Adsorption of Copper Ions from Water via Sorption Materials from Agricultural Wastes

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Abstract

Heavy metals such as copper are found in water supplies around the world. Exposure to high levels of heavy metals can lead to significant health risks, and effective methods of filtering water are needed. One method used for removing heavy metals from water is the use of sorption materials derived from agricultural waste. These materials include activated carbons, glucose hydrochars, CELF lignins from poplar, maple and bagasse, and subcritical water extraction coffee waste. Using an experiment designed to measure the adsorption of copper from an aqueous solution using a UV spectrometer, the adsorption capacities in mg Cu per gram of material was measured for each of these substances. It was found that the glucose hydrochars, the maplewood and bagasse lignins had the ability to absorb a small amount of copper ions. The other materials caused the test solutions to become discolored and rendered the experiment inconclusive. Activating the glucose chars using pyrolysis increased the adsorption capacity and eliminated the slight colorization of the solutions that occurred when using the raw char. This implies that these materials need additional processing in order to be used effectively as absorbents.

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Introduction

Heavy metals that are dissolved in freshwater are an issue of concern to many countries around the world. Toxic metals such as cadmium, mercury, lead, and copper are some of the most prevalent metals found in rivers. Most of these contaminants come from human activities such as mining and manufacturing.[1] The health risks of these metals are well documented, but the efforts to remove them from drinking water can be quite expensive. Some of the methods used to remove contaminants include metal precipitation, membrane filtration, and adsorption using natural zeolites, industrial byproducts, and agricultural wastes.[2] Precipitation methods are only useful for very high concentrations of heavy metals. This process is expensive and is only implemented for industrial waste streams[3]. Membrane filtration uses resins to exchange ions with the water stream. However, the resins are very selective and can be easily be fouled by other compounds present in freshwater.[4] Sorption techniques using different materials are far more versatile compared to resins. Some have the ability to absorb multiple compounds and ions simultaneously, and although their adsorption capacity is small, the abundance of these materials makes them useful for adsorbing the small concentrations of metals in drinking water that could present health risks to humans and the environment.

Agricultural wastes are by far the most abundant of the sorption materials. Many studies have been done on turning different waste materials into activated carbons for adsorbing different compounds ranging from heavy metals to pesticides from water streams. Another type of sorption materials that have recently become a focus of study are hydrothermal chars. These

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[1] Garbarino, J., Hayes, H. C., Roth, D. A., Antweiler, R. C., Brinton, T. I., & Taylor, H. E. (n.d.). Heavy Metals in the Mississippi River.

[2] Barakat, M. (2011). New trends in removing heavy metals from industrial wastewater. Arabian Journal of Chemistry, 4(4).

[3] Ibid, p. 363

[4] Ibid, p. 366

chars are created under a water environment and therefore allow a wet precursor to be used without the need for a drying step. These hydrothermal chars have properties that are similar to activated carbons, even before the activation steps are implemented.

In this project, four types of sorption materials were tested for their ability to absorb copper ions from an aqueous solution. These materials were activated carbons, hydrothermal chars, byproducts of subcritical water reactions, and CELF lignin samples. The purpose of this project is to test the uses of several products that can be produced from agricultural waste and to quantify their usefulness in adsorbing copper from water. Commercially available activated carbons were used as a control to create a copper adsorption test method and provide a comparison against the other materials. The hydrothermal chars were prepared at Worcester Polytechnic Institute. The subcritical water byproducts were taken from a study done in collaboration with Tania Forster-Carneiro from the University of Campinas. Lastly, the CELF lignin samples were provided by the Center for Environmental Research and Technology (CE-CERT).

Additionally, the some of the glucose chars prepared were physically activated using pyrolysis to test for any changes in the adsorption capabilities of the material. If the adsorption capabilities were improved using pyrolysis, it could mean that the performance of other hydrothermal chars could do so as well.

Background

Biomass

Biochar originally comes from biomass, which is made from organic materials like wood and agricultural remnants. What makes biomass unique is that it has the ability to be modified into three stages of matter.[5] The Earth provides an abundant supply of biomass, which makes it a valuable resource. Biomass is used in "energy production, carbon sequestration and, as an essential element for the production of hydrochars and activated carbons."[6] There are two kinds of biomass: wet biomass and dry biomass. Wet biomass has over a 30% moisture content and includes a variety of materials such as wastes from sewage and vegetables, algae, and sludge. Dry biomass, on the other hand, has a moisture content below 30%, and includes different species of wood and agricultural residues.[7] It is helpful to the environment to use this waste biomass as a feedstock in the production of biochar and hydrochar.[8]

Slow Pyrolysis

Slow pyrolysis is a method that is used to produce biochar under "dry condition[s]."[9] The process of pyrolysis can be done in slow, intermediate, fast or flash methods. In slow pyrolysis the feedstock is degraded with heat at high temperatures ranging from 300ºC to 650ºC without oxygen. This process leads to having a carbon rich-product and gases such as CO, CO_3, CH_4, and

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[5] Harpeet Singh Kambo, and Amish Dutta, "A Comparative Review of Biochar and Hydrochar in Terms of Production, Physico-Chemical Properties and Applications," ScienceDirect.com, http://dx.doi.org/10.1016/j.rser.2015.01.050, 2015, Accessed July 2015, p. 360.

[6] Akshay Jain, Rajasekhar Balasubramanian, and M.P. Srinivasan, "Hydrothermal Conversion of Biomass Waste to Activated Carbon With High Porosity: A Review," ScienceDirect.com. http://dx.doi.org/10.1016/j.cej.2015.08.014, 2015, Accessed on July 2016, p. 790.

[7] Kambo et.al, p. 361.

[8] Ibid., p. 362.

[9] Ibid, p. 369

H$_2$. Slow-pyrolysis with a relatively low operating temperature often leads to a greater yield of solid product and the heating rate will affect the surface area of the biochar. The components and properties of the biochar are dependent on the heating rate, the temperature of the process, the reaction time, and the moisture content of the raw material.[10] It is ideal to run pyrolysis at relatively lower temperatures of 300 to 650 °C and long operating times ranging from 5 minutes to 12 hours in order to get a relatively high solid mass yield of 25 to 35 %.[11]

The pyrolysis method has some negative effects on the environment in that during the process of pyrolysis "biomass releases harmful gases (CO, CH$_4$ and PAHs) and oils to the atmosphere."[12] Another drawback to pyrolysis lies in the fact that the process involves using extensive equipment to deal with these emissions that are generated when biochar is produced. In addition to these harmful effects on the atmosphere, there also exists the danger when using the slow pyrolysis method that the self-ignition of biochar may occur, because the "anaerobic microorganism activity in a biochar pile" can produce a great amount of heat.[13] A slow pyrolysis method is not ideal for making biochar if the feedstock is a wet biomass because this would require a pre-drying step.

Hydrothermal Carbonization (HTC)

Hydrothermal carbonization, HTC, offers an attractive alternative to pyrolysis because it uses a variety of biomass feedstocks and that do not require any "pre-drying" when producing the char[14]. Over the last few years, hydrothermal carbonization has been used to make carbon material from biomass and this method of production "has received considerable attention due to

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[10] Ibid, p. 362.
[11] Ibid.
[12] Ibid, p. 369.
[13] Ibid.
[14] Ibid.

its ability to produce hydrochars with attractive characteristics that promote efficient utilization for a variety of applications such as adsorption, bio imaging, catalysis, activated carbon synthesis, etc."[15] Using biomass waste to make hydrochars is appealing in that it is a positive way to deal with "solid waste management" because it directly decreases the cost of the raw materials while offering some positive "solutions for [the] solid waste management" problems that exist.[16]

In comparison to biochar, hydrochar has lower ash content.[17] Ash content refers to the "mineral content and other inorganic matter in biomass."[18] Hydrochar has a higher heating value than biochar when it is "produced at the same operating process temperature."[19] Hydrochar is made as a slurry, a solid and liquid two-phase mixture, in a process known as hydrothermal carbonization (HTC).[20] HTC is a thermochemical process that converts an organic material into a solid product that is very rich in carbon. The process occurs at a temperature range that falls between $180°$ to $260°$ C where biomass is placed into water and is then heated in a closed system at a pressure of 2 to 6 MPa, which is self-generated in the sealed container, for a time span of 5 to 240 minutes[21]. The hydrothermal carbonization process is not affected by the feedstock's high moisture content since it occurs within the presence of water. This makes HTC a beneficial process because it does not require a pre-drying step. The pre-drying step, on the other hand, requires a lot of energy and adds an enormous financial expense, which is incurred in the pre-

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[15] Jain et al, p. 790.

