Adsorption of Copper Ions from Water via Activation of Hydrothermal

Carbonization of Glucose

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Abstract

In many water bodies across the globe there is the presence of heavy metals such as copper. This contamination can be very detrimental to individuals as it can lead to significant health risks. A fairly new investigated area of this kind of water remediation is the use of sorption materials than can adsorb the heavy metals from the water bodies and aqueous solutions. Investigated in this project, possible sorption materials include hydrothermal carbonization (HTC) of glucose and its activation via potassium hydroxide (KOH) and a one-step HTC of glucose in the presence of acrylic acid monomer. Using measurements of copper adsorption from aqueous solutions, it was found that the best sorption material of these three was the KOH activated hydrochar.

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Introduction

In many bodies of water across the globe, there are heavy metals dissolved within them. This occurrence can very harmful to many countries if the water is to be consumed or used for other purposes. The method in which these heavy metals arrive in these water bodies is by human activities including manufacturing, mining, and improper use of locations for waste disposal. There are several health risks associated with consuming heavy metal-contaminated water, such as: toxic kidney effects, intestinal damage, anemia, and possibly cancer (Garbarino et al., 1992). Although this is a very serious problem, a large issue in attempting to remove these contaminants from water bodies is that the process is quite costly. Common methods used for removing heavy metals from water include: chemical precipitation, ion exchange, membrane filtration, and adsorption (Kurniawan et al., 2006). Of these four, it is known that adsorption is the most effective, especially when using activated carbon (Madhava Rao et al., 2006). But, even though it has been proven that activated carbon is an adsorbent for removing metals, using it is expensive and causes the search for a more affordable adsorbent. Because of this, many other alternative, low-cost, adsorbent materials capable of removing heavy metals from aqueous solutions have been attempted to be produced for wide use.

An alternative sorption material that has been thoroughly studied is hydrothermal char. The adsorption properties and capabilities of hydrothermal char are very similar to that of activated carbons. In this project, three different types of hydrothermal char were tested for their adsorption properties of copper ions within water in an aqueous solution. The three types of char used are: regular hydrothermal carbonization of glucose (referred to as glucose chars), potassium hydroxide-activated glucose chars (referred to as KOH char), and HTC of glucose in the presence of acrylic acid (referred to as acrylic char). The intent of this experiment is to observe

the adsorption capacity of each of the different char materials and to understand the effect on adsorption for varying reaction times of 8, 16, and 24 hr chars. All of the chars were prepared in the chemical engineering laboratories at Worcester Polytechnic Institute. The adsorption capability comparison was done by comparing the milligrams of copper adsorbed for every gram of char for each char type. Additionally, the adsorption capability of four batches of one of the char types was tested and observed to confirm reproducibility.

Background

Hydrothermal Carbonization (HTC)

Hydrothermal carbonization (HTC) is a technique that has received considerable attention because of its ability to produce hydrothermal chars (hydrochars) with characteristics that promote efficient utilization for many applications including: adsorption, bio imaging, catalysis, and activated carbon synthesis among others (Jain & Srinivasan, 2016). A great thing about hydrochars is that they can be made from biomass waste, meaning that converting this waste into hydrochar can reduce increasing amounts of solid waste. Additionally, hydrochars can use a variety of biomass materials such as feedstock, sewage slide, animal wastes, and agricultural wastes (Kambo & Dutta, 2015). Other characteristics of hydrochar that highlight its efficient utilization include high ash content and product yield at relative low temperatures. Ash content is the mineral content and other inorganic matter that is present in biomass (Sluiter et al., 2008). The process of HTC occurs at temperatures between $180°C$ and $250°C$, which does not require much energy for most ovens to reach and maintain for long periods of time. In order to yield hydrochar product within the 40% to 70% range, the reaction should be held between $180°C$ and $250°C$ and a residence time of at least 240 minutes (Kambo & Dutta, 2015).

The HTC process occurs when hydrochar is made as a solid and liquid two-phase mixture, also known as a slurry, that experiences a thermochemical conversion of organic material into a solid product that is carbon rich. This slurry is made by adding water to the biomass. This mixture is heated in a closed system within the temperature range detailed and experiences a pressure of 2 to 6 MPa. The pressure is not added, but instead is generated as the reaction occurs at the temperature range. From this reaction, three major products are produced:

the solid hydrochar, the liquid bio-oil/water solution, and a small fraction of gases, a majority of which is carbon dioxide. Before this raw material product can be used as a useful energy source, it must undergo further steps including: washing, filtering, and drying, in order to be made into its final, ready-to-use form.

Using HTC as an alternative method for creating adsorption materials is becoming more popular since it is safer for the environment as it does not produce any toxic emissions (Kambo & Dutta, 2015). The chemical structure of hydrochars include aromatic structures that contain many oxygen-containing functional groups, which give the advantage of further functionalization for hydrochar by the previously mentioned methods (adsorption, catalysis, and activated carbon synthesis). Specifically, in hydrochars, its many oxygen-containing functional groups present on the surface and lower carbon content allow for a reduction in environmental contaminants in addition to making it a more sought-after method for producing more affordable adsorbent material (Sun et al., 2015). Because of this, the process of HTC has the potential of being used as an environmentally-conscious method for producing a variety of adsorption materials for industrial use and heavy metals in water remediation.

In the thermochemical reaction of the HTC process, biomass is converted by a series of hydrolysis, condensation, decarboxylation, and dehydration reactions. Since this process is fairly new, the formation of aromatic compounds during HTC at different temperature stages from various feedstocks is highly complex and not fully understood (Demir-Cakan et al., 2009). The chemical properties of hydrochars are characterized as being dominated by aliphatic, aromatic, and alkyl groups, containing low degree of carbonization, low degree of aromaticity, and high proportion of functional groups on it surface. These oxygen-containing functional groups present

on the surface of hydrochars are the key aspects that allow for the removal of heavy metals in the aqueous solution.

The important characteristic of heavy metal adsorption in hydrochars has led to the method of attempting to remove dangerous elements from water streams, such as copper and lead. These two heavy metals, specifically, are detrimental if consumed in drinking water as they can lead to serious health issues including intestinal and brain damage (Garbarino et al., 1992). These metals enter water bodies by way of plumbing materials or waste runoff streams from industrial sites. In 1991, the Environmental Protection Agency (EPA) created the 'Lead and Copper Rule' that controls the amount of copper and lead that is allowed in drinking water. This rule allows for systems to monitor the drinking water at customer taps and if it occurs that anyone or business exceeds the allowed level (15 ppb lead and/or 1.3 ppm copper) then they would be labeled and immediate actions would occur to correct the concentration of lead and copper to the maximum allowable concentrations (EPA, 2016). As a result of the placement of this rule, a majority of drinking water service lines were replaced to remedy the issue that was also made present in corrosive pipes transporting the water (EPA, 2016).

Sorption Materials

Since the goal of this project was to observe the relationship between copper adsorption from an aqueous solution and different char types and reaction times, there were two methods of activation used to activate the hydrochars to create more variation within the hydrochar species. The two methods of hydrochar activation were activation by potassium hydroxide and activation

by the presence of acrylic acid during HTC. With these three different char types and three different reaction times (8, 16, and 24 hours)

Glucose Chars

The precursor for the hydrochars that was used specifically in this project was D-glucose. Glucose was used since it is commonly used in previous studies of the HTC process and it is a substance that is plentiful from the hydrolysis of cellulose found in agricultural waste. Glucose was used as the precursor also because it is the most abundant substance that reacts in cellulose-based material in organic waste. Glucose was a prime compound to use since it is also the basis that determine the functional groups present in the hydrochar's surface and therefore the adsorption characteristics. During HTC with glucose, the glucose will experience decomposition, dehydration, and fragmentation. The decomposition of glucose leads to the formation of organic acids such as: acetic, lactic, propenoic, levulinic, and formic. Dehydration and fragmentation give rise to different soluble products, such as furan-like compounds, acids, and aldehydes. Even further decomposition of the furan-like compounds produces acids, aldehydes, and phenols (Sevilla & Fuertes, 2009). After this break down of glucose, the intermediate compound of these reactions then undergoes polymerization or condensation reactions which lead to the formation of soluble polymers. From this, the formation of aromatic clusters can also be produced (by the condensation and intermolecular dehydration reactions) of aromatized molecules that were made in the decomposition of glucose (Sevilla & Fuertes, 2009). Since the temperatures for which HTC occurs, the processes of aromatization and polymerization are favored. Because of this, the diameter of the pores of the hydrochar increase which can allow for more surface contact availability when mixed with aqueous solutions. Although hydrochar has been proven to be an

effective adsorption material, it still does not always adsorb to its fullest potential since often hydrochar product has blocked pores which hinder access to all of its surface area.

