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# Copper Adsorption on carbon surfaces

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*Copper Adsorption on carbon surfaces*

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

Submitted by:

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Simon Escapa

December, 15th 2016

Approved by:

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Dr. Michael Timko, Advisor

## ***Abstract***

Removing heavy metals from waste water has always been a challenge. The different techniques that are offered today are limited to using other solvents that can potentially release secondary toxic materials and affect the environment and human health. Promising research using activated carbons as wastewater treatment have shown that it is an ecological alternative to the current methods. The exact mechanisms of heavy metal adsorption remains unknown. This project will devise different mechanism theories that could explain certain behaviors and characteristics of chars.

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## ***Introduction***

Water is an essential element for every living organism on the planet. It enables crops to grow, industries to produce and people to work. However, freshwater isn't the most predominant form of water. Freshwater only represents a fraction of the water of the planet (about 3%).<sup>1</sup> On top of this, 69% freshwater is located in the poles in forms of ice<sup>2</sup>, so humans need to take care of water management. Traditionally, freshwater comes from rivers, but nowadays freshwater also comes from small freshwater pockets located underground.

From the source to our faucets, different processes treat the water to fit consumption. All of them use the same method of transportation: pipes. The pipes are made out of heavy metals to keep it strong for years to come. In short term, using heavy metals allows safe and reliant transportation of freshwater, but in the long term, it can have serious impact on the environment and human health. Indeed, copper and zinc corrode and sip in to the water supply, which is then used for different purposes that affects our daily life. These problems have already started to surface everywhere. In Bangladesh, there has been report of constant arsenic poisoning<sup>3</sup>, while in the United States the Flint water crisis<sup>4</sup> has been gaining headlines for the last two years. These two separate events, although miles apart from each other, originate from pipes degrading and releasing heavy metals in to the supply.

Heavy metals are a serious concern to health and safety, regardless of the metal. Currently, most filtration processes for treating freshwater require the usage of solvents<sup>5</sup> that produce secondary toxic materials. As companies and governments are trying to pursue implement regulations for a more sustainable future, these methods need to be replaced. Promising research on biomass based chars have shown that there are several alternatives to the current methods that is less energy and cost intensive.

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<sup>1</sup> Howard Perlman, "How Much Water Is There On, In, and above the Earth?," How Much Water Is There on Earth, from the USGS Water Science School"

<sup>2</sup> Ibid 1

Riaz Uddin and Naz Hassan Huda, "Arsenic Poisoning in Bangladesh," Oman Medical Journal

<sup>4</sup> Steve Carmody, "A Year Later, Unfiltered Flint Tap Water Is Still Unsafe To Drink," NPR

<sup>5</sup> Tjoon Tow Teng, Yusri Yusup and Ling Wei Low (2012). Heavy Metal Ion Extraction Using Organic Solvents: An Application of the Equilibrium Slope Method,

# ***Background***

## ***Motivation***

Freshwater contains most of the nutrient that are essential to life. Minerals are an essential part for the body renewal, and not consuming freshwater, the most abundant source of mineral, can be fatal. Having a secure supply of freshwater is the main objective of each population agglomerations. As mentioned above, human population has grown considerably and some agglomerations are far from rivers. In order to maintain a healthy lifestyle, freshwater needs to be imported. In some cases, the water comes from underground pockets, while others comes from a river far away. However, activities above ground such as intense farming and industrial waste can cause freshwater to be contaminated with heavy metals. Some heavy metals, such as iron, are essential to life. For the purpose of this project, heavy metals will refer to all those toxic heavy metals that are defined by the World Health Organization.<sup>6</sup>

Heavy metal contamination are a serious threat to human life, and by extension, to the environment. Biologically, human cannot remove heavy metals as effectively as other materials. As a result, metals accumulate inside a body and cause different conditions. For example, cadmium affects the respiratory track severely, while at the same time cause renal failure.<sup>7</sup> Another common heavy metal is copper, which can cause gastrointestinal diseases and damage the liver.<sup>8</sup> Currently, the most common treatment found is chelation therapy, however this procedure can cause serious side-effects, from removing essential minerals in a body to death.<sup>9</sup> Knowing this, it is of utmost important to remove heavy metals to ensure a safe and healthy society.