[16] Ibid.

[17] Kambo et al, p. 365.

[18] Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., "Determination of Ash in Biomass," NREL.gov, http://www.nrel.gov/docs/gen/fy08/42622.pdf, 2008, Accessed on: 1 March 2017, p. 1.

[19] Kambo et al, p. 359.

[20] Ibid, p. 361

[21] Ibid, p. 363

processing of biomass.[22] The benefit of hydrothermal carbonization over the conventional slow-pyrolysis method for producing biochar lies in the fact that HTC can use a variety of "biomass feedstocks, such as sewage sludge, animal and agricultural wastes without any pre-drying of feedstock for char production."[23] HTC is a useful method to produce hydrochar because it has a high product yield and the process operates at a relatively low temperature.[24] Three major products are produced in the HTC process and include "the solid (hydrochar), the liquid, (bio-oil mixed with water), and the small fractions of gases" which are for the most part CO_2. The hydrochar that is produced from the HTC process is in a wet state, a slurry, and must go through compressing, filtering, and drying in order to be a useful energy source.[25] It is ideal to run HTC at a temperature of 180 to 260 °C and a residence time of 5 to 240 minutes in order to get a high mass yield of hydrochar of 40 to 70%.[26]

Environmental Benefits of HTC

Hydrothermal carbonization is safer for the environment than the pyrolysis method is because it does not produce toxic emissions.[27] Hydrochar is made up of aromatic structures with high oxygen functional groups (OFG) that give "the advantage of further functionalization and makes hydrochar more hydrophilic for suitable applications including adsorption, catalysis, and as a precursor for activated carbon synthesis."[28] What makes the hydrochar unique is that these OFG groups have important characteristics that enable them to bring about chemical activation.[29]

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[22] Ibid.
[23] Ibid, p. 369.
[24] Ibid, p. 363.
[25] Ibid.
[26] Ibid.
[27] Ibid, p. 369.
[28] Jain et al, p. 799.
[29] Ibid.

Hydrochar's greater "concentrations of oxygen-containing functional groups" combined with its "lower carbon content" make it an attractive option as a lower-cost adsorbent for the elimination of "environmental contaminants."[30] Another benefit to the HTC process is that it has a "higher yield (30-60 wt. %) than fast or slow pyrolysis."[31]

Hydrothermal carbonization of biomass and waste materials offers a very promising method to produce environmentally friendly products. However, this process is still fairly new and needs to be further explored and researched. Hydrothermal carbonization has the great possibility of being used as an environmentally friendly process to produce different kinds of products.

Hydrochar's removal of heavy metals has been thought to be controlled by metal ions' interaction with oxygen-containing functional groups on the surface of the hydrochar.[32] This makes it a very appealing method to use to remove dangerous elements such as copper and lead from water streams. Heavy metals such as lead and copper get into drinking water from plumbing materials and any exposure to them can lead to serious health issues from stomach problems to brain damage.[33] The Environmental Protection Agency (EPA) in 1991 laid out a regulation, the Lead and Copper Rule (LCR), that controlled the amount of copper and lead that was allowed in the drinking water. The EPA requires that "systems monitor the drinking water at

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[30] Kejing Sun, Jingchun Tang, Yanyan Gong, and Hairon Zhang, "Characterization of Potassium Hydroxide (KOH) Modified Hydrochars From Different Feedstocks for Enhanced Removal of Heavy Metals From Water," Springer.com. doi:10.1007/s11356-015-4849-0, 2015, Accessed August 2016, p. 16641.

[31] Yingwen Xue, Bin Gao, Ying Yao, Mandu Inyang, Ming Zhang, Andrew R. Zimmerman and Kyoung S. Ro, "Hydrogen Peroxide Modification Enhances Ability of Biochar (Hydrochar) Produced From Hydrothermal Carbonization of Peanut Hull to Remove Aqueous Heavy Metals: Batch and Column Tests," ScienceDirect.com, http://dx.doi.org/10.1016/j.cej.2012.06.116, 2012, Accessed August 2016, p. 674.

[32] Ibid.

[33] "Drinking Water Requirements for States and Public Water Systems," EPA.gov, https://www.epa.gov/dwreginfo/lead-and-copper-rule, Accessed on 22 October 2016.

customer taps."[34] With the LCR rule in place, any customer tap that was found to have had lead levels that exceeded 15 ppb and 1.3 ppm of copper and lead respectively, would be flagged as a problem and immediate actions would have to be done to fix the corrosive problem. Additionally, in the year 2007, the EPA added to the original rule with the "Short-Term Revisions to the Lead and Copper Rule," which gave more protection to consumers by increasing the amount of monitoring and consumer advocacy. Also as a result, more service lines were replaced to help deal with these corrosive pipes.[35]

Activated Carbon Properties

In practice, activated carbons are very widespread in their applications. They are used in many industries including food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing[36]. Most of these uses involve absorbing some chemical species from either a gas or liquid stream. Activated carbons can be used to absorb pollutants from air, or used to absorb heavy metals and organics such as pesticides from water. There are three important properties that determine the use of activated carbons: the effective surface area, the pore sizes, and the functional groups present on the material.

Activated carbons have extremely high surface areas, ranging anywhere between 13 m^3/g[37] of activated carbon to 2410 m^3/g.[38] This high surface area is due to the abundance of pores throughout an activated carbon. These pores can vary in size, which are separated into three main categories, macropores, mesopores, and micropores. Macropores are pores of any

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[34] Ibid.

[35] Ibid.

[36] Ioannidou, O., & Zabaniotou, A. (2007). Agricultural residues as precursors for activated carbon production—A review. Renewable and Sustainable Energy Reviews, 11(9), p. 1981

[37] Yalçın, N., & Sevinç, V. (2000). Studies of the surface area and porosity of activated carbons prepared from rice husks. Carbon, 38(14), p. 1945

[38] Oh, G. H., & Park, C. R. (2002). Preparation and characteristics of rice-straw-based porous carbons with high adsorption capacity. Fuel, 81(3), p. 329

diameter greater than 50 nm. Mesopores have diameters between 2 and 50 nm. Finally, micropores have diameters of less than 2 nm.[39] The functional groups present on activated carbons are what reacts with the target species. While the exact mechanism of these surface reactions are unknown, high concentrations of certain functional groups have been shown to promote reactions with certain chemical species. Oxygen-containing functional groups have been shown to promote the adsorption of heavy metal cations in aqueous solutions[40] and phenols.[41] Nitrogen containing functional groups have been shown to greatly promote the adsorption of anions.[42] Additionally, the acidity or basicity of these functional groups affect many of the activated carbon properties. This includes electrochemical and catalytic properties as well as adsorptive properties.[43]

The surface area, pore distribution, and functional groups present on an activated carbon sample depend on the feedstock the carbon was produced from and the method of activation. Activated carbons can be produced from any solid carbonaceous material, most often an agricultural waste product such as corn hulls, rice husks, fruit pits, etc.,[44] which are often thrown away. The different chemical compositions of these feedstocks will produce activated carbons with different surface areas and pore distributions. The composition will also affect the functional groups that will be present on the activated carbon, but not as strongly as the activation method.

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[39] Rouquerol, J., Avnir, D., Fairbridge, C. W., Everett, D. H., Haynes, J. M., Pernicone, N., . . . Unger, K. K. (1994). Recommendations for the characterization of porous solids. Pure Appl. Chem.,66(8), p. 1745

[40] Li, Y., Lee, C., & Gullett, B. (2003). Importance of activated carbon's oxygen surface functional groups on elemental mercury adsorption. Fuel, 82(4).

