this time, the pH gradually decreased at a small rate of less than 3%. Because the pH test method did not show a significant difference, it was probably not the best measure of the changing chemistry in this case. Other analyses, such as chromatography, could be used to try to examine any changes in surface.

	Time (hours) and pH				Percent changes between hours		
Char Type	*0*	*3.5*	*8*	*17.5*	*0 - 3.5*	*3.5 - 8*	*8 - 17.5*
8hg A	3.12	2.86	2.78	2.72	8.33	2.80	2.16
8hg B	3.12	2.86	2.8	2.73	8.33	2.10	2.50
16hg A	3.23	3.01	2.94	2.87	6.81	2.33	2.38
16hg B	3.22	3.01	2.96	2.89	6.52	1.66	2.36
24hg A	3.27	3.04	2.97	2.92	7.03	2.30	1.68
24hg B	3.27	3.06	3.01	2.94	6.42	1.63	2.33
Initial	4.26	4.27	4.25	4.25	-0.23	0.47	0
Picachem	1.88	1.88 (5 hours)			0		

Table 5: pH changes during adsorption experiments

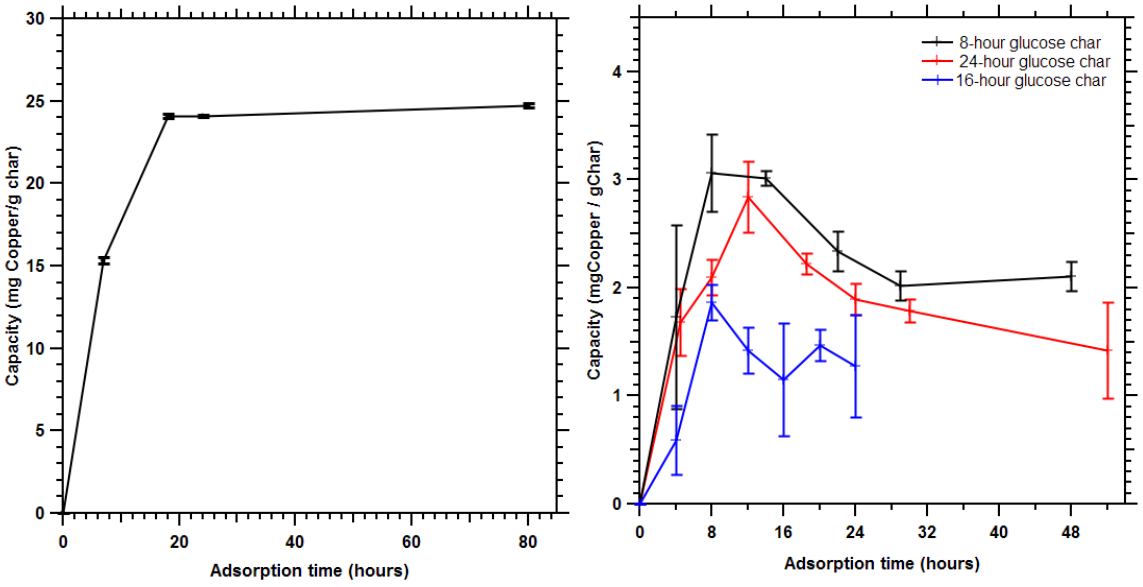


Figure 2: Equilibrium Curves for Picachem HP-120 (left) and hydrochars (right)

Adsorption Capacity by Mass

The chars studied in this experiment were 4-, 8-, 12-, 16-, and 24- hour glucose chars, as well as the activated carbon Picachem HP-120. Each char and activated carbon was shaken for 24 hours in 20 mL of 0.06M copper nitrate solution. Figure 3 shows the adsorption capacity for each char and the activated carbon.