Activating the Hydrochar

As previously stated, the two methods for activating the hydrochar used in this experiment was activation by potassium hydroxide and activation by acrylic acid. The goal of activation in general is to enhance the hydrothermal char's surface in order to enable the char to have better adsorption capabilities. Activation of hydrochar by potassium hydroxide occurs by enhancing the porosity of the char and cleaning up the partially blocked pores of the hydrochar. By enhancing and cleaning the pores of the hydrochar, the surface area of the activated hydrochar can be increased which may enhance the adsorption capacity of the activated char. Past research studies of activation biochar with potassium hydroxide (KOH) has shown that copper adsorption increases with KOH strength. In one research article by Regmi et al. it was found that activating the biochar with a 2N KOH solution allowed the char to adsorb the metals from the aqueous solution at nearly 100% (Regmi et al., 2012). Additionally, in the same article, it was found that the pH value range for optimal copper adsorption from aqueous solutions occurred between pH values of 5.0 and 7.0. Using the results from Regmi et al., the hydrochar in this experiment was activated using 2N KOH solution and maintaining the pH of the activated char between a pH of 5.0 to 7.0. Maintaining the pH of the KOH activated char is important because it has an effect on adsorbent surface charge and ionization and influencing the degree of ionization and speciation of the adsorbate (Regmi et al., 2012). At a pH of 2, the adsorption capacity was found to have extremely low values (0% to 10% adsorption) likely due to the

linkage of protons with oxygen-containing functional groups that inhibit access for the metal ions, such as copper, present in the aqueous solution (Regmi et al., 2012).

Activation of the hydrochar with acrylic acid was a different process than activation with potassium hydroxide. The activation method using potassium hydroxide occurs by activating already made hydrochar via HTC. The method for activating the hydrochar via acrylic acid is different from the potassium hydroxide activation method in that the activate hydrochar is produced in a one-step approach using HTC of glucose in the presence of acrylic acid. The presence of acrylic acid means that the acrylic is a functional organic monomer (Demir-Cakan et al., 2009). Using acrylic as the functional organic monomer results in carboxylate rich absorbents that can be used to remove heavy metals in aqueous solutions. The HTC of glucose and acrylic acid causes the chemical reaction to produce a final activated hydrochar product that is carbonaceous and contains carboxylic acids all along the surface of the material. The benefit and purpose of activating hydrochar via acrylic acid, and organic monomers in general, is that the carbonaceous adsorbents may offer certain advantages due to their rigid porous structures and high chemical, thermal, and ionizing radiation stability (Demir-Cakan et al., 2009). Activation of hydrochar in this method was employed in this project because it required a small amount of acrylic acid and was a substance that is relatively cheap to create that has better adsorption capabilities than inactivated hydrochars.

Methodology

Creation of Hydrothermal Carbonization of Glucose

To prepare the glucose hydrochars at reaction times of 8, 16, and 24 hours, a 10% weight ratio of D-glucose (Sigma-Aldrich, 99.5%) was dissolved in a 100 mL solution of deionized water. This ratio was always approximately 25 grams of D-glucose mixed with approximately 85 mL of deionized water. The mixture was then stirred using a magnetic stir bar for approximately 15 minutes to produce a well-mixed solution and to ensure that all of the glucose completely dissolved. This mixture was then transferred to a 160 mL Teflon inlet which was then placed into a stainless-steel autoclave. The autoclave was then bolted down (pressure sealed) and placed in an oven at $180°$C. The autoclave was kept in the oven at this temperature for either 8, 16, or 24 hours depending on which reaction time was desired to use. After the reaction time was complete, the oven was turned off while not removing the autoclave from it since the water in the solution creates its own pressure and would cause the solution to burst out of the Teflon inlet if any pressure was released too quickly. After allowing the autoclave to cool and decrease in pressure for 12 hours, the reaction mixture was washed with 200 mL of 1:1 H_2O:EtOH solution. The mixture was stirred with this solution for 30 minutes. The solution mixture was then vacuum filtered via Buchner funnel and the residual char left behind was transferred to a tared, ceramic crucible. The crucible was then placed in an oven to dry for 24 hours at $65°$C. Once the char was dried, it was grinded up using a mortar and pestle and transferred to a tared, labeled vial; a vial large enough to contain all of the char that was produced.

Activation of Hydrochar via Potassium Hydroxide

To activate each type of already created hydrochar, 2 grams of the hydrochar type (8, 16, and 24 hr reaction times) were mixed with 500 mL of 2N KOH solution using a magnetic stir bar and stirred for 1 hour. After mixing with the solution, the mixture was vacuum filtered via Buchner funnel and the residual char behind was transferred to an Erlenmeyer flask. Then 50 mL of deionized water was added to the flask containing the residual char and this solution mixture was stirred using a magnetic stir bar for 30 minutes. After mixing, the pH of the solution was measured using a pH meter. The pH of the mixture was brought to a pH value that was within the range of 5.0 to 7.0 using 1N HCl and/or 1N NaOH solution. Once the desired pH was reached, the solution mixture was allowed to stir for an additional 30 minutes and its pH value measured again to ensure that the pH stabilized within the pH value limited range. If the pH was too low or too high, the pH was adjusted accordingly and the pH stabilization process was repeated until the pH was within the accepted range. Once the target pH value was reached, the solution was vacuum filtered via Buchner funnel and the residual char washed 3 times with 50 mL of deionized water while still in the Buchner funnel. The residual char was then transferred to a tared, ceramic crucible and placed in an oven at $100\,^{\circ}C$ to dry for 24 hours. After drying was completed, the now potassium activated hydrochar was grinded using a mortar and pestle and transferred to a tared, labeled glass vials.

Activation of Hydrochar via Acrylic Acid

To activate the glucose char via acrylic in a one-step HTC process, a solution mixture of 10% acrylic acid and 10% D-glucose by weight ratios was made with deionized water for a total

mass of approximately 100 grams. The mixture was then stirred using a magnetic stir bar for 15 minutes to allow for a well-mixed solution and to ensure that all of the glucose dissolved. This mixture was then transferred to a 160 mL Teflon inlet which was then placed into a stainless-steel autoclave. The autoclave was then bolted down (pressure sealed) and placed in an oven at 190˚C. The autoclave was kept in the oven at this temperature for either 8, 16, or 24 hours depending on which reaction time was desired to use. After the reaction time was complete, the oven was turned off while keeping the autoclave inside the oven. After allowing the autoclave to cool and decrease in pressure for 12 hours, the reaction mixture was transferred to an Erlenmeyer flask and mixed with 100 mL deionized water. This solution was stirred using a magnetic stir bar for 30 minutes and then vacuum filtered via Buchner funnel. The residual char was then transferred to a tared, ceramic crucible and placed in an oven to dry for 12 hours at 65˚C. After drying, the acrylic acid char was grinded using a mortar and pestle and transferred to a tared, labeled glass vial.

Copper Adsorption Measurement

To test the adsorption capabilities of each of the different hydrochars, 0.08 M stock solutions of copper nitrate in deionized water (using $Cu(NO_3)_2 \cdot 2.5\ H_2O$) were prepared. Due to the very limited amount of each hydrochar type, a ratio of 0.2 grams of hydrochar and 10 mL of the 0.08 M $Cu(NO_3)_2$ solution was added to a plastic 50 mL centrifuge tube and placed in a mechanical arm shaker. The shaker was set to agitate for a total contact time of 24 hours. After shaking, the plastic tubes were removed from the shaker and the aqueous portion of the mixture was extracted by vacuum filtration via Buchner funnel and syringe filtration via 0.45 µm pore sized syringe filters. Once the aqueous solutions were extracted from the mixtures, they were

diluted down to 488 ppb in order to be measured for the amount of copper concentration present in them. Each solution was diluted to a very low concentration since the apparatus used to determine the final copper concentration of each solution was inductively coupled plasma (ICP) in an environmental engineering laboratory at Worcester Polytechnic Institute. Different concentration of calibration samples using a Cu standard solution (Cu standard for IC, Sigma-Aldrich) were used to create a calibration curve to be used to interpret the data collected in the ICP. An example of the calibration concentrations and curve used in this experiment can respectively be seen below.

Table 1: Example of Calibration Curve points used for ICP data collection interpretation.