## ***Heavy metal removal***

Heavy metal removal has been a challenge to the industry. Most of the heavy metal that is removed from waste water require an external agent that changes the properties of the metal dissolved in the water, but require very specific equipment that can ramp up the cost. Among the

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<sup>6</sup> World Health Organization, "Ten Chemicals of Major Public Health Concern," World Health Organization

<sup>7</sup> United States Department of Labor. "Safety and Health Topics: Cadmium"

<sup>8</sup>Casarett & Doull's Toxicology, The Basic Science of Poisons, Fifth Edition, Edited by Curtis D. Klassen, Ph.D., McGraw-Hill, New York. pp 715.

<sup>9</sup> "Nonstandard Uses of Chelation Therapy," The Medical Letter: On Drugs and Therapeutics 52, no. 1347



variety of different techniques, four of them stand out among the rest because of their usage: chemical precipitation, ion exchange, filtration and adsorption.

Chemical precipitation refers to using a reagent that sticks to the heavy metal and creates a solid mass that can be separated. It is a simple process and inexpensive to operate, however certain limitations that can impact the environment. For copper, the most widely spread precipitation technique used is the hydroxide precipitation.<sup>10</sup> It involves using a hydroxide compound (either NaOH or Ca(OH)<sub>2</sub>) that binds with the copper(II) cation and forms a precipitate. Because of this, the copper can be removed easily by either sedimentation or flocculation. However, this technique is very limited to high concentrations of heavy metal, while wastewater treatment usually only treats very small amounts of copper. Using chemical precipitation in low concentration solutions can result in a sludge, which can present a challenge when being removed. Additionally, in most cases the wastewater has a combination of different metals, and the precipitate that form can vary depending on the pH, leaving traces of metal in the water.<sup>11</sup>

Another widely used treatment for heavy metal removal is ion exchange. Ion exchange involves using a resin that binds to the metal cation by releasing a proton. Resins can be either naturally or synthetically produced, and yield a very good result, however this technique is heavily reliant on properties such as pH, temperature and initial concentration.<sup>12</sup> Promising research in zeolites, silicate minerals, could accelerate several of these constraints, however the technique is still in its infancy and needs time before any industrial usage.<sup>13</sup> Additionally, resins need to be regenerated after its usage, which can cause secondary pollution.<sup>14</sup>

Filtration of heavy metals involves passing the wastewater through a membrane that only allows certain ions to pass. The filtration techniques vary depending on what technique is used,

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<sup>10</sup> Fenglian Fu and Qi Wang, "Removal of Heavy Metal Ions from Wastewaters: A Review," *Journal of Environmental Management* 92 (March 2011)

<sup>11</sup> S. Ahmad Mirbagheri and Seyed Nezamedin Hosseini, "Pilot Plant Investigation on Petrochemical Wastewater Treatment for the Removal of Copper and Chromium with the Objective of Reuse," *Desalination*

<sup>12</sup> Fethiye Gode and Erol Pehlivan, "Removal of Chromium(III) from Aqueous Solutions Using Lewatit S 100: The Effect of PH, Time, Metal Concentration and Temperature," *Journal of Hazardous Materials*

<sup>13</sup> T. Motsi, N.a. Rowson, and M.j.h. Simmons, "Adsorption of Heavy Metals from Acid Mine Drainage by Natural Zeolite," *International Journal of Mineral Processing*

<sup>14</sup> *Ibid* 10

but are almost the same in their core. For example, ultrafiltration of heavy metals involves using a primary filter to obtain only the smallest particles. By adding polymers that binds to the heavy metals, the complex cannot pass through the nano-filters, hence filtering out the heavy metal. The primary advantage of this technique is that is highly efficient, as the polymers can be reused. However, the problem with this technique is, once again, that the most efficient removal depends on the polymer used and the solution's properties, both are specific to each metal. This breaks the wastewater treatment into individual treatments, which increases the cost of the process and therefore becomes less cost-effective.