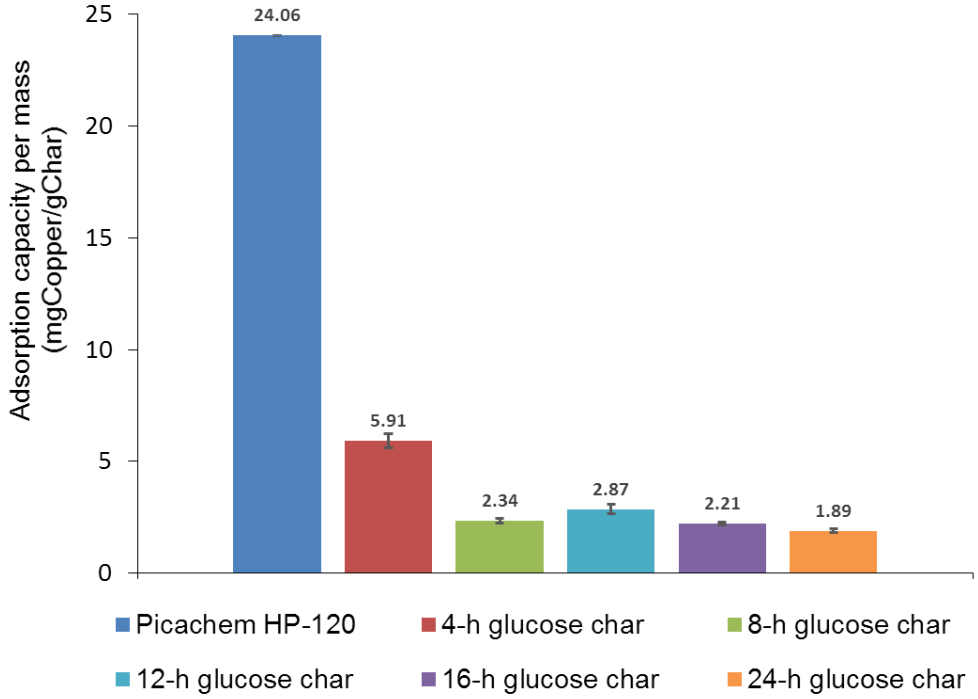


Figure 3: Adsorption Capacity by Mass

Figure 3 shows that Picachem HP-120 has a much higher the capacity compared to the chars, and 4-hour glucose char has the highest capacity among the chars. We furthered this analysis by comparing the surface area of each char with its adsorption capacity to see how much of an influence the surface area had on the adsorption capacity. The surface areas were calculated by DFT fit of nitrogen adsorption isotherm. Figure 4 below displays our findings.

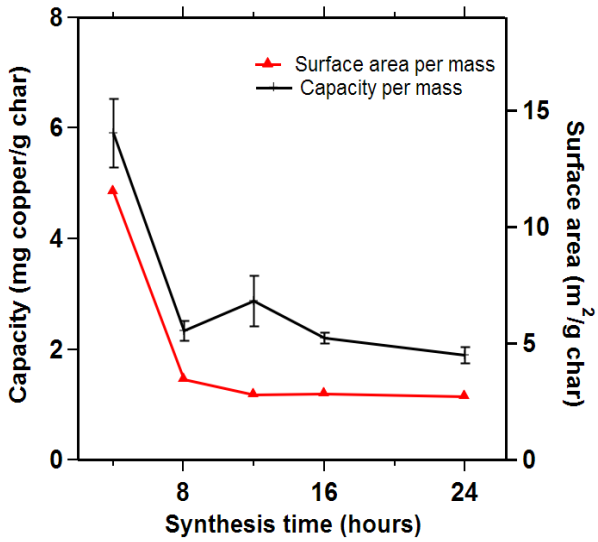


Figure 4: Relationship between the adsorption capacity and surface area of hydrochars.

Char type	DFT Surface Area (m^2/g)
4-hour glucose	11.531
8-hour glucose	3.445
12-hour glucose	2.801
16-hour glucose	2.826
24-hour glucose	2.732
Picachem HP-120	1454

Table 5: Surface Area of Chars

A first glance at figure 4 suggests that the surface area and adsorption capacity are positively correlated. Since 4-hour char has the highest surface area, it would make sense that it would also have the highest adsorption capacity per mass. A similar argument would stand for the capacity difference between the activated carbon and the chars. The surface area of the Picachem HP-120 is 1454 m^2/g compared to 11.5 m^2/g of the 4-hour glucose char (the char with the largest surface area). However, it should be noted although the surface area of the

activated carbon is ca. 100 times larger than that of the char, its adsorption capacity is only 5 times larger. This means that the surface of the char is able to interact much more with the heavy metals.

Adsorption Capacity by Surface Area

The data from our experiments was analyzed to determine which char had the best adsorption capacity per surface area. Figure 5 below displays our results.

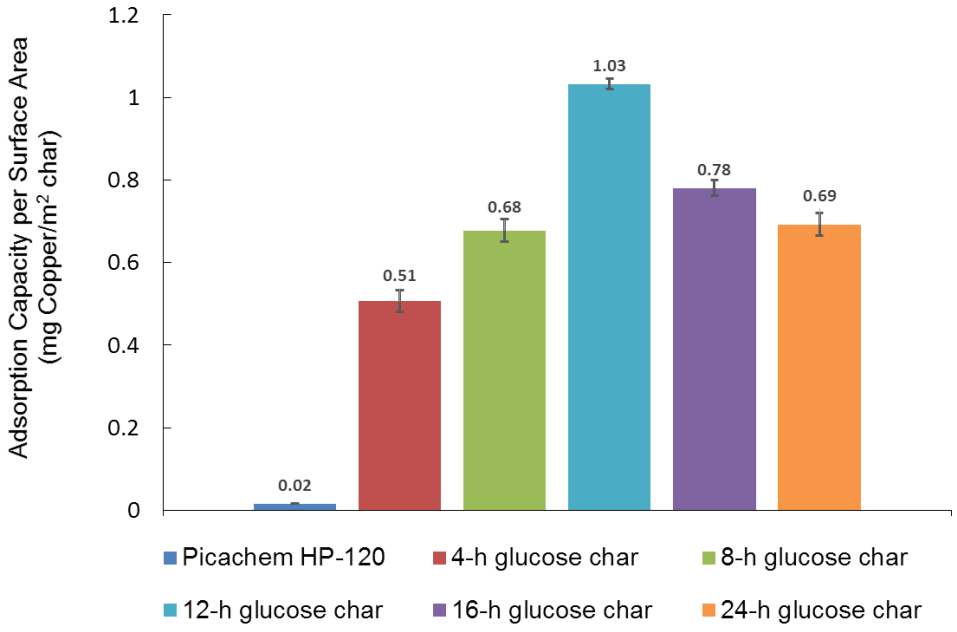


Figure 5: Adsorption Capacity by Surface Area

As expected, the activated carbon was outperformed by the chars on a surface area basis. In fact, the chars were better by a factor of 50. However, it was not expected that the 12-hour glucose char would perform better than the 4-hour glucose char, especially after looking at the trend in Figure 4. This confirms that available surface area alone is not responsible for the adsorption of copper ions. Rather, surface chemistry plays an important role in adsorption. To get a better idea of why the adsorption capacity per surface area is so much greater for the

chars, infrared (IR) spectroscopy was used to look at the surface functional groups present.