Cu Concentration (ppb)	ICP value (ppb)	ICP value (M)
10	10.000	0.0016
50	50.338	0.0082
100	99.065	0.0162
200	201.616	0.0330
400	408.065	0.0669
500	496.885	0.0814

Cu(NO_3)_2 Calibration Curve

$y = 6103.4x + 6E\text{-}14$
$R^2 = 1$
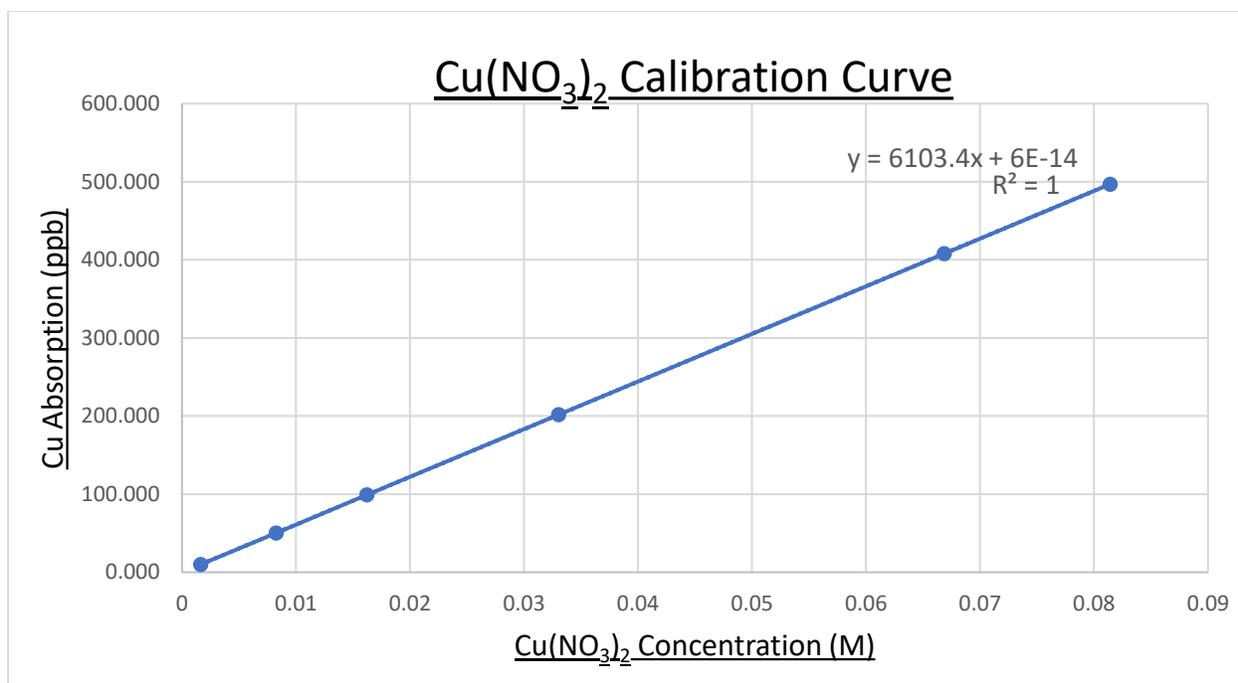
Figure 1: Example of calibration curve used to interpret collected ICP data for all hydrochars.

In addition to agitating the hydrochars for 24 hours, 10 mL of just copper solution for each stock solution made for each hydrochar type also underwent all of the same agitation to dilution steps and was used to compare and determine how many milligrams of copper were adsorbed for 1 gram of each char type. Once all data were collected via ICP, the concentration values of copper in each solution were scaled back up to a concentration in units of molarity.

Measurement of pH

The pH of each hydrochar was measured by agitating 0.2 grams of hydrochar with 10 mL of deionized water for 30 minutes. After this, the chars were measured using a pH meter calibrated between pH values of 4.0 and 7.0. The pH meter was washed in between each new measurement

recording for each hydrochar type with deionized water and carefully removing any droplets from the previous pH measurement.

Reproducibility of Hydrochar

To test the reproducibility of creating new hydrochars throughout this experiment and being able to test newly made hydrochars to achieve the same or very similar results, three other batches of 8-hour glucose chars were used and copper adsorption tested. The additional three batches were provided by a graduate student, John Hobson, who had recently created fresh batches of 8-hour glucose chars. However, Hobson did not wash all glucose chars three times with water as outlined in the protocol. Because of this, it would be expected that not all of the collected ICP data of copper adsorption capacity would be accurate for this char type.

Rama Spectroscopy Analysis

All hydrochar types were observed using Raman spectroscopy in order to learn more about the functional groups present on the surface of each of the hydrochars. The Raman apparatus was set to use a green laser (at 532 nm) with a grating value of 1800. Each hydrochar type had 7 different spots of its surface that were observed under Raman spectroscopy. The spectra produced for each char type was then substituted by using the non-peaks (continuous spectral line) as a baseline adjustment correspondent to better measure the intensities of the distinct peaks produced in the spectra.

Results and Discussion

First Copper Adsorption ICP Data

The first copper adsorption data collected via ICP was for the 8, 16, and 24-hour reaction times for each the glucose hydrochar, KOH hydrochar, and acrylic acid hydrochar. The results for the first trial of ICP data collection is shown in Figure 2 below.
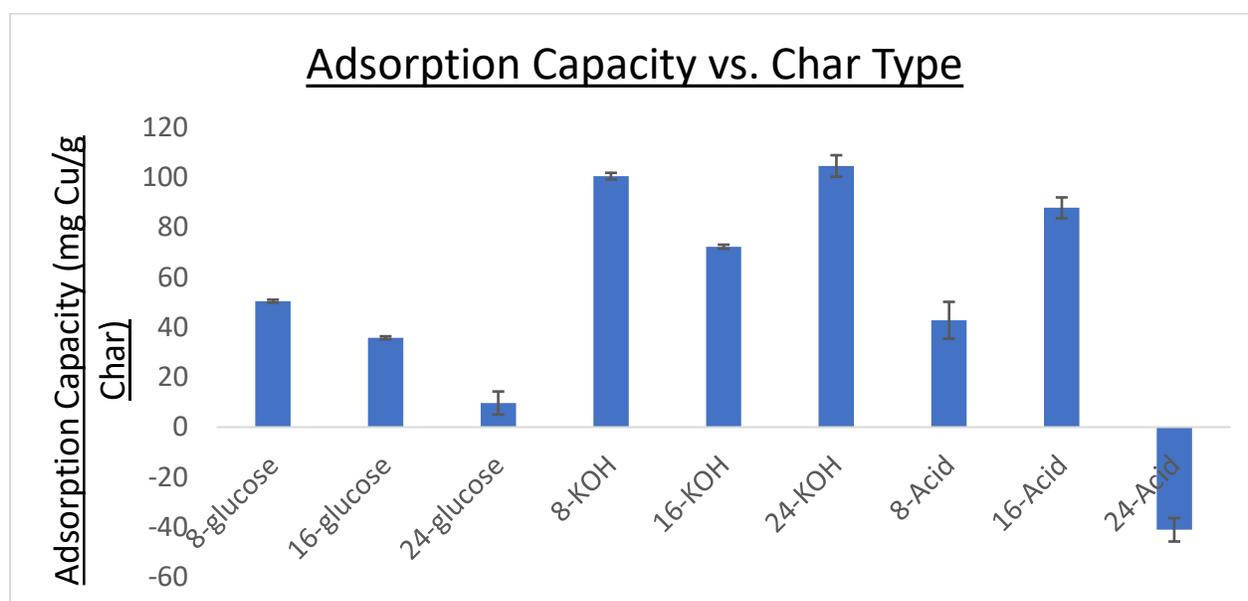
Figure 2: First trial of ICP data collected for all char types.

As can be seen in Figure 2 above, the adsorption capacity for several of the hydrochar types are between 50 mg Cu/g char and 100 mg Cu/g char. The noticeable anomaly in this data set is that for the 24-hour acrylic acid hydrochar, the data shows that there is a negative adsorption of approximately -41 mg Cu/g char. Table 2 below shows just how much concentration of copper that each hydrochar type adsorbed during this trial.

Table 2: Copper adsorption for each hydrochar type - 1st Trial.

Hydrochar Type	Change in Cu Concentration (M)
8 hr Glucose	0.0159
16 hr Glucose	0.0113
24 hr Glucose	0.0030
8 hr KOH	0.03169
16 hr KOH	0.0228
24 hr KOH	0.0329
8 hr Acid	0.0135
16 hr Acid	0.0277
24 hr Acid	-0.0130

As can be seen by the data shown in Table 2 above, all but two different hydrochar types have a difference in copper concentration of more than 0.01 M. In order to measure a very significant change in adsorption of copper, it was decided that adsorption values should be more than 0.01 M. Values within a magnitude of 0.01M or less about 0 means that the hydrochar was not well at measuring copper adsorption and that the ICP data was resembling that the hydrochar was simply fluctuating about 0 mg Cu/g char. Like any data, at least three ICP data sets were collected for each hydrochar type to ensure statistical significance of each hydrochar type.