[41] Tessmer, C. H., Vidic, R. D., & Uranowski, L. J. (1997). Impact of Oxygen-Containing Surface Functional Groups on Activated Carbon Adsorption of Phenols. Environmental Science & Technology, 31(7)

[42] Biniak, S., Szymański, G., Siedlewski, J., & Świątkowski, A. (1997). The characterization of activated carbons with oxygen and nitrogen surface groups. Carbon, 35(12)

[43] Ioannidou & Zabaniotou, 2011, p. 1981

[44] Ibid, p. 1979

Creating Activated Carbons

Activated carbons are created in two steps: the carbonization step and the activation step. The most common carbonization step is slow pyrolysis, which was mentioned previously. After the feedstock is heated and the volatile components have been removed, a char is what remains. This char needs to be activated in order to form the functional groups needed for its intended application. The activation step also helps develop the surface area and pore distribution of the resulting activated carbon. There are two methods for activation: physical activation and chemical activation. Physical activation involves gasification at high temperatures above 700 °C in the presence of an oxidizing gas such as steam, CO_2, air, or a mixture of the three.[45] Chemical activation combines the carbonization and activation step into one. The process involves an activating reagent such as K_2CO_3, Na_2CO_3, KOH, NaOH, $ZnCl_2$, or H_3PO_4-. The feedstock is mixed with the reagent and water, then the mixture is kneaded. The mixture is dried via heating at a low temperature then heated up in a furnace to carbonization temperatures similar to those used in physical activation. Once the mixture has been heated for a set time, it is washed several times to remove the reagent and then dried.[46]

Comparison Between Hydrochars and Activated Carbon

Hydrochars are similar to activated carbons, but they are not the same. The carbonization step for hydrochars occurs in the presence of water, which consequently creates some oxygen-containing functional groups within the char, before any activation step is performed. The presence of these functional groups may cause the hydrochars to exhibit some properties of

[45] Demiral, H., Demiral, I., Karabacakoğlu, B., & Tümsek, F. (2011). Production of activated carbon from olive bagasse by physical activation. Chemical Engineering Research and Design,89(2), p. 203

[46] Hayashi, J., Kazehaya, A., Muroyama, K., & Watkinson, A. (2000). Preparation of activated carbon from lignin by chemical activation. Carbon, 38(13), p. 1874

activated carbons, without the energy and resource intensive activation steps. Since oxygen-containing functional groups promote the adsorption of heavy metal ions in aqueous solutions, this project will focus on investigating the adsorption capability of hydrochars.

Like activated carbons, the precursor for the hydrochar plays a key role in determining the types of functional groups present on the final product. Agricultural feedstock contains three important components: cellulose, hemicellulose and lignin. Only the cellulose and hemicellulose portions will react under hydrothermal conditions to produce oxygen-containing functional groups. Lignin will remain mostly unaffected, and other components such as amino acids, proteins, and other organics will undergo side reactions.[47]

Sorption Materials Used

The goal of this project is to quantify a use for sorption materials from different sources. Using the available equipment in the lab, a procedure for measuring the levels of copper in aqueous solutions was developed. These sorption materials were used to absorb copper ions and the treated solutions were measured for their copper content. The materials used were: commercially available activated carbons, glucose chars produced via HTC, processed coffee waste from a hydrolysis study, and lignin wastes from a study using the CELF process.

The activated carbons used in this project are available for purchase on the market. These carbons follow industrial standards and are rated for use in specialized applications. Depending on the brand, the different types of activated carbons have different precursors and activation methods to prepare them for certain uses. The carbons used in this experiment were Norit SX-1, Norit Darco KB-G, and Picachem HP 120.

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[47] Titirici, M., White, R. J., Falco, C., & Sevilla, M. (2012). Black perspectives for a green future: hydrothermal carbons for environment protection and energy storage. Energy & Environmental Science, 5(5), p. 6800

The precursor for the hydrochars used was D-glucose. D-glucose is widely used in the study of hydrothermal chars because it is the most abundant compound derived from the hydrolysis of cellulose found in agricultural waste.[48] These chars were prepared in the labs at WPI and chars with 8, 12, and 16 hour synthesis times were tested for their ability to absorb copper.

The coffee "chars" tested were byproducts from another study working to hydrolyze waste from coffee production facilities. Using subcritical water, sugars and phenolic compounds were extracted from coffee powder and defatted coffee cake. The subcritical water experiments ranged from 150°C to 250°C, 22.5 to 30 MPa, and had residence times of approximately 30 minutes[49]. These waste products were subjected to water under conditions reminiscent of the HTC process. Although the temperature and pressures were higher and the residence times lower for the coffee "chars." The chars were tested for their ability to absorb copper. This could indicate whether or not the subcritical water conditions are suitable for producing something with properties similar to hydrochars.

The samples used in this experiment from maple wood, poplar wood, and bagasse are waste products from a CELF lignin experiment. Co-solvent-enhanced lignocellulosic fractionation (CELF) is a process used to remove cellulose and hemicellulose from lignin within organic materials. Using tetrahydrofuran as the co-solvent, the cell walls of plant materials can be easily broken down and the lignin is removed from the cellulose. Then from this point, the cellulose is treated with enzymes that break it down to sugars and alcohol for use in creating fuels and the lignin is discarded. The lignins have few known industrial applications. One study

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[48] Ibid, p. 6798

[49] Mayanga-Torres, P., Lachos-Perez, D., Rezende, C., Prado, J., Ma, Z., Tompsett, G., . . . Forster-Carneiro, T. (2017). Valorization of coffee industry residues by subcritical water hydrolysis: Recovery of sugars and phenolic compounds. The Journal of Supercritical Fluids.

of lignin adsorption showed that lignin may be able to adsorb heavy metals from water. However, its ability to adsorb metals was dependent on its precursor.[50]

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[50] Carrott, P., & Carrott, M. R. (2007). Lignin – from natural adsorbent to activated carbon: A review. Bioresource Technology, 98(12), p. 2303

Experimental Procedures

Hydrothermal Carbonization of Glucose

Three types of hydrothermal glucose chars were tested in this project. The three chars had different carbonization times of eight, twelve, and sixteen hours. To prepare the chars, 24.8 grams of D-glucose (Sigma-Aldrich, 99.5%) was dissolved in 100 mL of distilled water. A beaker containing the distilled water was constantly stirred using a magnetic stir bar and the glucose was slowly poured in, to prevent residue from forming at the bottom. The mixture was then allowed to continue mixing for five minutes to ensure that the glucose is completely dissolved. Afterwards, the solution was transferred to a 160 mL Teflon-lined stainless steel autoclave. The autoclave was pressure sealed and placed in an oven at 180°C. The water in the solution creates its own pressure and this step is where the carbonization takes place. The three chars were baked at this temperature for eight, twelve, or sixteen hours. Once the carbonization time was completed, the autoclave was allowed to cool to room temperature. The resulting char was then collected and washed with 50 mL of ethanol and 50 mL of water. The char was then vacuum filtered. This process was repeated three times in total or until the filtration liquid remained clear. The char was then dried overnight on a petri dish in an oven set to 80°C. Once dried, the char was ground into powder using a mortar and pestle and stored in glass vials.

Pyrolysis of Glucose Char

The 8-hour glucose char was pyrolyzed to measure the effects on its ability to absorb copper from aqueous solutions. The 8-hour glucose char was chosen for pyrolysis for A sample of 8-glucose char was prepared using the HTC method. The char was then placed into small

ceramic weigh boats and placed in a Blue 1100°C single zone tube furnace. The furnace was set to a ramp speed of 10°C and a holding temperature of 900°C. The glass tube created a temperature gradient between the outer surface of the tube, where the furnace measures temperature, and the inner surface where the samples were contained. The temperature of the inner portion of the tube was measured using an Omega Thermometer Calibrator (CL3512A) with a thermocouple. At the set point of 900°C on the furnace, the effective pyrolysis temperature in the tube was 650°C. The samples were pyrolyzed under a flow of nitrogen.