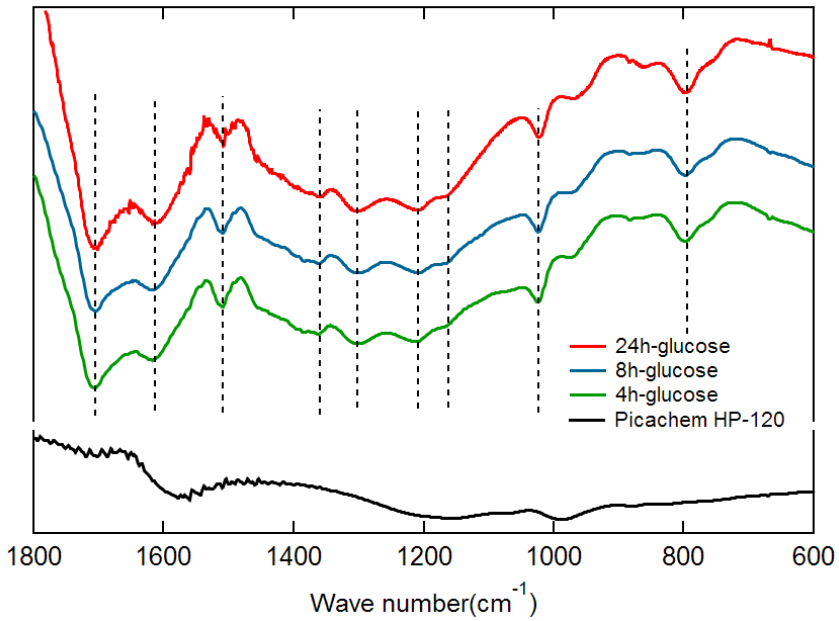


Figure 6: IR Spectrum of different hydrochars compared with Picachem HP-120.

It can be seen that the hydrochars have significantly more oxygen-containing functional groups. Figure 6 above shows the IR spectrum of three glucose chars and Picachem HP-120. The activated carbon seems to have significantly less functional groups compared to the glucose char. In particular, the glucose chars have strong carbonyl (C=O) and hydroxyl (-OH) signals. These negatively (or partial negatively) charged oxygen groups in the carbonyl/hydroxyl groups engage in ionic interactions with the copper (II) ions in solution, and account for the increased adsorption. The lack of these functional groups in particular in the activated carbon explains why the adsorption capacity per surface area is so low. These results are significant because it confirms the possibility that glucose char could be used as an alternative for activated carbon.

The IR spectrum does a good job in explaining the difference in surface chemistry between the glucose chars and Picachem HP-120. However, it cannot be used to compare the surface chemistry between the different glucose chars because the IR spectra of each of these are essentially identical.

In order to look at the differences between the surface chemistry of these chars, various characterization techniques involving Raman Spectroscopy, X-ray photoelectron spectroscopy (XPS) and Nuclear Magnetic Resonance (NMR) spectroscopy could be utilized. An example of a Raman spectrum for an 8-hour glucose char is shown below. The two major peaks shown in figure 7 are the defect peak (D-peak) around 1350 cm^{-1} and the Graphite peak (G-peak) around 1550 cm^{-1}.

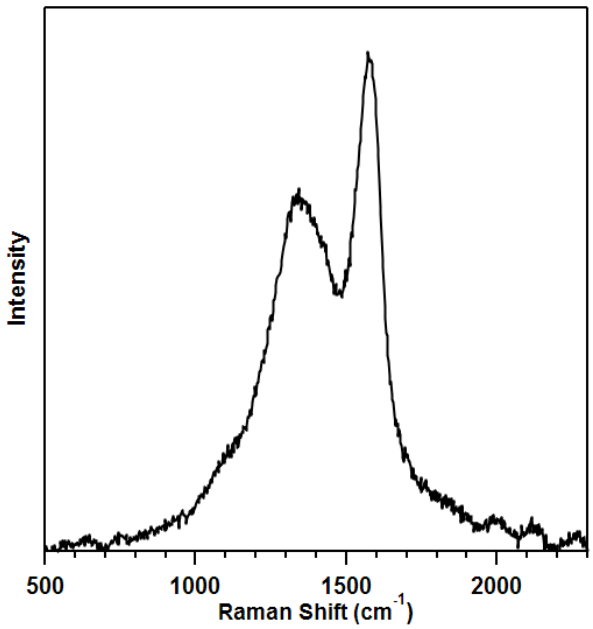


Figure 7: Raman Spectrum of 8-hour glucose hydrochar showing the D and G peaks.

Proper analysis of a Raman spectrum is important to determine the functional groups present. The spectra has to be fitted with different peaks corresponding to the different functional groups, such that sum of the area of the fitted individual peaks equal the area of the overall Raman spectrum. There are several peak assignment techniques, some of which are described by Li et al.[‡] and Sadezky et al.[§] This was, however, beyond the scope of this MQP.

[‡] X. Li, J.-I. Hayashi and C.-Z. Li, Fuel, 2006, 85, 1700-1707.
[§] A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl, Carbon, 2005, 43, 1731-1742.