Second Copper Adsorption ICP Data

The results for the second trial of ICP data collection is shown in Figure 2 below for all hydrochar types.
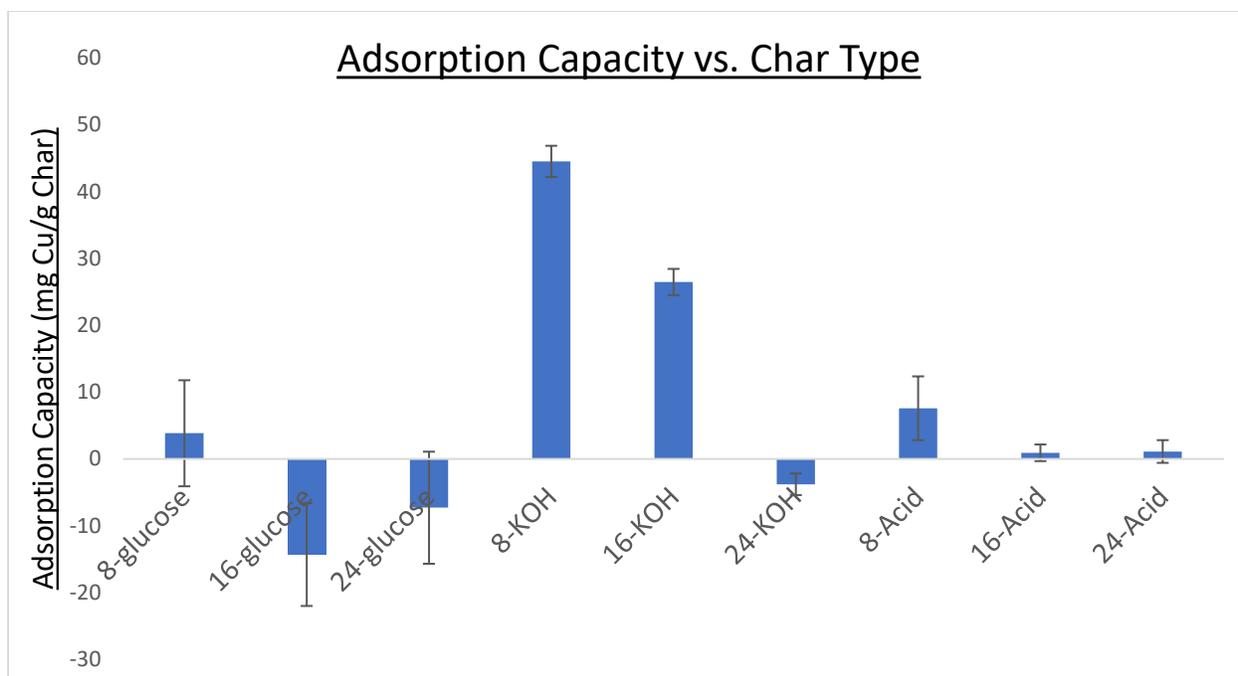
Figure 3: Second trial of ICP data collected for all char types.

As can be seen in Figure 4 above, the second trial of ICP data for all of the same hydrochar is shown. In this data set, there are 3 hydrochar types that show negative adsorption. Since each of the negative adsorption values are less than 0.01 M Cu in magnitude, the data is simply showing that the ICP was unable to properly measure a 0 M (no change) change in copper concentration for the hydrochar type. To better understand how much copper was adsorbed for each hydrochar type, Table 3 below shows the change in copper concentration for each hydrochar type.

Table 3: Copper adsorption for each hydrochar type - 2nd trial.

Hydrochar Type	Change in Cu Concentration (M)
8 hr Glucose	0.0012
16 hr Glucose	-0.0045
24 hr Glucose	-0.0023
8 hr KOH	0.0140
16 hr KOH	0.0083
24 hr KOH	-0.0012
8 hr Acid	0.0024
16 hr Acid	0.0003
24 hr Acid	0.0004

Although Figure 3 above shows that the highest bars (data for 8-hour and 16-hour KOH hydrochars) are approximately 50 mg Cu/g char adsorption capacity, the more correct values and determination of how much copper is being adsorbed for each hydrochar type is shown in Table 3 above. Shown in Table 3, the maximum changes in copper concentration of the data set correspond to 8-hour and 16-hour KOH hydrochars, as expected based on Figure 3, but they are just about equal to 0.01 M each. This means that although each of these two specific hydrochars showed good results when compared to the data set they were in, they do not show compelling enough values of copper adsorption concentration that suggests that this data point is not also a fluctuation about 0 and that the ICP was finding it difficult to measure the adsorption capacity difference.

Third Copper Adsorption ICP Data

The final trial of ICP data collection was collected for the third trial of ICP. The results for this trial are shown in Figure 4 and Table 4 below.
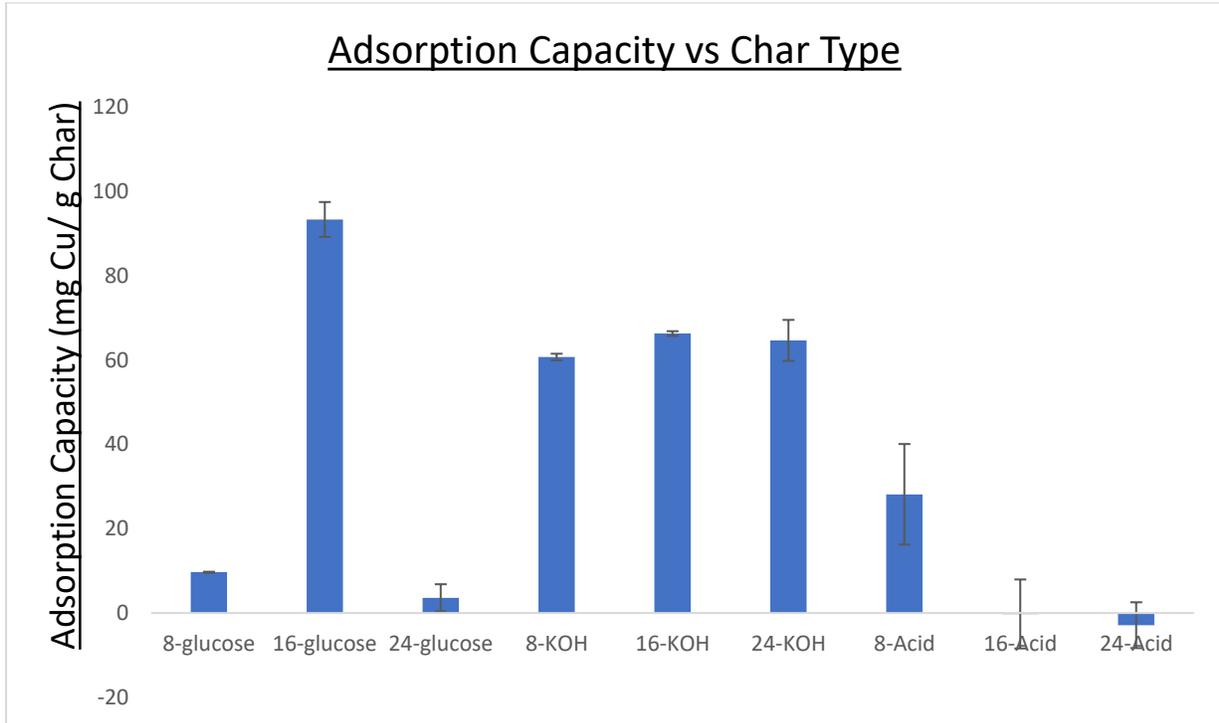

Figure 4: Third trial of ICP data collected for all char types.

Table 4: Copper adsorption for each hydrochar type – 3rd trial.

Hydrochar Type	Change in Cu Concentration (M)
8 hr Glucose	0.0031
16 hr Glucose	0.0294
24 hr Glucose	0.0011
8 hr KOH	0.0191
16 hr KOH	0.0209

24 hr KOH	0.0204
8 hr Acid	0.0089
16 hr Acid	-0.7007E-4
24 hr Acid	-0.0009

As shown in Figure 4 and Table 4 above, the ICP collected data for all hydrochar types show, for a majority of the samples, high adsorption capacities of copper. For the 16-hour and 24-hour acrylic acid hydrochar types there are negative adsorption values, meaning that these hydrochar types did not adsorb copper. Of the three different hydrochar types of material, excluding reaction time, the KOH hydrochars show the most promising copper adsorption capacity data trends since in this third trial and in the previous two trials, the adsorption capacity values have been consistent and higher than the rest of the hydrochars. A further investigation for why it is that the KOH hydrochars produce the best copper adsorption capacity data was explored by analyzing the Raman spectroscopy data results. To assess the reproducibility of this experiment, the copper adsorption capacities of the three additional batches of 8-hour glucose prepared by Hobson were also analyzed via ICP.