Three samples were made using three different holding times: two, four, and six hours. After the samples were held at 650°C for their allotted times, they were allowed to cool to room temperature under nitrogen. Once cool, the samples were removed from the furnace and weighed. The samples typically lost almost a third of their original mass, therefore, using three crucibles yielded approximately 0.2 grams to perform the Cu(II) adsorption procedure. The pyrolyzed char was placed in a 20 mL vial and the adsorption tests were performed for 24 hours. The un-pyrolyzed char was also tested as a control to measure the affect the pyrolysis had on the adsorption capacity.

Calibration Curve

As mentioned previously, copper nitrate absorbed a portion of the light. The absorbance of the solution can be correlated with the concentration of the compound. In order to do that, a known concentration has to be made and measured using the UV spectrometer. The unit used for this project was a Hewlett Packard G1103A UV spectrometer. At first, x amount of copper nitrate has been added to 50mL of DI water and mixed for twenty minutes to get a well-mixed solution of 0.08M. Once well mixed, 5 mL of the present solution was retrieved and run through the UV spectrometer before being disposed. DI water has been added to the main copper nitrate

solution with 50 mL to get another concentration, which was then stirred for twenty minutes before sampling again. The glass cuvette was rinsed twice with DI water, then cleaned with ethanol before every sampling. This same procedure has been done from 0.08 M to 0.01M with increments of 0.01 M. The table below represents the concentrations used along with the wavelength for the adsorption. A graph was made for adsorption against concentration in order to use the results obtained from the UV spectrometer.

Table 1: Calibration curve for aqueous copper nitrate solutions using UV spectrometer

Concentration (M)	Wavelength (nm^{-1})	Absorption (Au)
0.01	813	0.119788
0.02	813	0.238829
0.03	815	0.358782
0.04	806	0.467596
0.05	807	0.575400
0.06	810	0.692980
0.07	813	0.805777
0.08	810	0.916305
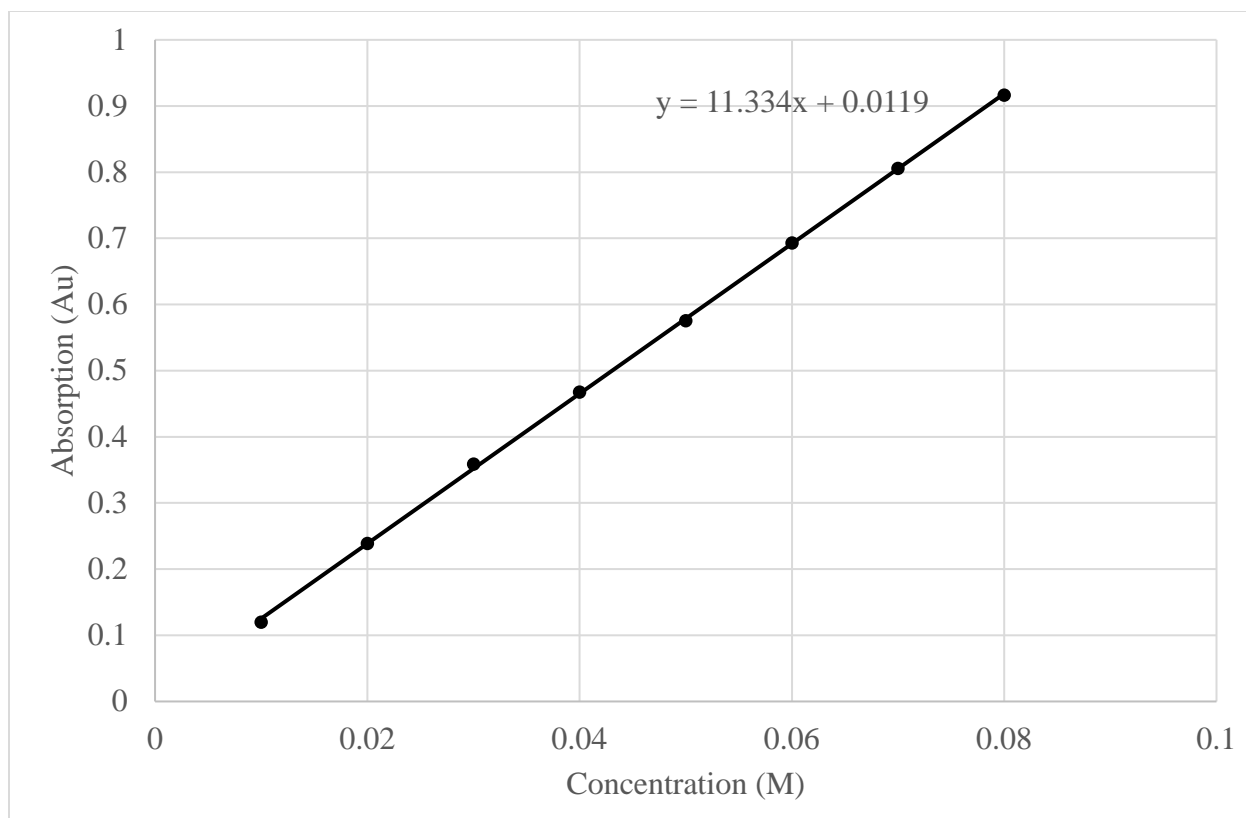
Figure 1: Calibration curve of aqueous copper nitrate

Cu(II) Adsorption Measurement

To test the adsorption capabilities of the hydrochars, 0.04 M stock solutions were prepared using copper nitrate ($Cu(NO_3)_2 \bullet 2.5\ H_2O$) and deionized water. Since there were very limited amounts of each char, 0.2 grams of char was added to 20 mL glass vials with 10 mL of the stock solution. Each vial was then placed in a wrist action shaker for 24 hours to agitate the mixtures and allow the chars to absorb the copper. After 24 hours, the vials were removed from the shaker and the aqueous portion was extracted by running the mixture through a Buchner funnel and Whatman (qualitative grade 1) filter paper using a filtering flask and vacuum pump. The aqueous portion of each solution was then filtered a second time using Scientific Strategies 0.45 µm syringe filters to remove fine char particles. The filtered solutions were placed in a glass cuvette and the absorbance was measured using the UV spectrometer. After each sample was

measured, the solution was disposed of and the cuvette was rinsed twice with deionized water. The UV adsorption test was performed twice for each sample to minimize the effect of the error from the UV spectrometer on the final results. A vial of stock solution was also placed in the shaker along with the char samples. The absorption reading for the stock solution was used as the basis for the adsorption capacity for each char. The adsorption capacity of each char was calculated by taking the highest UV absorption reading between 800 and 815 nm for each of the two tests, taking the average, and using the calibration curve to get a concentration in units of mol/L. Then, the concentration of the stock solution was determined using the same procedure. The difference between the concentrations of the stock solution and the char solution would be the moles of Cu(II) adsorbed by the char. Then, the adsorption capacity would be converted to grams of Cu(II) and divided by the mass of the char to get the capacity in grams Cu(II) per gram of char.

Results and Discussion

Activated Carbon Adsorptions

The first materials tested for copper adsorption were activated carbons. These activated carbons were used as the basis to test the copper adsorption method developed for this project, because their characteristics are well known, and are they available in large quantities. Three types of activated carbons were tested during this project: Norit SX-1, Norit Darco KB-G, and Picachem HP-120.

Table 2: Copper adsorption capacities measured for activated carbons using a 0.04 M solution of copper nitrate

Name	Mass (g)	mg Cu/g AC
Norit SX-1*	0.20	15.80 ± 1.32*
Norit Darco KB-G	0.20	1.76 ± 0.05
Picachem HP-120	0.20	21.40 ± 0.11

*stock solution concentration used was 0.08 M for Norit SX-1

Norit SX-1 is a multipurpose activated carbon that is useful for absorbing both organic and inorganic compounds.[51] This activated carbon was used heavily to test the effects of different concentrations of starting copper nitrate solutions with different masses of material. Unfortunately, the bottle of SX-1 was used up before a proper test could be run to compare against the other materials in the project. The most relevant results involved a run using 0.20 grams of SX-1 and a 0.08 M solution of copper nitrate. However, the mass used and the time in the shaker was the same as all the other samples. Although the solution of copper nitrate was a higher concentration than the other solutions used, it was found that the adsorption capacity of a

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[51] http://www.cabotcorp.com/solutions/products-plus/activated-carbon/powdered

material was affected more by its mass than the concentration of the solution it was in. Norit SX-1 had an adsorption capacity of 15.80 mg Cu per gram of activated carbon. This level of performance was expected due to uses of this product in industry.