Adsorption involves using a small particle, usually a char, that allows the cation to bind to the surface of the char. Chars are long organic that come from a variety of biomasses. Most of today's biomass goes on to produce biofuels as an alternative to fossil fuels, however some of it goes into producing biochar. Chars have been synthesized since the very beginning of time, however their application in different fields haven't been discovered until the late 1990s.<sup>15</sup> Depending on what feedstock is used, chars can have different visible properties such as color and structure changes, as well as chemical properties. Despite the variety of chars available, there are two main properties that are specific to all: porous structures and large surface area. Chars present very small pores that can be used as part of the desalinization of water, however the pores are too big for heavy metal adsorption.<sup>16</sup> Heavy metal adsorption is done on the surface of the char. Each char has a different surface area where the adsorption can take place.<sup>17</sup> This means that, by having more surface area, there is more likelihood of reactions to happen between the surface and the metal. What makes the usage of chars much more interesting than the other techniques is that it presents close to no limitations. Chars are low-cost materials that are reusable once the heavy metal cations desorb from its surface. The processes are very flexible, meaning that they do not involve using complex and heavy equipments, and is specifically successful at low-concentrations.

Chars are classified into two sections: raw and activated. Activated chars are those chars that have gone through an extra-processes in the production where more functional groups are

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<sup>15</sup> Maria-Magdalena Titirici et al., "Black Perspectives for a Green Future: Hydrothermal Carbons for Environment Protection and Energy Storage," *Energy & Environmental Science*

<sup>16</sup> Ibid

<sup>17</sup> Ibid

present. It has been showed that several functional groups are responsible for heavy metal adsorption<sup>18</sup>, however the exact mechanism remains unknowns. Activating a char can be done either mechanically or chemically, however a pre-treatment of the char called Co-solvent Enhanced Lignin-cellulosic Fractionation (CELf) has become object of interest for feedstock-based chars. Lignin is a group of chemicals that have an important function in plants. Being sturdy structures, they are the main skeleton of the plant and allows plants to be rigid. Lignin have long been problematic in development of ethanol, as they protect the cell walls of the plant and limits the interaction with water.<sup>19</sup> Accessing cellulose, the main reactant for the formation of ethanol, has been a daunting task until recently. A technique, using THF as a solvent, unfolds lignin structure, while makes the removal of it more simple and access the surface of the cell.<sup>20</sup> Being able to access cell walls has also helped adsorption research on chars, since lignin inhibited heavy metals from interacting with the surface.

### ***Theoretical Models and functional groups***

Despite extensive research done in the field of adsorption of heavy metals using a char, there are very few research papers that describe or proposes an adsorption mechanism. Instead, research has been focusing on characterizing the chars to identify functional groups. Chars are highly complex materials with many different functional groups at the surface, however it was possible to identify which functional groups are responsible of copper adsorption.

Functional groups are atom bonds that characterize the reactions of a compound. Functional groups are extensive, but can be classified depending on what atoms are present on it. At the same time, functional groups can be identified using an Infrared Spectrometer (IR). Each functional groups have different bonds between atoms which affects what energy they absorb. When passing a beam of light through a char, certain wavelengths will be absorbed, and each wavelength that has been absorbed can be traced back to a certain functional group.<sup>21</sup>

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<sup>18</sup> J.I Figueiredo et al., "Modification of the Surface Chemistry of Activated Carbons," Carbon

<sup>19</sup> Micholas Dean Smith et al., "Cosolvent Pretreatment in Cellulosic Biofuel Production: Effect of Tetrahydrofuran-water on Lignin Structure and Dynamics," Green Chem

<sup>20</sup> Ibid

<sup>21</sup>"IR Absorption Table." IR Absorption Table. <http://webspectra.chem.ucla.edu/irtable.html>.

It has been found that the functional groups that are responsible for the adsorption of copper are functional groups that have an oxygen atom.<sup>22</sup> Given this information, much of the mechanism that have been proposed involve around the idea of ion exchange. A proton detaches itself from an oxygenated functional group for it to bind with the copper. Given enough hydrogen, the metal would then adsorb to the surface and form bonds with those oxygens. The exact mechanism, where the intermediate steps are drawn, is still unknown and a theme of research.

The purpose of this project is to explore the ion exchange theory, as well as the adsorption for different chars. For this project, copper, one of the most predominant heavy metals found in freshwater, will be adsorbed on the surface of different chars. Each individual chars will be chemically analyzed, and the correlation between functional groups abundance and adsorption will be measured.