ICP Data of Additional 8-hour Glucose Batches

The copper adsorption capacity data for the three batches of the 8-hour glucose hydrochars produced by Hobson were quite peculiar, as shown in Figure 5 and Table 5 below.
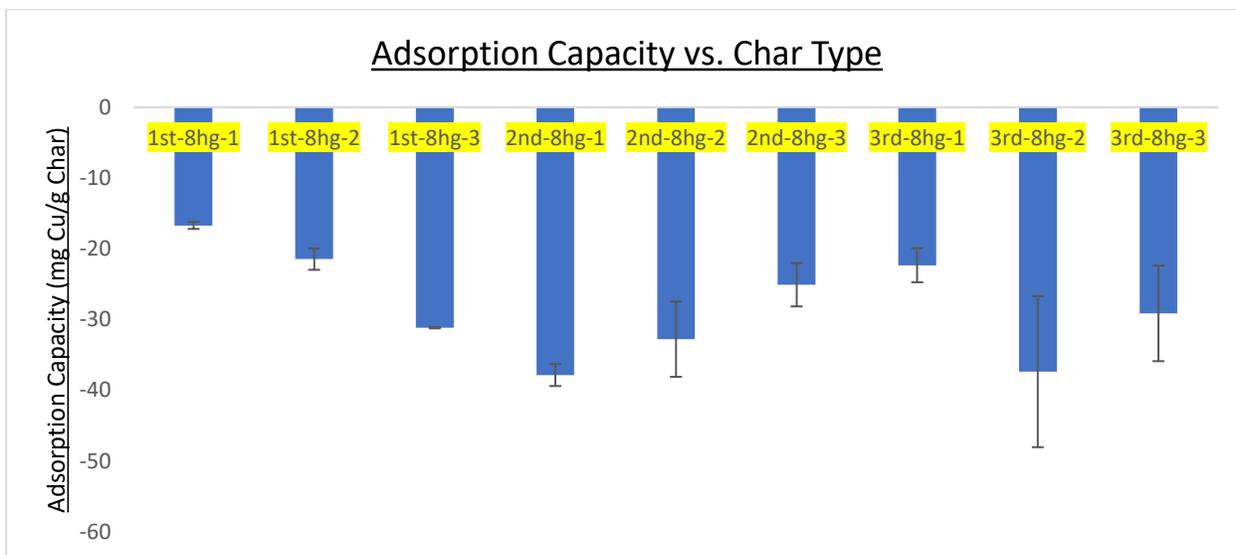
Figure 5: ICP data collected for all trials for the three batches of 8-hour glucose hydrochars.

The resulting data is very peculiar because all 3 trials of each batch of 8-hour glucose produces negative copper adsorption values, which can also be seen in Table 5 below.

Table 5: Copper adsorption capacity for each batch of 8-hour glucose prepared by Hobson.

8-hour Glucose Batch Type	Change in Cu Concentration (M)
1st Batch – 1st Trial	-0.0053
1st Batch – 2nd Trial	-0.0068
1st Batch – 3rd Trial	-0.0098
2nd Batch – 1st Trial	-0.0119
2nd Batch – 2nd Trial	-0.0103
2nd Batch – 3rd Trial	-0.0079
3rd Batch – 1st Trial	-0.0070
3rd Batch – 2nd Trial	-0.0118
3rd Batch – 3rd Trial	-0.0092

As can be noticed in both Figure 5 and Table 5 above, the copper adsorption capacities are consistently negative for all batches. This phenomenon was likely occurring because of contamination of copper during either the creation of the 8-hour glucose hydrochars or during the washing of the hydrochars. It was ensured that the correct copper solution blank was used in the calculation of the change in copper concentration for the hydrochars in this set of data. Therefore, the logical explanation for why every single batch type and batch trial had negative data was because of a contamination of exposure to copper nitrate during the preparation of the final product of the 8-hour glucose hydrochar. Unfortunately, because this portion of the experiment was to determine reproducibility, it is unknown whether or not the data can be reproducible.

Recorded pH Values

In addition to measuring the copper adsorption capacities of each hydrochar type as a means of learning how many milligrams of Cu each gram of hydrochar could adsorb, other analyses of the hydrochar's chemical makeup must also be conducted to better understand why the adsorption capacity capabilities are being observed. Figure 6 below shows the recorded pH values for each hydrochar type used in this experiment.

Table 6: Recorded pH values for each hydrochar type.

Char Type	pH Value
8-hour Glucose	3.69
16-hour Glucose	3.63
24-hour Glucose	3.58

8-hour KOH	6.70
16-hour KOH	6.21
24-hour KOH	6.69
8-hour Acrylic Acid	3.19
16-hour Acrylic Acid	3.04
24-hour Acrylic Acid	3.05
1st Batch – 8-hour Glucose	3.98
2nd Batch – 8-hour Glucose	3.92
3rd Batch – 8-hour Glucose	4.19

As seen in Table 6 above, the pH values for each type of hydrochar is very similar to each other. The pH for the acrylic acid activated glucose chars are the hydrochars with the lowest pH value due to the acidity of the carboxylate rich presence along the surface of this char type. As stated in the Background section of this report, the pH of the glucose hydrochars was expected to lower to approximately pH=3. The pH values observed for the 8-hour glucose char and the three batches provided by Hobson are all just slightly above a pH of 3. This can be a result of slight changes in the methodology of each specific batch but can still be concluded that the method of preparation of each batch was still relatively correct since the pH does not stray too far away from the expected literature value. Lastly, the pH of the KOH hydrochars is the highest due to mixing the glucose hydrochars with 2 N of KOH solution. The addition of alkali groups caused the pH to increase since alkali groups are very basic.

Raman Spectra

Wavenumber is essentially a unit of energy (a unit of wavelength) and describes the energy when the laser from the Raman apparatus is shined on the hydrochars. Since the green laser is a type of light that shines on the hydrochars at a specific wavelength (532 nm), the light emitted throughout the hydrochars is emitted at different wavelengths and depends on the adsorption of each of the hydrochars. Raman spectroscopy provides information on polarizability and is the main driving force for what peaks are observed at specific wavenumber locations. Because of this, molecules that have very strong dipole moments, such as a carbonyl, will not be present as a strong peak in Raman spectroscopy, but molecules that have very subtle polarizability changes can be observed in Raman. For example, observing the slight difference in polarizability between a carbon-carbon bonded to a carbon versus a carbon-carbon bonded to an oxygen will be shown as different peaks within Raman, allowing for a closer observation of the different structures present in each hydrochar. With this ability in Raman spectroscopy, it is possible to observe how the aromatic molecules are interacting on the surface of each hydrochar. Specifically, Raman spectroscopy allows for more insight on how the benzene and furan rings are interacting with each other and how they're motions of vibrating are affecting changes in polarizability.

In the Raman spectra collected for each of the hydrochars there are three peaks to pay particular attention to at Raman shifts of 1300, 1400, and 1600 cm^{-1}. The ratio of these three peaks describes the ratio of furan to benzene, the relative quantities of furan and benzene present on the hydrochar surface, and the aromatic structures present. A peak located at 1300 cm^{-1} describes how the chemical structure of the surface of the hydrochar is connected. This peak indicates the presence of condensed 6-membered aromatic rings, such as benzene, and describes

whether or not these aromatic rings are attached by aliphatic groups or if they are larger aromatic domains. A peak located at 1400 cm^{-1} indicates how much furan is present relative to benzene on the surface of the hydrochar. A peak located at 1600 cm^{-1} indicates the ratio of furan to benzene that is present on the surface of the hydrochar. Observing the Raman spectra must be done while looking at all three peaks together and not individually since the three peaks complement each other and paint a better picture of the true structure that is on the surface of the hydrochar. Figure 6 below shows the Raman spectra collected for all glucose hydrochar reaction times (8, 16, and 24 hr) and Figure 7, also below, shows the three batches of 8-hour glucose batches provided by Hobson for reproducibility.
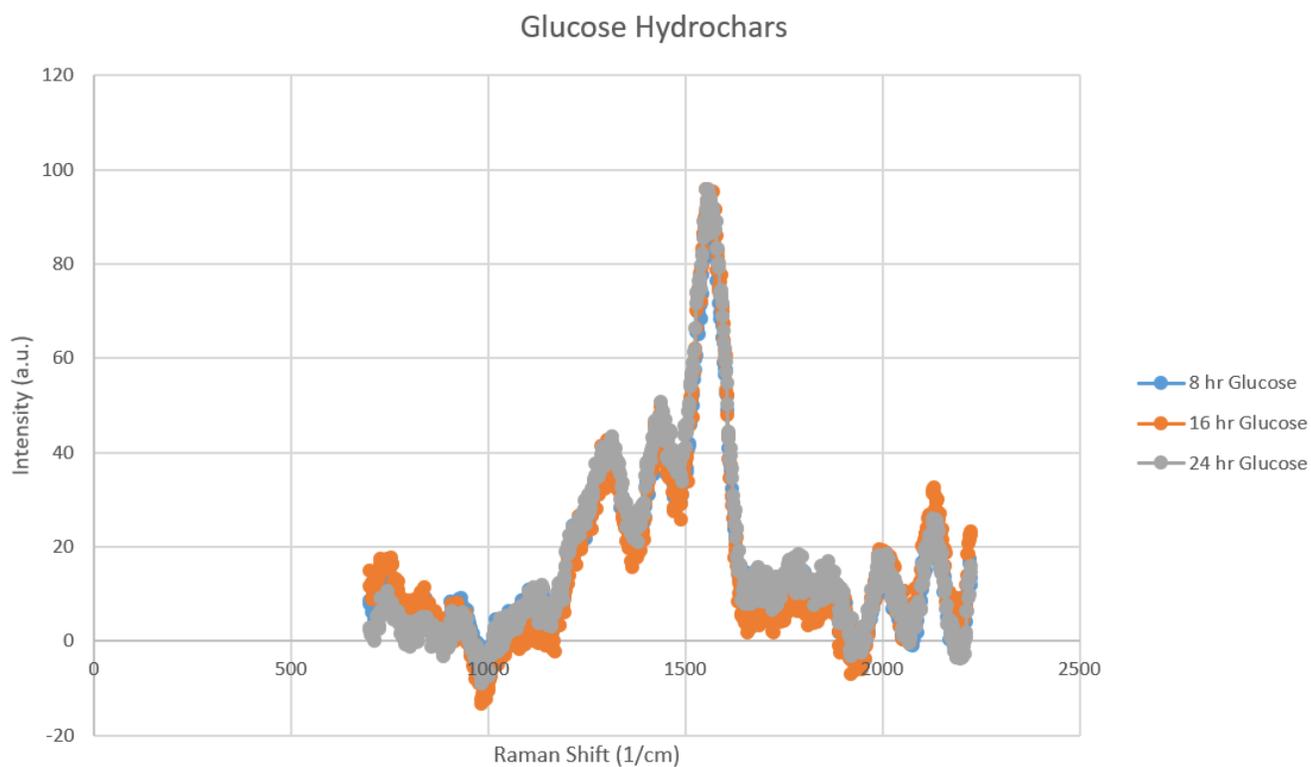