Norit Darco KB-G is used for the adsorption of large organic compounds with a high molecular weight such as proteins. Norit's mass was 0.2 g and was added to 0.04 M of copper nitrate solution that was shaken for 24 hours. Once shaking was done, the adsorption was 1.76 mg Cu/ g AC. The reason why Norit Darco KB-G did not get high adsorption for copper because the activated carbon must have larger pores compared to those of SX-1. Since Darco KB-G is used for absorbing large organic compounds, it would benefit from a having larger pores. However, these large pores will not perform well when trying to absorb small copper ions. For this reason, Darco KB-G did not perform as well in the copper tests.

The last activated carbon tested was Picachem HP-120. This activated carbon is a general purpose product used to remove impurities from water ranging from micro-molecules to macromolecules.[52] As with the other materials in this project, 0.20 grams of this carbon were measured and shaken in a vial with 10 mL of 0.04 M copper nitrate solution. As shown in Table 2 above, the adsorption capacity measured was 21.40 mg Cu/gram of activated carbon. As with Norit SX-1, this multipurpose activated carbon absorbed a large quantity of activated carbon. This is likely due to its high surface area. The HP-120 carbon perhaps has a higher concentration of functional groups and a higher surface area than the Norit SX-1, which would explain the slightly higher performance.

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[52]"Activated Carbon," Geofluid.com, http://www.geofluid.com/picaproducts.asp, Accessed on: 26 February 2017.

Hydrothermal Char Adsorptions

   Three different glucose chars were made that had different times for the carbonization step of 8, 12, and 16 hours to see what effect the time of carbonization had on the copper adsorption capacity. These glucose chars were then placed in vials with copper nitrate solution and shaken for 24 hours. The following table shows the copper adsorption capacities of the three glucose chars.

Table 3: Copper adsorption capacities measured for glucose hydrochars 0.04 M solution of copper nitrate

Name	Mass (g)	mg Cu/g AC
Glucose 8-hour HTC	0.20	3.72 ± 1.14
Glucose 12-hour HTC	0.20	2.75 ± 0.10
Glucose 16-hour HTC	0.20	3.66 ± 0.35

   The hydrochars created from D-glucose show some capacity for absorbing copper from aqueous solutions. Glucose is used as the model for hydrothermal chars because it is the most abundant substance that reacts from cellulosic material in organic waste. Ideally, researchers want precursors with larger quantities of cellulose and hemicellulose in their compositions. These two materials are the basis for the functional groups that determine the characteristics of the char or activated carbon that comes from that material. Table 3 above shows the adsorption capacity for D-glucose chars created using different carbonization times. The chars performed similarly for this range of carbonization times. It should be noted however, that the aqueous copper solutions acquired after filtering these chars were slightly green in color.[53] Since the UV

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[53] See Appendix B

spectrometer measures visible light, which in this case is a blue wavelength, the changed color of the solutions may have affected the data.

The green colorization of the solutions is most likely due to dissolved compounds from the carbonization process. There are many possible side reactions that take place during the carbonization step, when the glucose is exposed to water at high temperatures. The actual compounds that cause this green colorization is unknown at this point. It could be some organic compound from the char itself, a complex formed between an organic compound and the copper, or some combination of the two.

The char has some capacity for absorbing copper from water streams, but more testing needs to be done on the reason why the treated copper solutions become green instead of remaining blue. There is a possibility that these compounds may be toxic if ingested. An additional method for measuring the adsorption of copper would also be recommended, since the color change may have affected the accuracy of the results seen above.

CELF Lignin Adsorptions

Experiments were also performed on different CELF lignins to see how well these materials adsorbed copper ions. Table 4 shows the copper adsorption capacity for each CELF lignin.

Table 4: Copper adsorption capacities measured for CELF lignin samples using a 0.04 M solution of copper nitrate

Name	Mass (g)	mg Cu/g AC
Maplewood CELF Lignin	0.20	4.04 ± 0.97
Bagasse CELF Lignin	0.20	3.88 ± 0.44
Poplar Wood CELF Lignin	0.20	-10.84 ± 1.02
Poplar CELF Lignin (heat treated)	0.20	-3.59 ± 2.50

The maplewood and bagasse CELF lignins had adsorption capacities slightly higher than the glucose hydrochars tested. This is an important discovery since these lignins are a waste product from another process with few known industrial applications. They could perhaps be converted into viable activated carbons if an activation step were implemented. The other two poplar lignins did not perform well, however.

The absorption readings measured from the UV spectrometer showed that the absorbance of the test solutions from both poplar samples were higher than the initial absorption of the stock solution. This is only possible if some other compounds came from the lignin samples and dissolved or became suspended in the solution. In fact, the poplar lignin sample turned a very bright lime green color. Some decolorization was present in the glucose char solutions, but the

poplar solution color was far more saturated.[54] The heat treated poplar lignin sample did not decolorize the solution nearly as much as the normal poplar lignin.[55] However, the solution still had a higher absorbance than the stock solution. This means that there is either some other compound dissolving that is also blue in color, or that there are very fine particles suspended in the solution that the syringe filters were unable to remove. The poplar lignins would therefore be unfit for use in water filtration in this state. They may require additional processing to remove the compounds causing the discoloration to become usable.

Coffee Wastes from Subcritical Water Extraction

These coffee "chars" were produced by a study where a process for removing sugars and phenolic compounds from coffee waste products. This process involved using subcritical water, pressurized liquid water at high temperatures, to remove these compounds. After the sugars and phenols were extracted, the process leaves behind a waste material that resembles hydrothermal chars. These wastes were created under the presence of water, but at higher temperature and pressures than HTC, but also with lower exposure times to the water.

Table 5: Copper adsorption capacities measured for subcritical water by-product using a 0.04 M solution of copper nitrate

Name	Mass (g)	mg Cu/g AC
Coffee Powder (subCW)	0.20	-11.53 ± 1.32
Coffee Cake (subCW)	0.20	-16.58 ± 5.33
Coffee Raw Material (subCW)	0.20	-22.86 ± 1.75

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[54] See Appendix B
[55] See Appendix B

The measured absorbances from the UV spectrometer were higher than the initial absorption of the starting copper nitrate solution for all the coffee samples tested. Similarly, to the glucose chars and some of the lignin samples, the test solutions turned green after shaking for 24 hours. The color of the solution affected the UV spectroscopy readings greatly, resulting in a negative adsorption capacity for all three samples. The adsorption capacity testing for these materials is therefore inconclusive. Another testing method will need to be implemented in order to effectively measure the adsorption capacities in water. However, since the solution cannot be filtered easily, using these coffee chars to treat water for heavy metals is not recommended.

These results are not entirely surprising considering the conditions under which these materials were created. The coffee wastes used were produced from subcritical water experiments. Although they were exposed to water at high temperatures and pressures, the actual contact times were only about 9 minutes. It is unlikely that the reactions responsible for the oxygen-containing functional groups found on activated carbons and hydrochars can be completed in this small amount of time. The colorization of the test solutions is very likely caused by the compounds would be removed if the coffee material was carbonized using traditional methods.

Pyrolysis of Glucose Hydrochars

Glucose char that was used had an 8-hour long carbonization step. Three different samples of glucose hydrochar was put into the furnace for pyrolysis that had operating times of 2 hours, 4 hours, and 6 hours respectively. Once pyrolysis was done, the samples were taken out and put into copper nitrate solution to be shaken for 24 hours. Glucose char that did not go through pyrolysis was used as a control to compare to the other pyrolyzed chars. The following

table shows the results for the copper adsorption of the different glucose char samples that were pyrolyzed.