## ***Experimental Procedures***

The team designed and optimized several experiments that have been found in the literature. As part of the research, many different experiments have emerged based upon the results found in previous experiments. Additionally, optimization of the processes have been done using the most abundant chars and assuming that a similar behavior will be found when testing for other chars.

### ***Calibration curves for Copper Nitrate***

Copper nitrate will be used to model the copper content of water. 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 passed through the UV. At first, a 180 mL mother solution of 0.08M copper nitrate was made and stirred for twenty minutes<sup>23</sup>. Once well mixed, a small

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<sup>22</sup> J.I Figueiredo et al., "Modification of the Surface Chemistry of Activated Carbons," Carbon

<sup>23</sup> Appendix A: Sample Calculations

sample was run through the UV. In order to get 20 mL of each concentration, a certain volume of the mother solution was used. Additional DI water was also used to get to 20 mL which was then stirred for twenty minutes before sampling again. The cuvette was rinsed twice with DI water, then cleaned with ethanol and let to dry before every sampling. This same procedure has been done to get solutions from 0.07M to 0.01M. The table below shows how much DI water had to be added to the previous amount to get the desired concentration.

***Table 1: Calibration curve volume***

Copper concentration (Molar)	Mother solution removed (mL)	DI water (mL)
0.08	0	0
0.07	17.5	2.5
0.06	15	5
0.05	12.5	7.5
0.04	10	10
0.03	7.5	12.5
0.02	5	15
0.01	2.5	17.5

***Appropriate activated carbon to concentration ratio***

The UV Spec is a very sensitive equipment. Lower the absorbance change, more likely the readings will be similar. Therefore, a considerable change in absorbance needs to be observed for more accuracy. The purpose of this experiment is to find the right amount of char for any solution. Different mass of NORIT SX-1 were shaken with 20 mL of a 0.06M solution for six hours. Shaking is a better technique than stirring because the contact area with the copper nitrate is greater because of turbulent flow. The solution resulting solution was then first vacuum filtered then micro filtered using a 0.45  $\mu\text{m}$  syringe filter before being analyzed in the UV. The syringe filter is a necessary step because there are some micro particles the sip through the regular filter and makes the solution unreadable. Once analyzed, the best adsorption to mass ratio was picked for future experiments.

### ***Equilibrium time***

Equilibrium is the state of the solution at which the concentration of copper nitrate will remain constant. Given the limited amount of char, the equilibrium time taken from Norit SX-1 (Norit) and PICA HP-120 (HP-120) were assumed to be also the equilibrium time for other chars. In order to find this, 0.4g of both activated carbons were shaken with a 20mL of a 0.08M solution.

### ***Determining copper adsorption at equilibrium***

Vials containing PICA HP-120 and Norit SX-1 were shaken at the equilibrium time using the results from the second experiment. Once done, glucose based chars synthesized at different times were also shaken and sampled into the UV.

### ***Scale-down to 0.2g***

Some of the sample given to analyze didn't pass the 0.4 g mark. This means that a scale-down needed to be made to analyze these materials. Since glucose chars resemble more to the other raw-material chars, the eight-hour synthesis time glucose chars were used for the scale-down. For this, 30 mL vials and 15 mL vials were used for the scale-down to see the impact of using different vial sizes.

### ***Thermogravimetric Analyzer, Infrared Spectroscopy***

As said before, chars contain different functional groups. Much like analyzing the copper concentration using UV, functional groups can be identified using IR. Each char was analyzed in the IR to identify what functional groups are present. As for the amount of each functional group within a sample size, the Thermogravimetric Analyzer (TGA) was used to determine the composition of each functional groups. TGA takes a small sample and increments the ambient temperature slowly. At the same time, the mass of the char is weighted for different temperatures. As the temperature increases, functional groups will start to dissociate from the main structure, which will result in a change in mass. This change in mass will give out how much of each functional group is present in the different chars.

## *Uncertainty And Error*

As careful and precise instruments and procedures are, there are many sources of error that needs to be taken into consideration. For this project, most of the error analysis is performed for the amount of copper adsorbed per mass of char. Since multiple steps are done for each run, there are several sources of error that can have an influence on the interpretation of the result.