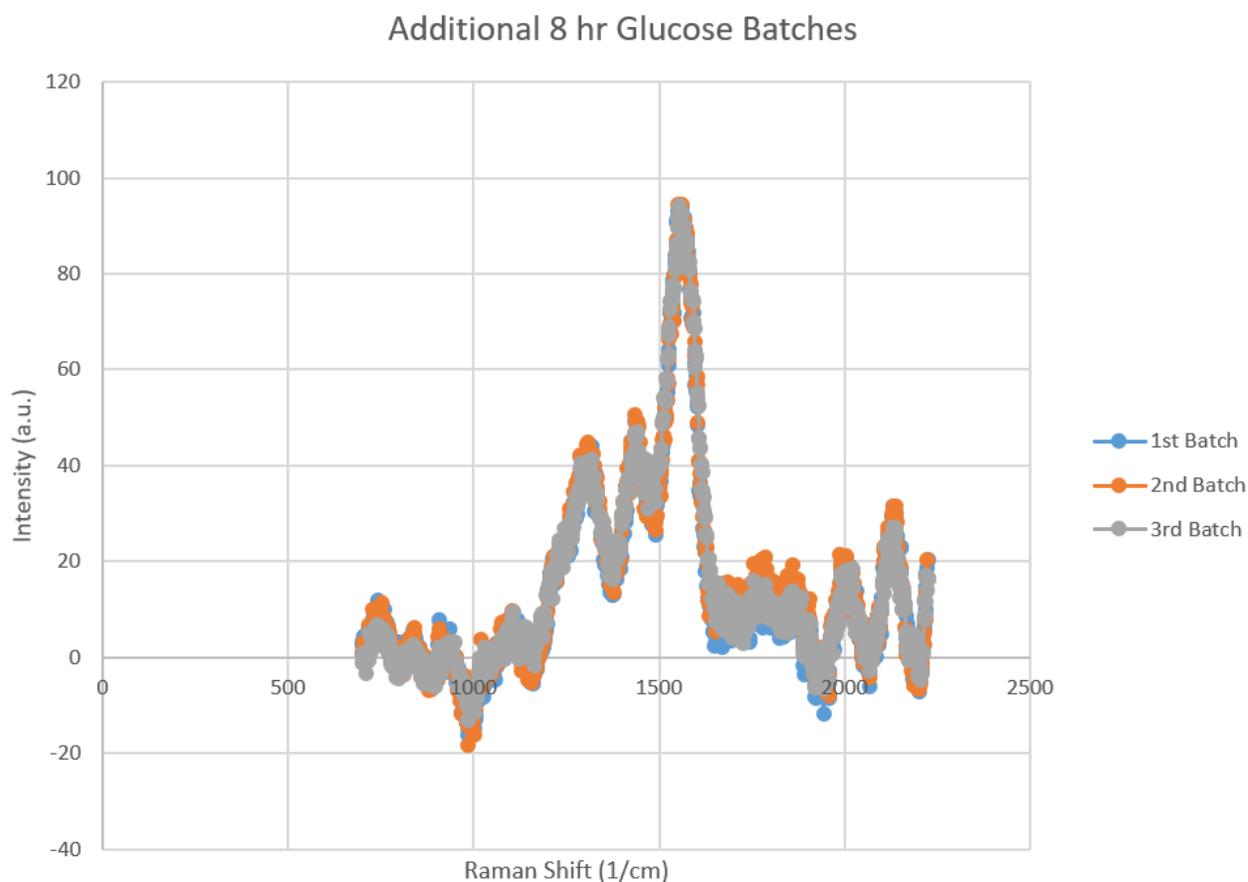Figure 6: Raman Spectra of Glucose Hydrochars.

Figure 7: Raman Spectra of 8-hour Glucose Batches.

As shown in Figure 6 and 7 above, the Raman spectra of the glucose hydrochars at all three reaction times do not really change as the reaction time increases. The strong peak at 1600 cm^{-1} indicates that there is both furan and benzene present in the surface structure. For Figure 6, the two peaks at 1300 cm^{-1} and 1400 cm^{-1} tell us that there is more furan than the aromatic domains present in the chemical structure. This means that the surface of these glucose hydrochars do not change very much chemically as reaction time changes. Similarly to Figure 7, the reaction times also do not seem to have an effect on the surface structure of each of the hydrochar types. In Figure 7, the two peaks also at 1300 cm^{-1} and 1400 cm^{-1} show that there may be more furan present than the aromatic domain since the peak at 1400 cm^{-1} is just slightly higher than the peak at 1300 cm^{-1}. However, this may also very well just be that the graph is too noisy. This result of

no noticeable change as reaction time changes is also corroborated by the collected ICP data for all glucose hydrochars. Since the ICP results and Raman spectra both do not show any indication of a trend in copper adsorption capacity advancement as reaction time increases, it can be determined that the glucose hydrochars do not adsorb copper well.

Figure 8 below shows the Raman spectra collected for all potassium hydroxide activated hydrochars used in this project.

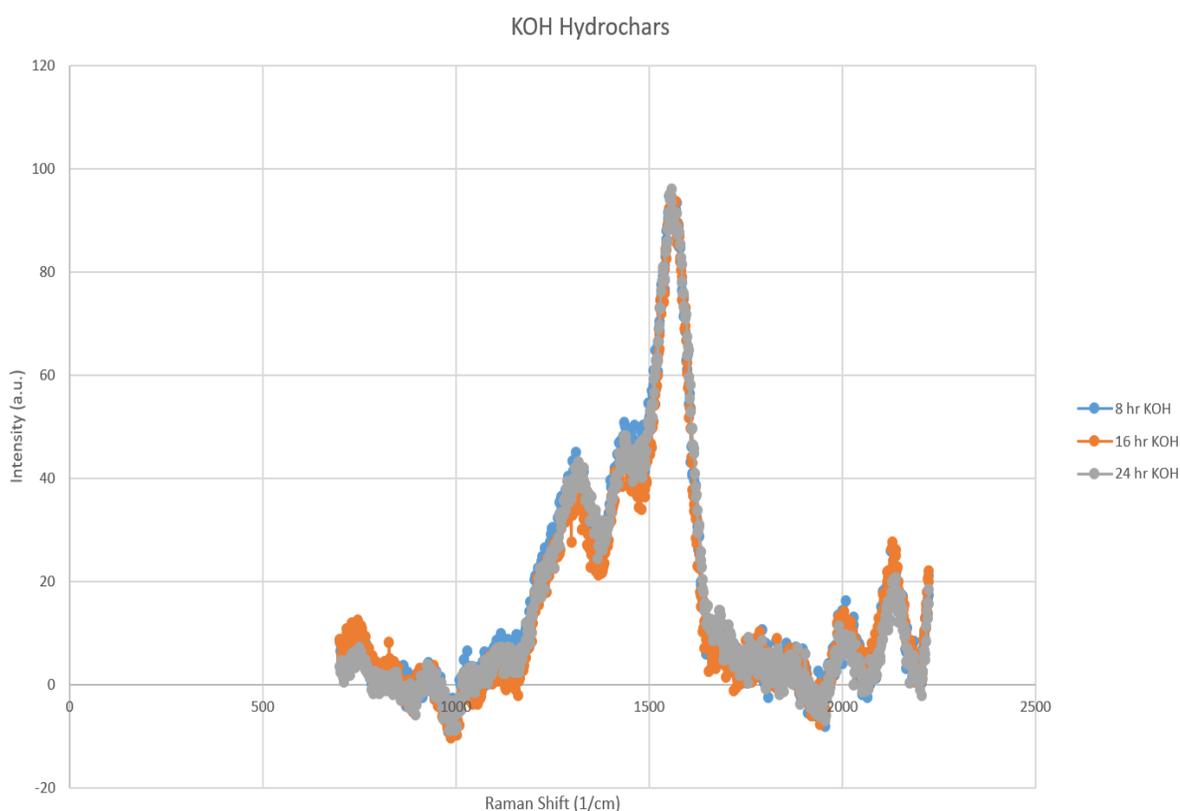
Figure 8: Raman Spectra of KOH hydrochars.