Conclusion and Recommendations

Although internal surface area is considered to be the major surface property that determines adsorption capacity, the results presented in this report show that there are more factors to consider. Surface chemistry, for example, plays an equal, if not more important, role in determining the amount of copper ions adsorbed onto the surface of the hydrochar. This argument was supported by the observation that the 4-hour glucose char, despite having the largest surface area of 11.5 m^2/g among the chars, performed poorly on a per surface area basis against all the other glucose hydrochars. However, despite having 100 times the surface area, Picachem only had 5 times the adsorption capacity per unit mass. In other words, the 12-hour glucose char performed more than 50 times better on a per surface area basis. This result was attributed to the electrostatic attraction between the Cu^{2+} ions in solution and the electronegative oxygen atoms present on the char surface relating to the aldehyde, hydroxyl, ketone, ester, phenolic and carboxyl functional groups. The specific role of each of these groups on the adsorption capacity, however, could not be determined because it required spectroscopic analysis outside the scope of this MQP.

An interesting behavior was also observed while determining the equilibrium time for the hydrochars. The adsorption capacity seemed to peak around the 8-hour adsorption time, and fell gradually until it reached a constant value after around 30 hours. This behavior was not observed for Picachem HP-120, suggesting that the char was interacting with water during the course of the experiment. The pH tests weakly proved this hypothesis as its value steadily decreased with adsorption time. However, because the difference in pH readings was low, another form of analysis, eg. Chromatography, could be employed to test this hypothesis.

There are many places to start if one wants to build on this work in the future. First of all, the functional group evolution on the char surface with reaction time can be studied to help explain the relationship with the adsorption capacities. Proper characterization of the chars is

therefore important in this regard. The second area that can be studied is the reaction of the chars with water during the adsorption experiments, especially in the time range of 8-16 hours and around the peak. The knowledge of the changing chemistry will prove to be vital because of the insights it can provide on the char structure. The third area to build on could be chemical treatment of the chars. Because of the presence of numerous oxygen groups on the char, it can be treated with acids or other chemicals to add more functionality to the surface. This added functionality could be used, in addition to adsorption site for heavy metals, as a heterogeneous catalyst. Another area to build on is changing the reaction parameters like temperature, concentration, reaction pressure, etc. and observe changes in the surface functionality, with an ultimate goal of maximizing the usefulness of the char.

Works Cited

[1] "Toxic Substances Portal - Copper." Centers for Disease Control and Prevention. Centers for Disease Control and Prevention, 30 Nov. 2016. Web.
[2] "Impacts From Lead and Copper Corossion." Water Research Foundation, n.d. Web. 30 Nov. 2016. <http://www.waterrf.org/knowledge/distribution-system-management/FactSheets/DistributionSystemMgmt_LeadCopper_FactSheet.pdf>
[3] Ibid.
[4] "Drinking Water." Centers for Disease Control and Prevention. Centers for Disease Control and Prevention, 01 July 2015. Web. 30 Nov. 2016. <https://www.cdc.gov/healthywater/drinking/private/wells/disease/copper.html>.
[5] "Impacts From Lead and Copper Corossion." Water Research Foundation, n.d. Web. 30 Nov. 2016. <http://www.waterrf.org/knowledge/distribution-system-management/FactSheets/DistributionSystemMgmt_LeadCopper_FactSheet.pdf>
[6] "Drinking Water." Centers for Disease Control and Prevention. Centers for Disease Control and Prevention, 01 July 2015. Web. 30 Nov. 2016. <https://www.cdc.gov/healthywater/drinking/private/wells/disease/copper.html>.
[7] Worch, Eckhard. *Adsorption Technology in Water Treatment: Fundamentals, Processes, and Modeling*. Berlin ; Boston: De Gruyter, 2012. Print.
[8] Mohan, Dinesh et al. “Organic and Inorganic Contaminants Removal from Water with Biochar, a Renewable, Low Cost and Sustainable Adsorbent – A Critical Review.” *Bioresource Technology* 160 (2014): 191–202. *CrossRef*. Web.
[9] Thompson, Kyle A. et al. “Environmental Comparison of Biochar and Activated Carbon for Tertiary Wastewater Treatment.” *Environmental Science & Technology* 50.20 (2016): 11253–11262. *CrossRef*. Web.
[10] Shackley, S.; Clare, A.; Joseph, S.; McCarl, B. A.; Schmidt, H.-P. “Economic evaluation of biochar systems: current evidence and challenges.” *Biochar for Environmental Management* (2015): 812−851. *CrossRef*. Web.
[11] Alibaba.com. 325 Mesh Powdered Activated Carbon Factory Price. Shanghai Feb. 12, 2016
[12] Wikberg, Hanne et al. “Structural and Morphological Changes in Kraft Lignin during Hydrothermal Carbonization.” *ACS Sustainable Chemistry & Engineering* 3.11 (2015): 2737–2745. *CrossRef*. Web.
[13] Román, S. et al. “Hydrothermal Carbonization as an Effective Way of Densifying the Energy Content of Biomass.” *Fuel Processing Technology* 103 (2012): 78–83. *CrossRef*. Web.
[14] "Renewables." *Bioenergy*. International Energy Agency, n.d. Web. 22 Apr. 2017. https://www.iea.org/topics/renewables/subtopics/bioenergy
[15] Kang, Shimin et al. “Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, d-Xylose, and Wood Meal.” *Industrial & Engineering Chemistry Research* 51.26 (2012): 9023–9031. *CrossRef*. Web.
[16] Ibid.
[17] Meyer, Sebastian, Bruno Glaser, and Peter Quicker. “Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review.” *Environmental Science & Technology* 45.22 (2011): 9473–9483. *CrossRef*. Web.
[18] Funke, Axel, and Felix Ziegler. "Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering." *Biofuels, Bioproducts and Biorefining*, vol. 4, no. 2, 2010, pp. 160-177
[19] Meyer, Sebastian, Bruno Glaser, and Peter Quicker. “Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review.” *Environmental Science & Technology* 45.22 (2011): 9473–9483. *CrossRef*. Web.