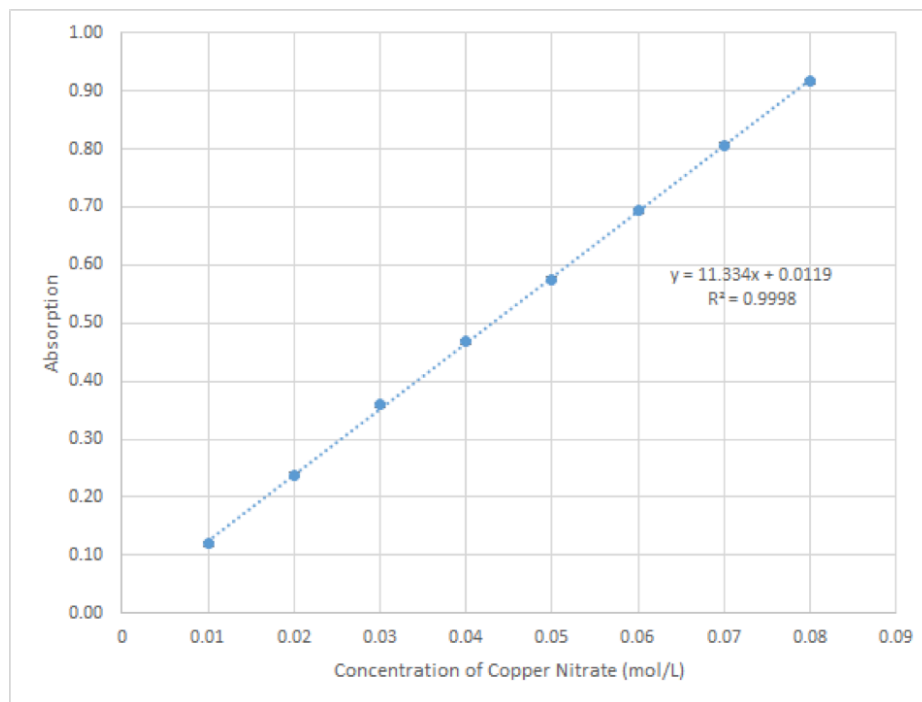
The first source of error was the UV. The UV spectrometer, although it is not as fragile as other analyzing equipment such as Raman, has different electrical components that can cause error. Mainly, a same sample can have different readings. For a same sample of 0.08M, it was found that the UV had an error of 0.004 in between each run. This error will be taken into account when doing calculations for the copper adsorbed. This amount of copper adsorb will be also referred throughout the paper as the capacity of the char.

The second source of error came from all the instrumentation that have been used. Every instruments used have a small error, whether it is in the weigh of the amount of copper nitrate added to the mother solution, weight of char in each vial, measuring the volume of DI water added and Copper Nitrate extracted. For each one of these individual steps, small fluctuations needs to be taken into account. For the balance, the fluctuation of mass for any material was 0.001g above and below. Therefore, the middle point between those two readings was assumed to be the most accurate amount, and an error or 0.0005g was considered for all masses calculated.

Lastly, another source of error and uncertainty was on the glucose chars. Since the experiments used a lot of glucose-based chars were used, different batches of glucose chars were used. Each batch, although they had the same synthesis time, were chemically different as reproducing the same exact char twice is impossible. Knowing this, each glucose run had to be carefully analyzed.

## Results And Discussion

### Preliminary results



**Figure 1: Absorption curve for Copper Nitrate.**

The absorption curve shows a linear correlation between the absorbance and the concentration of the solution for this Ultra violet spectrometer. The solutions used were decided based on literature value. Indeed, as the concentration tends towards a 0.01 M and 0.09 M, there is a change in curvature that occurs.<sup>24</sup> At those points, the absorbance of the solution will remain constant regardless of the concentration. This calibration, specific for the UV, will be the basis of the calculations done to determine the concentration of copper in a solution.