As shown in Figure 8 above, the Raman spectra is very consistent across all reaction times. At 1400 cm^{-1} the peak is slightly higher than the peak at 1300 cm^{-1} which may indicate that there is

more furan present than the aromatic domain structure, but, as previously described, since the peaks are closed in intensity, it may simply be that the data is too noisy. Additionally, since the Raman spectra is very similar across all reaction times for KOH hydrochars, it means that the copper adsorption capacity results should also be similar across all reaction times. That is exactly what we can observe in the ICP data for KOH hydrochars. Potassium hydroxide activated glucose hydrochars are the best hydrochar material that can adsorb the most copper while also being the only hydrochar type with the most consistent data throughout the project.

Figure 9 below shows the collected Raman spectra for the acrylic acid activated hydrochars via a one-step HTC process with glucose.
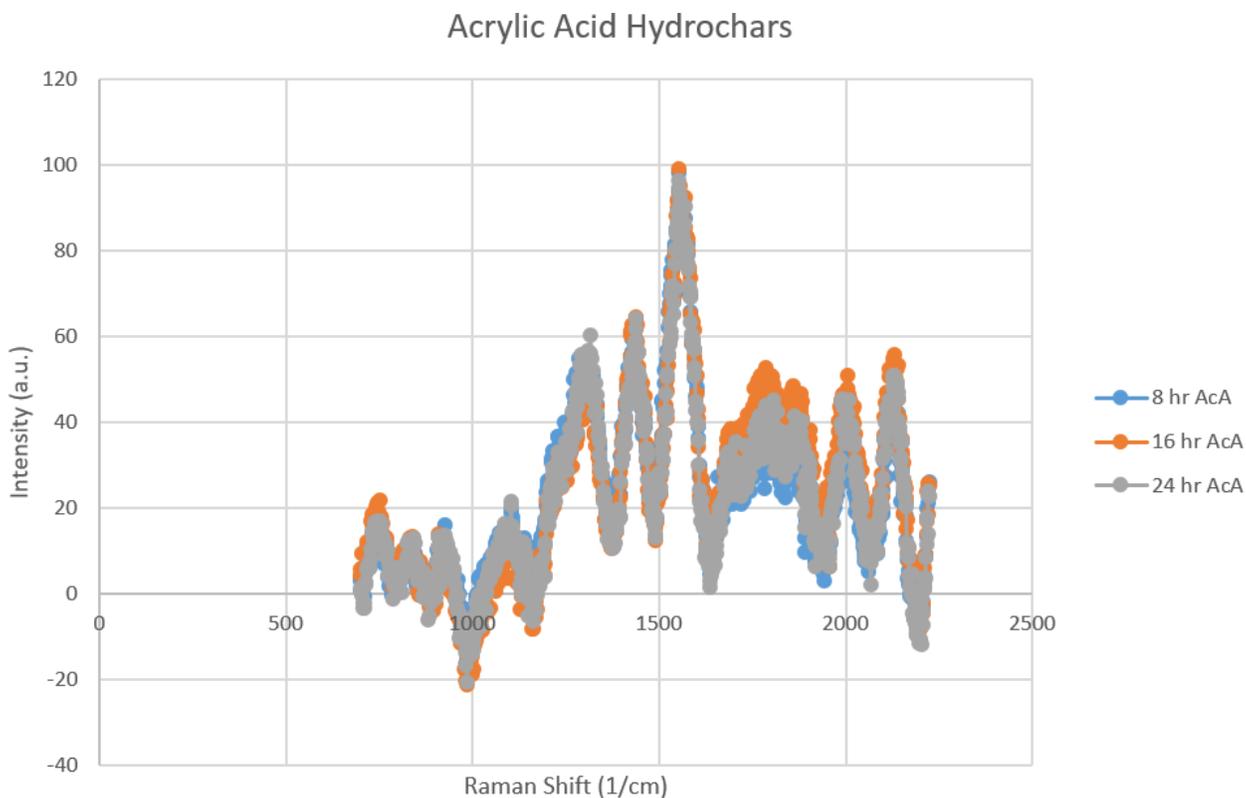

Figure 9: Raman Spectra of Acrylic Acid hydrochars.

The Raman spectra shown in Figure 9 above shows that the spectra of each reaction time overlap very well. Similar to the previous two types of hydrochar, the acrylic acid hydrochar does not show any indication of changing its chemical surface structure over time and so is not more effective in copper adsorption capacities at one reaction time more than another. However, there are noticeable difference in each of the types of hydrochars for each of the three reaction times.

Figures 10, 11, and 12 show the Raman spectra for all of the hydrochar types, separated by reaction time.
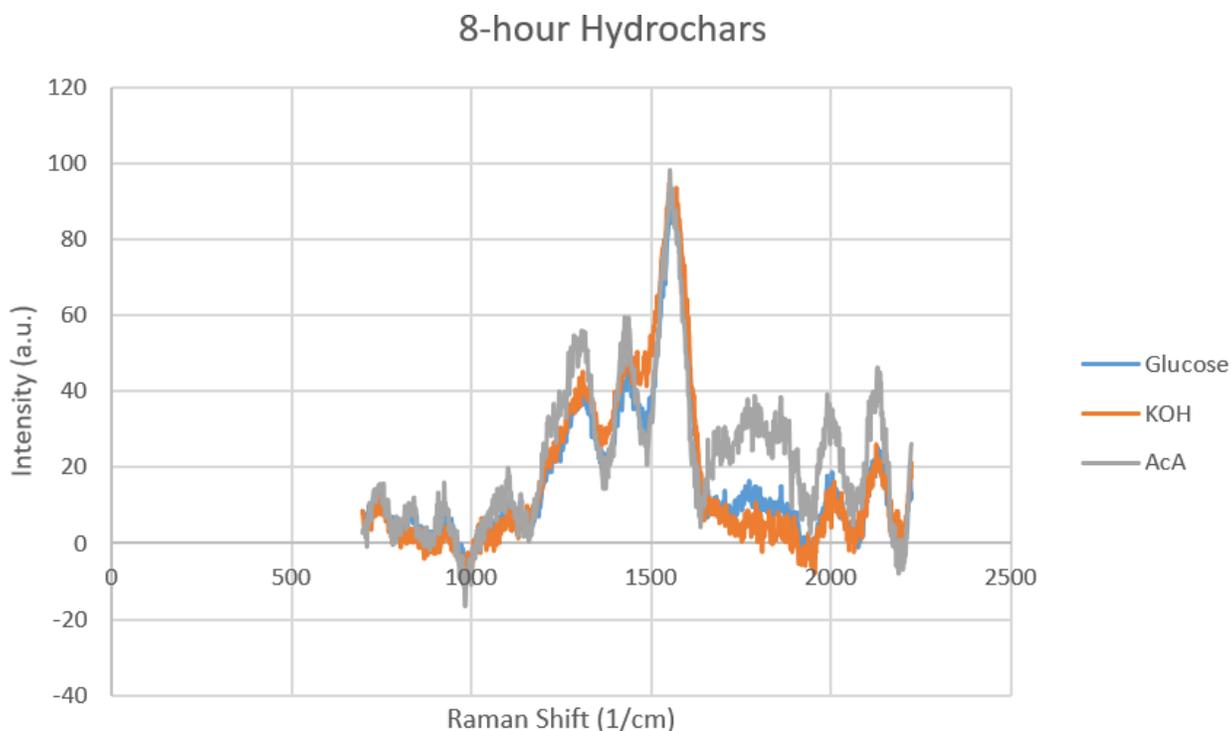