[20] Ibid.
[21] Aydıncak, Kıvanç et al. “Synthesis and Characterization of Carbonaceous Materials from Saccharides (Glucose and Lactose) and Two Waste Biomasses by Hydrothermal Carbonization.” *Industrial & Engineering Chemistry Research* 51.26 (2012): 9145–9152. *CrossRef*. Web.
[22] Kambo, Harpreet Singh, and Animesh Dutta. “A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications.” *Renewable and Sustainable Energy Reviews* 45 (2015): 359–378. *CrossRef*. Web.
[23] Funke, Axel, and Felix Ziegler. "Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering." *Biofuels, Bioproducts and Biorefining*, vol. 4, no. 2, 2010, pp. 160-177
[24] Ibid.
[25] Sevilla, M. and Fuertes, Antonio B. (2009), Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides. Chem. Eur. J., 15: 4195–4203.
[26] Meyer, Sebastian, Bruno Glaser, and Peter Quicker. “Technical, Economical, and Climate-Related Aspects of Biochar Production Technologies: A Literature Review.” *Environmental Science & Technology* 45.22 (2011): 9473–9483. *CrossRef*. Web.
[27] Kang, Shimin et al. “Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, d-Xylose, and Wood Meal.” *Industrial & Engineering Chemistry Research* 51.26 (2012): 9023–9031. *CrossRef*. Web.
[28] Titirici, Maria-Magdalena et al. “Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage.” *Energy & Environmental Science* 5.5 (2012): 6796. *CrossRef*. Web.
[29] Ibid.
[30] Aydıncak, Kıvanç et al. “Synthesis and Characterization of Carbonaceous Materials from Saccharides (Glucose and Lactose) and Two Waste Biomasses by Hydrothermal Carbonization.” *Industrial & Engineering Chemistry Research* 51.26 (2012): 9145–9152. *CrossRef*. Web.
[31] Falco, Camillo et al. “Hydrothermal Carbon from Biomass: Structural Differences between Hydrothermal and Pyrolyzed Carbons via 13C Solid State NMR.” *Langmuir* 27.23 (2011): 14460–14471. Print.
[32] Lin, Yousheng et al. “A Mechanism Study on Hydrothermal Carbonization of Waste Textile.” *Energy & Fuels* 30.9 (2016): 7746–7754. *CrossRef*. Web.
[33] Cai, Huaming et al. “One-Step Hydrothermal Synthesis of Carbonaceous Spheres from Glucose with an Aluminum Chloride Catalyst and Its Adsorption Characteristic for Uranium(VI).” *Industrial & Engineering Chemistry Research* 55.36 (2016): 9648–9656. *CrossRef*. Web.
[34] Kang, Shimin et al. “Characterization of Hydrochars Produced by Hydrothermal Carbonization of Lignin, Cellulose, d-Xylose, and Wood Meal.” *Industrial & Engineering Chemistry Research* 51.26 (2012): 9023–9031. *CrossRef*. Web.
[35] Baccile, Niki et al. “Structural Characterization of Hydrothermal Carbon Spheres by Advanced Solid-State MAS ^{13}C NMR Investigations.” *The Journal of Physical Chemistry C* 113.22 (2009): 9644–9654. *CrossRef*. Web.
[36] Titirici, Maria-Magdalena et al. “Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage.” *Energy & Environmental Science* 5.5 (2012): 6796. *CrossRef*. Web.
[37] Aydıncak, Kıvanç et al. “Synthesis and Characterization of Carbonaceous Materials from Saccharides (Glucose and Lactose) and Two Waste Biomasses by Hydrothermal Carbonization.” *Industrial & Engineering Chemistry Research* 51.26 (2012): 9145–9152. *CrossRef*. Web.