Table 6: Copper adsorption capacities measured for pyrolyzed glucose hydrochars using a 0.04 M solution of copper nitrate

Name	Mass (g)	mg Cu/g AC
8-hour glucose (made 2/17)	0.19	1.15 ± 0.25
2-hour Pyrolysis Sample	0.20	3.94 ± 0.16
4-hour Pyrolysis Sample	0.19	9.89 ± 0.01
6-hour Pyrolysis Sample	0.15	2.88 ± 0.67

The results show that when the glucose goes through pyrolysis for 2 hours, the copper adsorption capacity increases compared to the control. The copper adsorption capacity went up again when pyrolysis was run for 4 hours, but then went down for 6 hours. One thing that was observed about the samples for each solution was that the regular 8-hour glucose char in copper nitrate solution was green after 24 hours of shaking, while the pyrolyzed glucose chars in copper nitrate solution were blue. One possible explanation as to why the pyrolyzed chars were blue is that pyrolysis must have decomposed volatile groups from the glucose char to make the solution have the same color as copper nitrate solution.

One possible theory as to why copper adsorption capacity increased when using pyrolysis for 2-4 hours is because the glucose char's volatile components were broken down to improve the surface area of the glucose char and therefore enhance the surface chemistry between the char's surface and the copper ions. What could have happened with running pyrolysis for 6 hours was that when pyrolysis ran for a longer period of time, more functional groups that were on the

surface of the glucose char were removed, which hurt the interactions between the char's surface and the copper ions

Adsorption Capacity at Different Operating Times

In this experiment, the adsorption capacity over time was observed for two activated carbons: Norit Darco KB-G and Picachem HP 120. During the course of the previous experiments, it was found that some samples may have different equilibrium times, where the maximum amount of copper absorbed was found to take place when the samples were left in the shaker for longer than 24 hours. To explore the behavior of adsorption at different shaking times, the copper adsorption procedure was performed from 24 to 96 hours in 12 hour increments. The results are summarized below.

Table 7: Copper adsorption capacities for Norit Darco KB-G at different operating times

Time (hrs)	Mass (g)	mg Cu/g AC
24	0.20	1.76 ± 0.05
36	0.20	12.18 ± 0.69
48	0.20	1.85 ± 0.76
60	0.20	5.57 ± 0.11
72	0.20	3.16 ± 0.55
96	0.20	5.99 ± 0.46

Running the adsorption process for a longer period of time increased the copper adsorption capacity for Norit Darco KB-G. One possible theory is that Norit Darco KB-G's large pores are broken down into smaller pores, which made it easier to adsorb copper ions into the material.

Table 8: Copper adsorption capacities for Picachem HP-120 at different operating times

Time (hrs)	Mass (g)	mg Cu/g AC
24	0.20	21.40 ± 0.11
36	0.20	12.15 ± 0.69
48	0.20	19.44 ± 0.03
60	0.20	19.87 ± 2.10
72	0.20	22.28 ± 0.05
96	0.20	21.88 ± 0.21

Table 8 shows that the copper adsorption capacity of Picachem HP-120 stayed relatively the same over time. One possible theory could be that Picachem already is saturated and that the pores are already filled up with copper ions and that the surface of Picachem is already covered with copper ions.
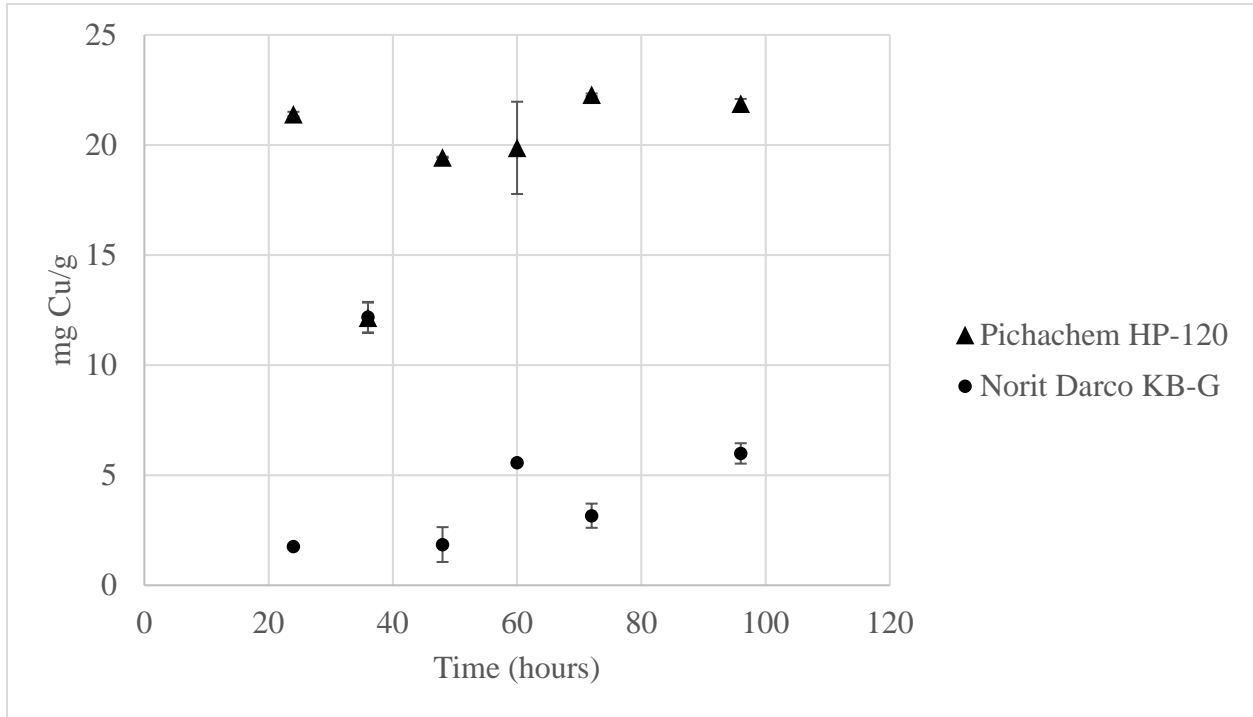

Figure 2: Copper Adsorption Capacities of Norit Darco KB-G and Picachem HP-120 at different adsorption times

Looking at Figure 2 above, it can be seen that there is a significant outlier at 36 hours. The exact cause of the outlier is unclear, but it is certainly not consistent with any of the data for either the Norit or Picachem carbons. Not accounting for the outlier, the adsorption capacity for Picachem remained relatively constant over the course of the experiments. The first point at 24 hours had one of the highest capacities. The points for Picachem at 72 and 96 hours were also close to the value reported 24 hours. There is no real reason for the slightly lower performance observed at 48 hours. The data point at 60 hours had a considerable deviation, which could explain why the value was lower in this instance.

The Norit Darco KB-G carbon did not absorb as much copper as the Picachem HP-120, as stated before. The trials at 24 and 48 hours had the lowest adsorptions at around 1.8 mg Cu/g. The results at 60 and 96 hours have higher adsorptions at over 5 mg Cu/g. This increase can be considered significant, since it is twice that found during the 24 and 48 hour trials. This can be interpreted as a weak positive trend in adsorption capacity for this char as the trial time increases. This may imply that some chars may have an equilibrium point with copper that far exceeds 24 hours. Although interesting, this phenomenon may be attributed to the characteristics of the material being studied. In this case, Darco KB-G is designed to be used for absorbing large organic molecules. The pore distributions and functional groups required for this task are not the same as the ones required for ion adsorption, which was shown in the comparison between HP-120 and SX-1.

Perhaps what is occurring is a slow mass transfer step between the copper ions and the functional groups on Darco KB-G. The larger pores would make it more difficult for ions to make contact with the appropriate groups and adhere to the surface of the carbon. Therefore, it would take much longer for a set amount of copper to adsorb onto the surface of the activated

carbon. Again, this behavior may only be present on materials with a weak affinity for copper. In contrast, the capacities measured over time for Picachem were very high and consistent.