Figure 10: Raman Spectra of all hydrochars with a reaction time of 8 hours.
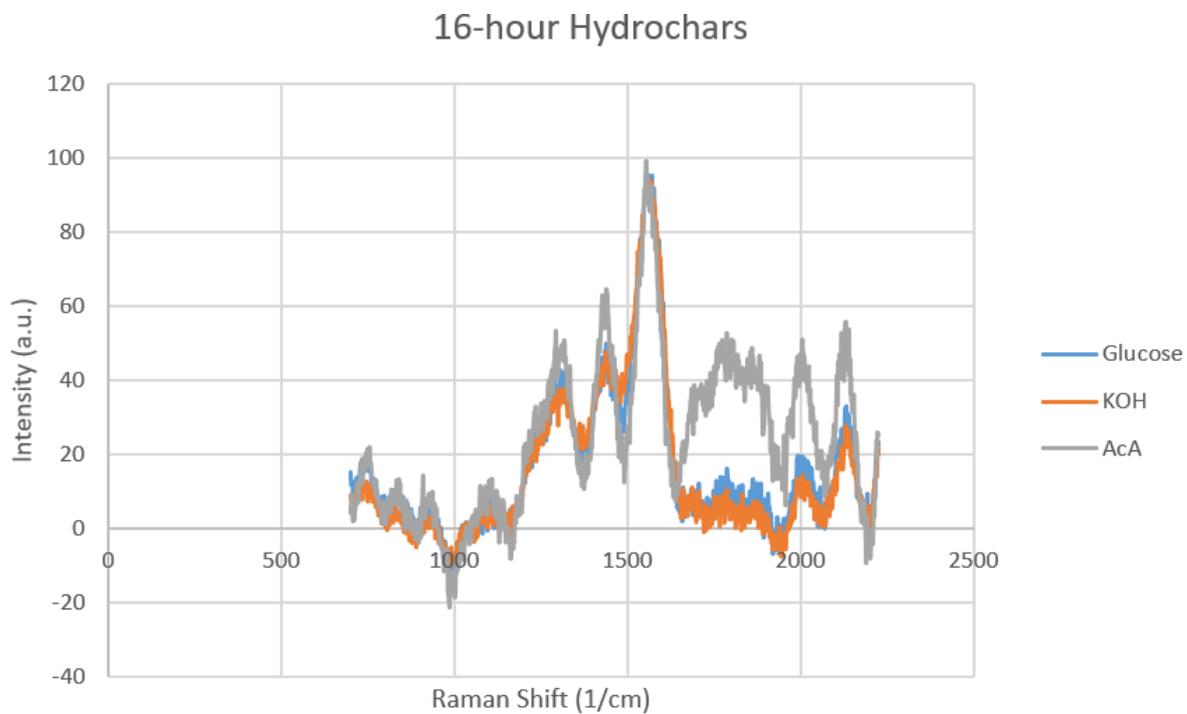
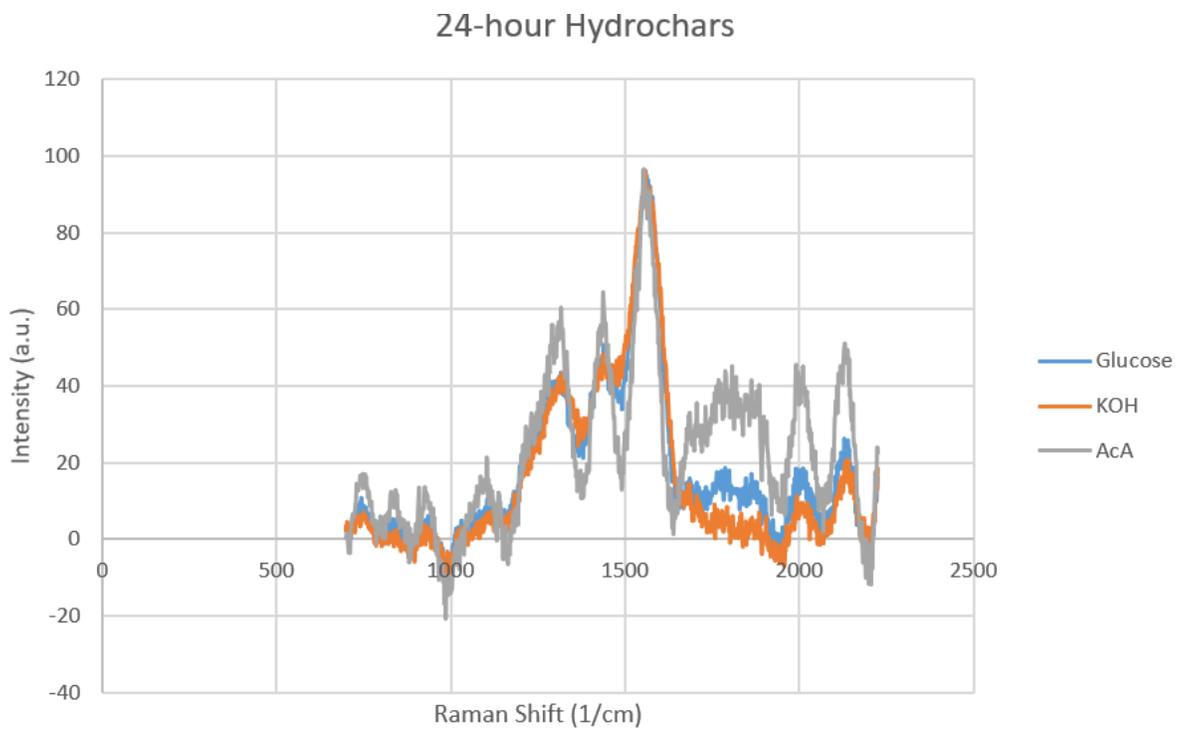Figure 11: Raman Spectra of all hydrochars with a reaction time of 16 hours.

Figure 12: Raman Spectra of all hydrochars with a reaction time of 24 hours.

As clearly seen in Figure 10, 11, and 12 above, all three of the types of hydrochar materials (glucose, KOH, and acrylic acid) contain a relatively even mixture of furan and large aromatic domains for all reaction times. The intensity of the peaks for each reaction time across all three hydrochar materials does not change and remains in a consistent trend for all three reaction times. The acrylic acid hydrochars still indicate a slightly higher quantity of furan to aromatic domains when compared to the glucose and KOH hydrochars. Although this appearance in peak intensity may still be noise, it is a more noticeable difference between the peaks at 1300 and 1400 cm^{-1} than these pair of peaks for both glucose and KOH hydrochars alike.

Conclusions and Recommendations

Sorption materials have proven to be very useful in removing heavy metals and metal ions from water bodies and aqueous solutions. In an ever-increasing society in which half of the population seems to always have doubts about and remain in disbelief about pollution, it is important to employ the best efforts towards decreasing pollution and cleaning the environment as much as possible before there really is no turning back from the downhill slope our society inclines towards. Products made from processes such as HTC have also been shown to have great uses towards adsorption of metal ions such as copper from these contaminated aqueous solutions.

Hydrothermal carbonization provides a simple and easy to make sorption material that has some capacity for adsorbing metals without requiring further processing. The product hydrochars are able to adsorb a small portion of the copper present in the aqueous solution and consist of very affordable raw materials. As shown in this project, the activation of glucose hydrochars does change the chemical structure of the surface of each hydrochar and can adsorb more milligrams of copper ion per gram of activated HTC glucose hydrochars. Unfortunately, in this project it was concluded that the glucose and acrylic acid hydrochars were not good hydrochar types to test with the adsorption of copper from aqueous solutions.

The potassium hydroxide activation method of glucose that has gone through the HTC process has proven to be a better sorption material than glucose hydrochar. This was because the KOH hydrochars had better pore availability (and therefore more surface area availability), were maintained at a more desirable pH that did not interfere with distinguishing the metal removal phenomena due to adsorption, and were optimized by activating the glucose hydrochar with 2 N

KOH solution instead of a lower concentration of KOH. The results of this project also were most consistent with the KOH hydrochars. The Raman spectra and ICP results support the conclusion that the KOH hydrochars were the best sorption material for either of the reaction times since it is the material that consistently removes approximately 0.02 M of copper from the aqueous solution and had consistent Raman spectra that only reinforced the results from ICP.

Although increasing reaction time does increase pore size, it was not a strong factor in allowing for more copper adsorption capabilities since the ICP results had data that mainly fluctuated around no adsorption of copper (~0 M copper adsorbed) and since the Raman spectra did not show significant changes by changing reaction time and keeping the hydrochar material constant.

Recommendations for future projects that could possibly stem from this project include retesting the 8-hour glucose hydrochar batches provided by Hobson with the same batch of 0.08 M $Cu(NO_3)_2$ solution used to first test all three trials of each of the three batches. Since the ICP data for these hydrochars were not a mixture of positive and negative adsorption bars, which could have suggested statistical variation, it is very likely that there was copper contamination at either the synthesis of the hydrochar or during Hobson's wash of the already made batches. Another recommendation is to further investigate the acrylic acid hydrochars adsorption capabilities. Several articles showed the benefit of creating a HTC glucose hydrochar in the presence of the acrylic acid monomer since it produces a carboxylate rich carbonaceous material. This material is shown to have higher adsorption capabilities than that of biochars. Lastly, another recommendation for future work on this experiment can be to see if the same adsorption (mg Cu/g hydrochar) is observed for different concentration of copper stock solution. It is assumed in this report that the maximum amount of copper is being adsorbed to the hydrochar

materials but perhaps this is something that is not consistent when the concentration of the copper stock solution is changed. Similarly, the adsorption of copper for each of the hydrochar materials can be tested in the presence of other heavy metals and/or metal ions also present in the aqueous solution along with copper. This could show favorability, if any, of certain ions based on size and formal charge for each of the different hydrochar types.

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