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<sup>24</sup> Curve flattening



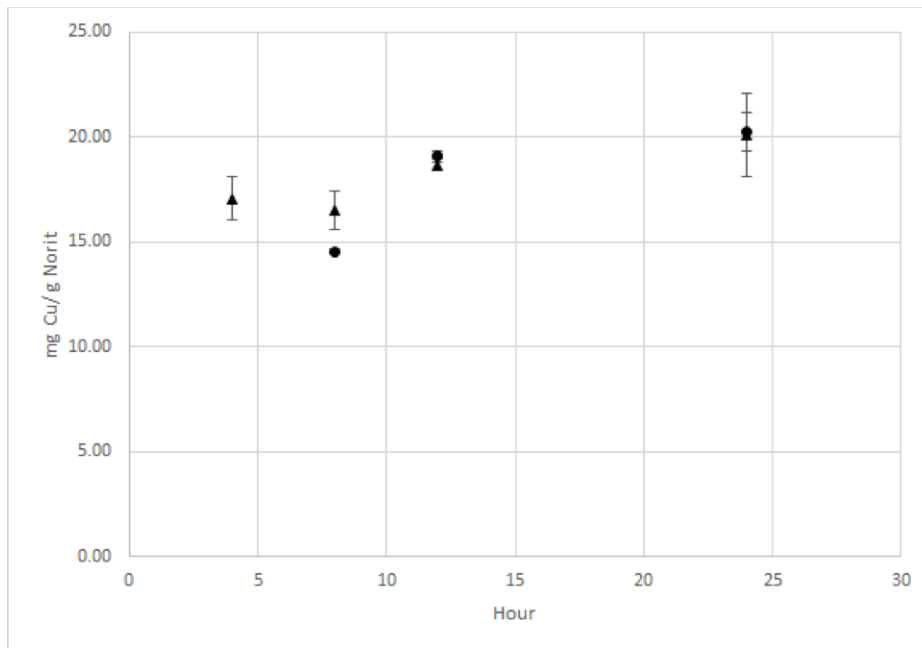
**Table 2: Absorbance difference for different masses of Norit SX-1 with 20 mL solution of 0.08M**

Mass of carbon (g)	Absorbance
0.2005 ± 0.0006	0.0199 ± 0.0022
0.4006 ± 0.0005	0.0506 ± 0.0024
0.8003 ± 0.0007	0.1105 ± 0.0008
1.6004 ± 0.0007	0.2510 ± 0.0114

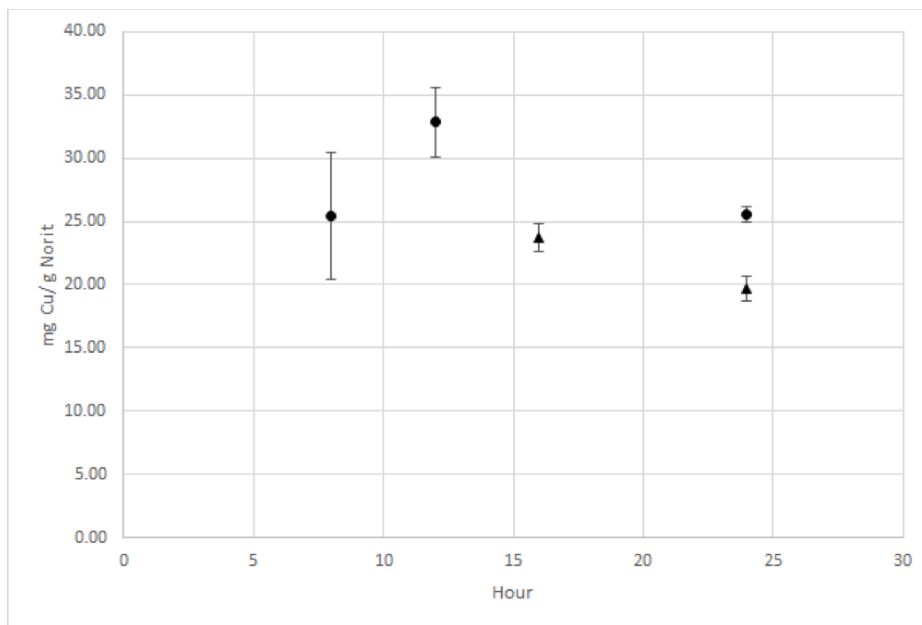
From the experiments run, by increasing the amount of char, the absorbance increases. Although having higher mass of carbon would show a much more distinct change in absorbance, it is too much char for one single vial. Knowing the limited amount of chars that are available, the best was determined to be 0.4000 g of char for the absorption. From here, all the experiments will be using a mass of char being equal to 0.4 g.