Error Analysis

One of the possible sources of error in this project is that there was evaporation of copper nitrate solution in our stock solution if it was left out. Another source of error was from absorption of copper nitrate into the walls of the vials as well as evaporation of the copper nitrate solution during shaking. To deal with this, some copper nitrate solution was put into a vial and shaken with the test samples. This copper nitrate solution was then used as the baseline for the adsorption capacities, since it endured similar conditions to the test samples. One other possible source of error was how accurate the UV readings were for the sample solutions. In addition to the error of the spectrometer between reading the same sample, cleaning the cuvette introduced a small amount of water that would slightly affect the adsorption readings. One way to avoid the error was to repeat each absorption twice per sample. First, about 4 mL of solution was syringe filtered and transferred to the cuvette. Next, the UV absorbance was measured. Then the cuvette was emptied and another 4 mL of the test solution was syringe filtered and transferred to the cuvette. The UV absorbance was measured again. Finally, the cuvette was emptied, rinsed twice with DI water and this process was repeated for the next test solution. This method reduced the error caused by the tiny droplets of water remaining after the cuvette was cleaned and also accounts for the slight variance in the UV measurements. The error of the absorption results was calculated by finding the standard deviation of the two absorbance measurements recorded for each sample taken during the course of the project. This deviation was then converted from an absorbance value to units of mg Cu/g of material.

Conclusion and Recommendations

Agricultural waste products have more utilities than most people realize. Even after processing the waste down to nothing but char, even then there are still uses for it. Traditionally, agricultural waste has been used to create activated carbons that can be used for many different applications depending on the precursor material and activation method. However, even products from other processes such as HTC and CELF have been shown to have some uses such as the adsorption of copper from aqueous solutions.

Hydrothermal carbonization provides material with some capacity for absorbing heavy metals without further processing. The chars can absorb a small amount of copper without the need for an activation step, however, it may not be very useful for purification of drinking water since they turned the test solutions slightly green. The chars may have removed some copper from the solution, but some unknown substance was also added that may negatively impact the quality of the water. Performing a physical activation step can greatly increase the amount of copper absorbed by the material. Even more exciting, is the fact that whatever compound was discoloring the solution either burned off or decomposed during the heating process. While the solutions should still be tested for other compounds present in the solution coming from the char, it seems that the pyrolyzed material would be suitable for water filtration. This has great implications for providing activated carbons from materials without the need to dry the starting material.

The CELF process is used in an effort to convert usable materials from organic waste into fuel. A use for the lignins left behind should also be researched. It was shown that some of the lignins such as the ones from maple wood and bagasse showed adsorptions even higher than the HTCs. However, the other lignins had the colorization issue, so their performance could not be

quantified using this procedure. Since the test solutions were decolorized by the lignins similarly to the glucose chars, further processing may be required to use this material for heavy metal adsorption. Perhaps an activation step to convert the lignins to activated carbons would yield better results without decolorization.

The copper adsorption experiments for the subcritical water coffee products were also inconclusive, due to the green colorization of the solutions. More testing will have to be done on this material to confirm whether or not the material contains the functional groups necessary to absorb heavy metals. Since the residence time of the coffee was so low, it is very likely that these groups are not present on the surface of the material. Additionally, there are still many organic compounds present in the material causing the solution to become green and cloudy. Further processing of this material is indeed necessary for it to be used effectively for purifying drinking water.

The pyrolysis method using nitrogen gas helps to decompose volatile parts of chars such as glucose chars. The process shows that running pyrolysis for multiple hours improves the adsorption of copper ions for glucose char. More trials for pyrolysis and running pyrolysis for longer periods of time would help to get a better idea as to how pyrolysis affects the copper adsorption of the glucose chars. It would also be interesting to see if glucose chars that were made with longer carbonization steps would have better copper adsorption capacities after pyrolysis compared to the 8-hour glucose char. It would also be interesting to see how pyrolysis with air or CO_2 would affect the adsorption capacities. The presence of oxygen in the gas may cause more functional groups to form and increase performance.

The experiment of adsorption of Norit Darco KB-G and Picachem HP-120 from 24 to 96 hours shows that different materials may have different equilibrium times. These experiments

should be repeated to confirm that the results are reproducible. Moreover, additional materials such as Norit SX-1 should be tested in this manner to see whether or not chars with high affinity for copper ions reach equilibrium quickly and maintain the same adsorption capacity over long periods of time like HP-120. Also, materials with low relative adsorption capacities should be tested as well to see if the same phenomenon that happened with Darco KB-G occurs. Another activated carbon designed for use primarily with organics would be an appropriate candidate.

Other future experiments could involve looking for another metal ion to adsorb such as lead and see how well activated carbons and hydrochars adsorb lead ions. Another experiment would involve the uses of some of these materials for absorbing organic compounds such as pesticides. Since these materials show some capacity for absorbing heavy metal ions, they may also perform well when tasked with removing organics from water streams.

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Appendix

Appendix A: Cumulative Adsorption Results

Table 9: Copper adsorption capacities measured for all 16 different materials using a 0.04 M solution of copper nitrate

Name	Mass (g)	mg Cu/g AC
Norit SX-1*	0.20	15.80 ± 1.32*
Norit Darco KB-G	0.20	1.76 ± 0.05
Picachem HP-120	0.20	21.40 ± 0.11
Glucose 8-hour HTC	0.20	3.72 ± 1.14
Glucose 12-hour HTC	0.20	2.75 ± 0.10
Glucose 16-hour HTC	0.20	3.66 ± 0.35
Maplewood CELF Lignin	0.20	4.04 ± 0.97
Bagasse CELF Lignin	0.20	3.88 ± 0.44
Poplar Wood CELF Lignin	0.20	-10.84 ± 1.02
Poplar CELF Lignin (heat treated)	0.20	-3.59 ± 2.50
Coffee Powder (subCW)	0.20	-11.53 ± 1.32
Coffee Cake (subCW)	0.20	-16.58 ± 5.33
Coffee Raw Material (subCW)	0.20	-22.86 ± 1.75
8-hour glucose (made 2/17)	0.19	1.15 ± 0.25
2-hour Pyrolysis Sample	0.20	3.94 ± 0.16
4-hour Pyrolysis Sample	0.19	9.89 ± 0.01
6-hour Pyrolysis Sample	0.15	2.88 ± 0.67