[38] Kambo, Harpreet Singh, and Animesh Dutta. “A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications.” *Renewable and Sustainable Energy Reviews* 45 (2015): 359–378. *CrossRef*. Web.
[39] Ibid.
[40] Ibid.
[41] Ibid.
[42] Mahtab Ahmad, Anushka Upamali Rajapaksha, Jung Eun Lim, Ming Zhang, Nanthi Bolan, Dinesh Mohan, Meththika Vithanage, Sang Soo Lee, Yong Sik Ok, Biochar as a sorbent for contaminant management in soil and water: A review, Chemosphere, Volume 99, March 2014, Pages 19-33, ISSN 0045-6535
[43] Kambo, Harpreet Singh, and Animesh Dutta. “A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications.” *Renewable and Sustainable Energy Reviews* 45 (2015): 359–378. *CrossRef*. Web.
[44] Barakat, M.A. “New Trends in Removing Heavy Metals from Industrial Wastewater.” *Arabian Journal of Chemistry* 4.4 (2011): 361–377. *CrossRef*. Web.
[45] Ibid.
[46] Aziz, Hamidi A., Mohd. N. Adlan, and Kamar S. Ariffin. “Heavy Metals (Cd, Pb, Zn, Ni, Cu and Cr(III)) Removal from Water in Malaysia: Post Treatment by High Quality Limestone.” *Bioresource Technology* 99.6 (2008): 1578–1583. *CrossRef*. Web.
[47] Kurniawan, Tonni Agustiono et al. “Physico–chemical Treatment Techniques for Wastewater Laden with Heavy Metals.” *Chemical Engineering Journal* 118.1–2 (2006): 83–98. *CrossRef*. Web.
[48] Barakat, M.A. “New Trends in Removing Heavy Metals from Industrial Wastewater.” *Arabian Journal of Chemistry* 4.4 (2011): 361–377. *CrossRef*. Web.
[49] Kurniawan, Tonni Agustiono et al. “Physico–chemical Treatment Techniques for Wastewater Laden with Heavy Metals.” *Chemical Engineering Journal* 118.1–2 (2006): 83–98. *CrossRef*. Web
[50] Kambo, Harpreet Singh, and Animesh Dutta. “A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications.” *Renewable and Sustainable Energy Reviews* 45 (2015): 359–378. *CrossRef*. Web.
[51] Alibaba.com. 325 Mesh Powdered Activated Carbon Factory Price. Shanghai February 12, 2016

Appendices

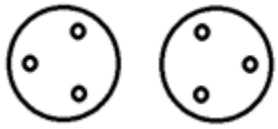
Appendix I- Detailed Lab Procedure

Preparing the samples

1. The copper nitrate solution used is 0.06M. The amount of water and copper nitrate is based on the number of samples being tested. For each experiment, there are two vials containing char and copper nitrate solution, and one vial containing just the initial copper nitrate solution.
    a. The amount of copper nitrate used was 0.2791 g per sample. The copper nitrate was measured in an Erlenmeyer flask using a balance*.
    b. Once the appropriate mass was in the beaker, 20 mL of DI water multiplied by the number of samples was measured out using a graduated cylinder*. The water was then added to the flask and stirred with a magnetic stirrer for 20 minutes. The flask was covered with parafilm to ensure no vapor escaped.
2. While the solution is being stirred, measure out 0.4000 $\pm$0.008g of char in each vial*.
3. Using a pipette, transfer 20 mL of copper nitrate solution into each vial.
4. Place the vials into the shaker and turn the wrist-action shaker on.

Analyzing the Samples

1. After the samples have been shaken for the desired amount of time, take both samples and the vial containing its initial solution out of the shaker.
2. Transfer the contents of the vials into their own plastic vial. The plastic vial is designed for the centrifuge which will be used for filtration.
3. The vials are then placed in the centrifuge as described in the figure below. It is important to keep the centrifuge balanced. If only three samples are going into the centrifuge, fill three plastic vials with about 20 mL of water each and place on the other side.



4. Set the centrifuge to 4000 rpm and run for 5 minutes.
5. After the centrifuge has come to a complete stop, take out the plastic vials. The solid char should be at the bottom and liquid copper nitrate solution at the top of the vial. Using a syringe, suction out the copper nitrate solution and place it in a clean glass vial. Do this for each vial.
6. Start the UV machine, and before opening up the Software, make a new folder with its name as the date.
7. DI water is used as a blank before any samples can be tested.
8. Using a syringe, suction out some of the solution from the vial. Place the filter on the syringe and then transfer the liquid into the cuvette. Place the cuvette with the logo facing towards the machine, and use the software to run the machine. Find the peak of the curve*.

a. Repeat this at least two more times for this sample** Shake the vial for about 5 seconds before doing another reading to ensure the copper is equally distributed throughout the solution.
    i. Example for saving the file: 8HG12HA (8-hour glucose 12 hour shake)
    ii. Clear data on software before collecting data from other samples
b. Repeat step 8 for sample b and the initial solution.

*Record in notebook

**Do more readings if a lot of variation

Appendix II- Calibration Curve Raw Data

Concentration	AU 1	AU 2	St dev	Error
0.08	0.915881	0.916729	0.000424	0.000299813
0.07	0.80658	0.804975	0.0008025	0.000567453
0.06	0.691442	0.694518	0.001538	0.00108753
0.05	0.577569	0.573232	0.0021685	0.001533361
0.04	0.468702	0.46699	0.000856	0.000605283
0.03	0.36121	0.356354	0.002428	0.001716855
0.02	0.23962	0.238038	0.000791	0.000559321
0.01	0.11933	0.120246	0.000458	0.000323855

Appendix III- Amount of Char Used Raw Data

0.4 grams of 5/8 8-hour glucose char, 12 and 24h shakes — Date of UV-Vis: 9/9/16

Vial#	Hours	AU 1	AU 2	AU 3	Average Capacities	Averag	Average % Copper Adsorbed
8A	8	0.68295	0.67829	0.67882	1.079408901	0.0589	0.5734
8B	8	0.67796	0.67826	0.67808	1.620484402	0.0588	0.8592
8OA	8	0.67547	0.67655	0.67547	2.257072937	0.0586	1.197
Pure/Initial		0.68386	0.68355	0.68421			
12A	12	0.62972	0.63951	0.623321	9.504029438	0.0546	5.2139
12B	12	0.65226	0.645209	0.640969	5.261421285	0.056	2.8713
24A	24	0.6459	0.64795	0.653417	4.423770524	0.0562	2.4208
24B	24	0.66715	0.66348	0.667239	-0.297359514	0.0577	-0.162
Pure/Initial		0.67453	0.656441	0.663723			