*stock solution concentration used was 0.08 M for Norit SX-1

Appendix B: Photographs Comparing Filtered Test Solution Colors
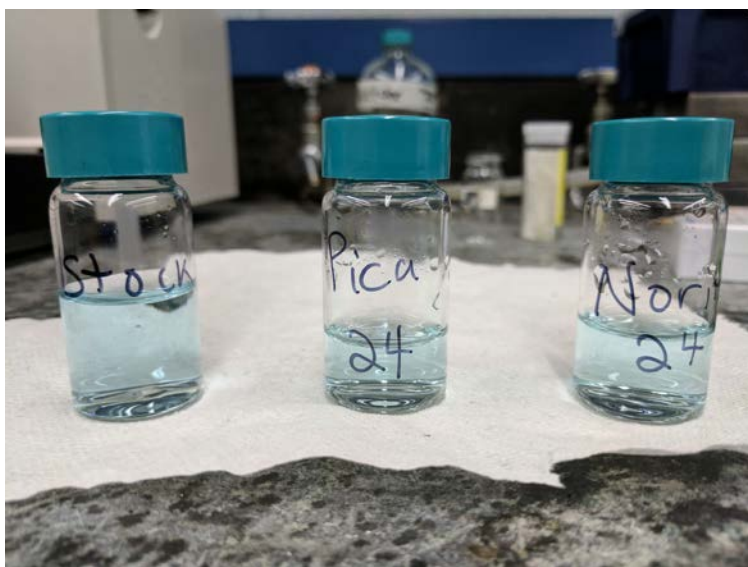
Figure 3: Comparing colors of filtered solutions of Picachem HP-120 and Norit Darco KB-G
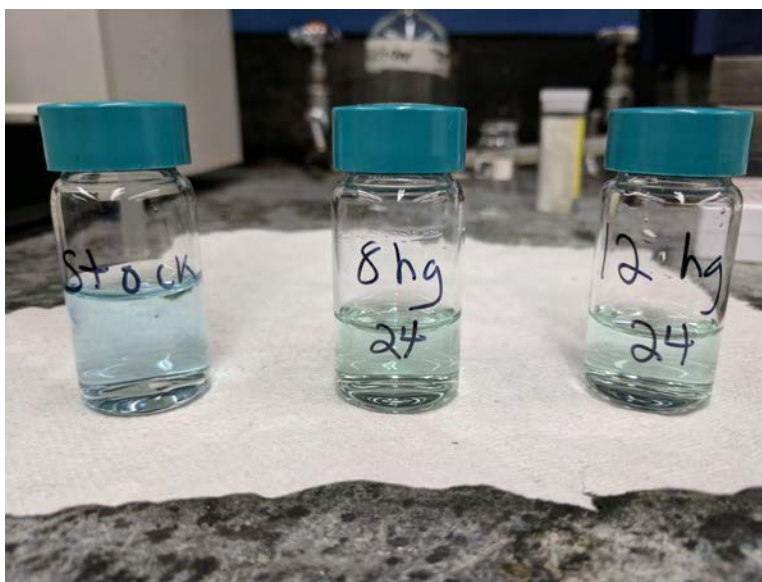
Figure 4: Comparing colors of filtered solutions of 8 and 12 hour glucose hydrochars
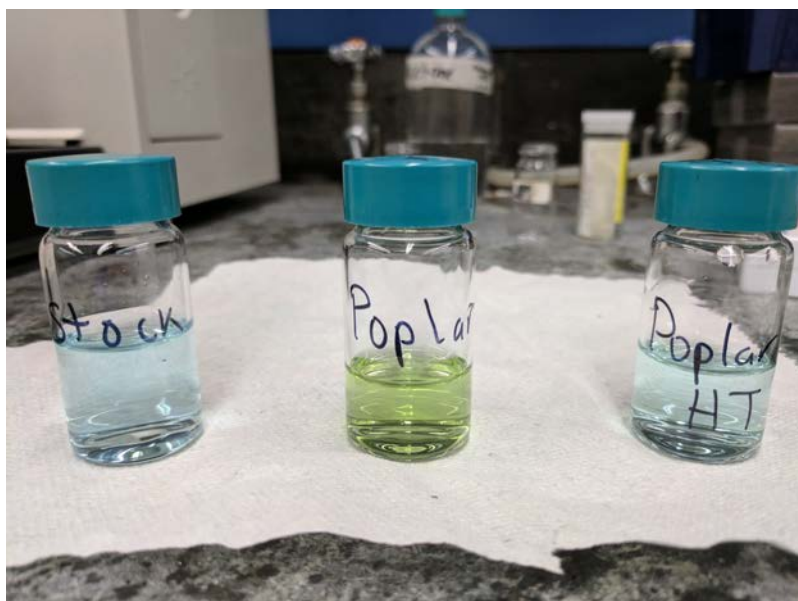
Figure 5: Comparing colors of filtered solutions of poplar and heat treated poplar CELF lignins
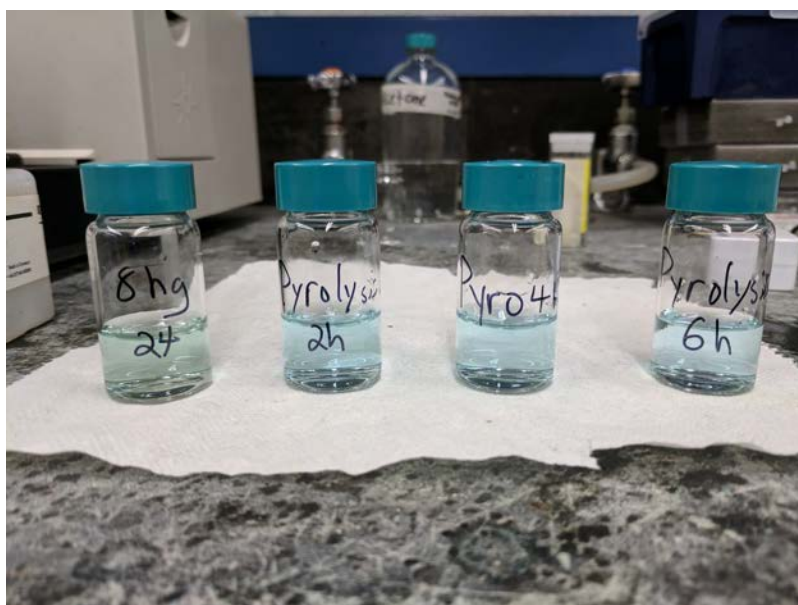
Figure 6: Comparing colors of filtered solutions of 8 hour glucose and the 2, 4 and 6 hour pyrolyzed samples

Appendix C: Spectroscopy Data

Table 10: Raw UV Spectroscopy Data

Trial	Mass AC	Initial Abs.	Final Abs. 1	Final Abs. 2
8 hr glucose A	0.2005	0.428960	0.417489	0.412586
8 hr glucose B	0.1999	0.428960	0.412586	0.405538
8 hr glucose B	0.2002	0.428960	0.422782	0.423032
12 hr glucose	0.2005	0.464452	0.454443	0.454806
16 hour glucose	0.2012	0.464452	0.450685	0.451934
Coffee Cake A	0.1999	0.467470	0.527950	0.565230
Coffee Cake B	0.2005	0.467470	0.507140	0.506440
Coffee RMR2	0.2006	0.467470	0.564450	0.552010
Coffee Powder	0.2002	0.467470	0.511050	0.506326
Coffee RM2 B	0.2008	0.467470	0.540470	0.540560
Maplewood A	0.2009	0.455060	0.438717	0.444070
Maplewood B	0.2013	0.455060	0.438854	0.440479
Bagasse A	0.2001	0.455060	0.437830	0.439310
Bagasse B	0.2013	0.455060	0.444617	0.442920
Poplar CELF Lignin	0.2020	0.479686	0.520596	0.516905
Poplar lignin (heat treated)	0.2019	0.479686	0.497111	0.488120
8hg (made 2/17)	0.1930	0.485553	0.482016	0.481151
2hr pyrolysis	0.2003	0.479686	0.465326	0.465910
4hr pyrolysis	0.1937	0.485553	0.451410	0.451376
6hr pyrolysis	0.1460	0.479686	0.473067	0.471311
Norit Darco 24hr	0.2003	0.489150	0.482771	0.482963
Norit Darco 36hr	0.2005	0.489150	0.444356	0.446832
Norit Darco 48hr	0.2006	0.467829	0.462639	0.459807
Norit Darco 60hr	0.2005	0.471512	0.451404	0.451798
Norit Darco 72hr	0.2007	0.489771	0.469891	0.467928
Norit Darco 96hr	0.2003	0.473650	0.453074	0.451418
Pica HP-120 24hr	0.2008	0.489150	0.412313	0.412703
Pica HP-120 36hr	0.2010	0.489150	0.444356	0.446832

Pica HP-120 48hr	0.2001	0.467829	0.398403	0.398503
Pica HP-120 60hr	0.2005	0.471512	0.404208	0.396714
Pica HP-120 72hr	0.2002	0.489771	0.410316	0.410104
Pica HP-120 96hr	0.2006	0.473650	0.395744	0.394984
Norit SX-1	0.2	0.71404	0.665125	0.672193
Norit SX-1	0.1999	0.71404	0.647822	0.645463

Appendix D: Sample Calculations

Sample calculations to find the copper Adsorption Capacity

$V := 10 \quad mL \qquad MWCu := 63.5 \quad g/mol$

$masschar := 0.1930 \quad g$

$initialabs := 0.485553 \qquad finalabs1 := 0.482016 \quad finalabs2 := 0.481151$

$finalaverage := \dfrac{(finalabs1 + finalabs2)}{2} = 0.482$

Note: the calibration curve is Abs = 11.334*(concenctration)+0.0119

$initialconcentration := \dfrac{(initialabs - 0.0119)}{11.334} = 0.042 \quad M$

$finalconcentration := \dfrac{(finalaverage - 0.0119)}{11.334} = 0.041 \quad M$

$initialcopper := initialconcentration \cdot \dfrac{V \cdot MWCu}{1000} = 0.027 \quad g$

$finalcopper := finalconcentration \cdot \dfrac{V \cdot MWCu}{1000} = 0.026 \quad g$

$Capacitance := \dfrac{(initialcopper - finalcopper) \cdot 1000}{masschar} = 1.152 \qquad mg\ Cu/g\ AC$