0.6 grams of 8hg & Picachem HP 120 — Date of UV-Vis: 9/14/2016

Vial#	Hours	AU 1	AU 2	AU 3	Average Capacities	Averag	Average % Copper Adsorbed
12A	12	0.6655	0.67153	0.670788	2.136443642	0.058	1.7101
12B	12	0.65991	0.670964	0.670837	2.515983525	0.0578	2.0146
Pure/Initial		0.66387	0.689031	0.689229			
24A	24	0.64895	0.643041	0.641638	2.648206636	0.0558	2.1914
24B	24	0.65639	0.652966	0.630929	2.235687398	0.056	1.8485
Pure/Initial		0.64657	0.65533	0.674257			

0.2 grams of 5/8 8-hour glucose char & oven dried same char — Date of UV-Vis: 9/4/16

Vial#	Hours	AU 1	AU 2	AU 3	Average capacities	Averag	Average % Copper adsorbed
8C	8	0.67958	0.68208	0.68054	1.757857655	0.059	0.4673
8D	8	0.67893	0.67978	0.67968	2.467606344	0.0589	0.6563
8OB	8	0.67826	0.67842	0.67711	3.317303122	0.0588	0.8845
Pure/Initial		0.68386	0.68355	0.68421			

0.06 grams of 5/8 8-hour glucose char — Date of UV-Vis: 8/31/2016

Vial#	Hours	AU 1	AU 2	AU 3	Average capacities	Averag	Average % Copper adsorbed
4A	4	0.69572	0.69747	0.69656	-2.789200635	0.0604	-0.217
4B	4	0.69736	0.69788	0.69694	-4.265539784	0.0605	-0.335
5A	5	0.69598	0.69986	0.69895	-5.876311051	0.0606	-0.463
5B	5	0.69811	0.69909	0.69744	-5.792938309	0.0606	-0.455
Pure/Initial		0.69578	0.69483	0.6947			

Appendix IV- Centrifuge vs. Vacuum Filtration Raw Data

Vial#	Hours	AU 1	AU 2	AU 3	Average Capacity	Final Capacity	Error
19A cent	19	0.606206	0.605648	0.605776	23.79455		
19B cent	19	0.607662	0.606864	0.607821	23.30655	23.55055	0.106973
19C (filt)	19	0.612567	0.612038	0.61118	24.11676		
19D (filt)	19	0.622119	0.618215	0.607034	23.01221	23.56448	0.565401

Appendix V- Equilibrium Curve Raw Data

8-hour glucose hydrochar							
Vial#	**Hours**	**AU 1**	**AU 2**	**AU 3**	**Average Capacity**	**Final Capacity**	**Error**
4A	4	0.68996	0.689356	0.691997	3.797334		
4B	4	0.704525	0.705103	0.705861	-0.3329	1.732216	0.849187
8A	8	0.687842	0.688097	0.687739	3.875468		
8B	8	0.693451	0.695867	0.692032	2.244261	3.059864	0.357088
14A	14	0.677163	0.677215	0.678828	3.086873		
14B	14	0.678313	0.678342	0.678016	2.946855	3.01686	0.069866
22A	22	0.694569	0.693853	0.696004	2.729896		
22B	22	0.697221	0.696986	0.698666	1.940193	2.335044	0.186599
29A	29	0.681287	0.685472	0.684958	6.924086		
29B	29	0.67344	0.675395	0.675292	9.491891	2.017993	0.131555
48A	48	0.699479	0.699298	0.7011	2.103738	2.103738	0.130933
					Average Initial		
Init 4	4	0.704909	0.703872	0.703149	0.703977		
Init 8	8	0.700786	0.702425	0.702096	0.701769		
Init 14	14	0.68811	0.688648	0.689441	0.688733		
Init 22	22	0.704688	0.704531	0.704443	0.704554		
Init 29	29	0.708596	0.707739	0.709573	0.708636		
Init 48	48	0.706471	0.70738	0.708573	0.707475		

16-hour glucose hydrochar							
Vial#	**Hours**	**AU 1**	**AU 2**	**AU 3**	**Average Capacity**	**Final Capacity**	**Error**
4A	4	0.702638	0.709387	0.710889	0.891726		
4B	4	0.708702	0.71007	0.710653	0.284191	0.587959	0.322431
8A	8	0.694995	0.710134	0.712787	2.12522		
8B	8	0.712567	0.713604	0.71379	1.604909	1.865065	0.163635
12A	12	0.704705	0.709737	0.709677	1.633223		
12B	12	0.709245	0.709898	0.709577	1.202383	1.417803	0.211222

Vial#	Hours	AU 1	AU 2	AU 3	Average Capacity	Final Capacity	Error
16A	16	0.702017	0.710752	0.712524	2.005421		
16B	16	0.714259	0.714839	0.715469	0.289416	1.147419	0.524663
20A	20	0.69243	0.702971	0.702983	1.709339		
20B	20	0.706034	0.704545	0.703491	1.229847	1.469593	0.507702
24A	24	0.692358	0.701871	0.711514	1.956775		
24B	24	0.710792	0.71264	0.713315	0.399801	1.178288	0.870381
					Average Initial		
Init 4	4	0.711019	0.710485	0.71096	0.710821		
Init 8	8	0.71732	0.71907	0.720746	0.719045		
Init 12	12	0.713048	0.712899	0.71565	0.713866		
Init 16	16	0.716253	0.715587	0.714898	0.715579		
Init 20	20	0.70953	0.708645	0.709076	0.709084		
Init 24	24	0.713433	0.713057	0.714528	0.713673		
24-hour glucose hydrochar							
Vial#	**Hours**	**AU 1**	**AU 2**	**AU 3**	**Average Capacity**	**Final Capacity**	**Error**
4A	4.5	0.70488	0.705272	0.706203	2.355614		
4B	4.5	0.708666	0.711992	0.710993	1.002028	1.678821	0.305317
8A	8	0.690001	0.690175	0.691942	2.422055		
8B	8	0.692338	0.692603	0.694218	1.770331	2.096193	0.164997
12A	12	0.698321	0.699246	0.701491	3.403007		
12B	12	0.701762	0.702081	0.707379	2.265825	2.834416	0.330251
18A	18.5	0.703932	0.704678	0.706436	2.346998		
18B	18.5	0.705998	0.705733	0.706003	2.096383	2.22169	0.099522
24A	24	0.675905	0.679855	0.676509	1.876001		
24B	24	0.676503	0.677893	0.677496	1.905074	1.890537	0.148591
30A	30	0.712474	0.711176	0.713025	1.940709		
30B	30	0.712324	0.713688	0.713875	1.63952	1.790115	0.104171
					Average Initial		
Init 4	4.5	0.713333	0.713333	0.714904	0.713857		
Init 8	8	0.703036	0.698692	0.696381	0.699370		
Init 12	12	0.711342	0.711292	0.712805	0.711813		
Init 18	18.5	0.712718	0.712188	0.715313	0.713406		
Init 24	24	0.684206	0.684142	0.683972	0.684107		
Init 30	30	0.719884	0.717967	0.719577	0.719143		

Appendix VI- Each char at 24 hour shake Raw Data

Vial#	AU 1	AU 2	AU 3	Average Capacity	Final Capacity	Error
4A	0.68509	0.69386	0.69521	7.090568908		
4B	0.69921	0.7003	0.70119	4.735174305	5.912872	0.627907
8A	0.694569	0.693853	0.696004	2.729896075		
8B	0.697221	0.696986	0.698666	1.940192538	2.335044	0.186599
12A	0.76018	0.761581	0	3.91291835		
12B	0.767797	0.768504	0.768656	1.82302199	2.86797	0.462678
16A	0.675372	0.675696	0.675592	2.39838555		
16B	0.675896	0.677992	0.67686	2.015784824	2.207085	0.104996
24A	0.675905	0.679855	0.676509	1.876000736		
24B	0.676503	0.677893	0.677496	1.905074164	1.890537	0.148591
12A (0.04M)	0.459834	0.456036	0.457542	1.706064423		
12B (0.04M)	0.456983	0.457597	0.45874	1.710393991	1.708229	0.139649
24A	0.639585	0.639209	0.639911	23.92889817		
24B	0.638505	0.638215	0.639627	24.18564715	24.05727	0.075655
				Average Initial		
Init 4	0.71838	0.71499	0.71667	0.71668		
Init 8	0.704688	0.704531	0.704443	0.704554		
Init 12	0.774265	0.774914	0.775253	0.774811		
Init 16	0.684206	0.684142	0.683972	0.684107		
Init 24	0.684206	0.684142	0.683972	0.684107		
Init 12 (0.04M)	0.467223	0.460811	0.463599	0.463878		

Appendix VII- Sample Calculations

For the following calculations, the data for Vial# 4A and 4B listed in the table in Appendix VII are used:

Vial#	AU 1	AU 2	AU 3	Average Capacity	Final Capacity	Error
4A	0.68509	0.69386	0.69521	7.090568908		
4B	0.69921	0.7003	0.70119	4.735174305	5.912872	0.627907
				Average Initial		
Init 4	0.71838	0.71499	0.71667	0.71668		

In order to determine the final capacity of the hydrochar from the UV-Vis absorption data, each of the three Absorption Units (AU 1, AU 2 and AU 3) were first converted, using the calibration curve equation, to concentration:

$$\frac{0.68509 - 0.0119}{11.334} = 0.059395624 \text{ M}$$

This value is then converted to grams of Copper by first determining the number of moles of copper nitrate solution and then multiplying it by the molar mass of copper:

$$(0.059395624\ M * 0.02\ L) * 63.546\ g/mol = 0.075487086\ g$$

Similarly, for the initial value of 0.71838:

$$\frac{0.71838 - 0.0119}{11.334} = 0.062332804 \text{ M}$$

Converting to grams of copper

$$(0.062332804\ M * 0.02\ L) * 63.546\ g/mol = 0.079220007\ g$$

Now, calculate the mass of copper adsorbed, divide by the mass of hydrochar used, and multiply by 1000 to convert to milligrams:

$$\frac{0.079220007g - 0.075487086\ g}{0.4\ g} * 1000\frac{mg}{g} = 8.855735574\frac{mg\ Copper}{g\ char}$$

These steps were applied to all the 6 readings in vials 4A and 4B, and the average capacities calculated. The errors were calculated using:

$$Error = \frac{Standard\ deviation\ of\ all\ the\ calculated\ capacities}{\sqrt{(Number\ of\ observations)}}$$