**Table 3: Capacity in function of time for Activated Carbon**

Time (hours)	Norit SX-1 (mg Cu/g)	HP-120 (mg Cu/g)
4	17.1±2.0	N/A
8	15.7±1.3	25.4±5.8
12	18.9±0.5	32.8±3.1
16	N/A	23.7 ± 1.1
24	20.19±2.4	22.6 ± 3.9



*Figure 2: Adsorption in function of time for Norit SX-1 (Activated Carbon). Triangular and circles represent different runs at different days*



*Figure 3: Adsorption in function of time for HP-120 (Activated Carbon)*

As expected, the capacity of the activated carbon to adsorb the char changes over time. For Norit, the adsorption increases and starts converging towards equilibrium. Although when taking

the overall capacity for each run the error bars are big, the individual error bars are quite small at 24 hours. It is important to note that for one of the runs, only two recordings were made instead of three. This increases the error bar, however when looking at the overall picture, at 24 hours, the solution is at equilibrium. Same goes for HP-120. The error bars at 24 hours are extremely small that the system can be considered to be at steady-state. What is different about HP-120 is that the capacity increased until 12 hours and starts declining afterwards. The capacity of adsorption reaches 32 mg/g before decreasing to 25.1 mg/g. This trend is an anomaly, as the char shouldn't be able to pass equilibrium and come back down. The only explanation for this is that there is a second mechanism that happens at 12 hours when using HP-120 that does not affect Norit. A possible mechanism will be proposed later in the paper. Nevertheless, regardless of this issue, it can be concluded that steady-state for 0.4g of activated carbon is around twenty-four hours given the error bars.

### *Scale-down and other chars*

*Table 4: Capacitance dependance on mass run for 24 hours*

Char used	mass (g)	Capacity (mg Cu/ g Char)
HP-120	0.4	12.5 ± 1.2
HP-120	0.2	21.0 ± 2.9
8 hour glucose	0.4	6.6 ± 3.6
8 hour glucose	0.2	3.7 ± 1.8

Although the equilibrium time was determined to be 24 hours for activated carbons, the equilibrium time need to be determined for glucose. At the same time, 8 hour glucose is the most abundant char available to the team that has a similar structure to the rest of the chars that need to be analyzed. The capacity of the activated carbon and the glucose char changes in function of the mass. This experiment was carried out without a styrofoam protector surrounding the shaker. This could have influenced the temperature, which can also affect the composition in the char. Indeed, temperature influences the amount of energy in the solution, and protons can be released from functional groups present on the char which can change the absorption done.

When considering the overall picture, if you have the same ratio of char to copper available, the capacity needs to remain constant. When this is not the case, it is possible that the solution hasn't reached equilibrium and this is why the contrast in values. For HP-120, there is a very big inflation of capacitance, a similar trend that was observed for determining the equilibrium time. For the glucose char, the capacity decreases. Therefore, when scaling down, the equilibrium time changes and needs to be determined for the scale-down to 0.2g.

**Table 5: Capacity for different masses HP-120 and 8 hour glucose for 0.04 M solution shaken for 96 hours. Asterix means that the runs for that mass were only run once.**

Char type	mass (g)	Capacity (mg Cu/ g)
HP-120*	0.2	17.3 ± 0.0
HP-120*	0.2	17.6 ± 0.0
8 hour glucose	0.4	4.05 ± 4.7
8 hour glucose	0.2	6.28 ± 5.2

Combining with a high capacity value and small error in the mass, the error bars were negligible. For 0.2g of HP-120, the solution is in equilibrium when shaken for 96 hours. The glucose chars have a very large capacity difference (fluctuating more than 5 mg/g). This is because there are two data points (one for each mass) that differs a lot from the other. This particular batch of glucose char had several small glassy structures that were hard to separate from the char. The two data points that are faulty could be due to having more of the glassy structure than others. Nevertheless, when looking at the other data points, they were relatively close to one another.<sup>25</sup> From this, it was assumed that, at 96 hours, the solution will be at equilibrium for 0.2 g of 8-hour glucose.

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<sup>25</sup> See Appendix B: Raw Data for Glucose 8 hours

**Table 6: Capacity for 0.2 g of different chars for a 0.04 M solution shaken for 96 hours. Chars with an Asterix have been run twice while a double asterix indicates only one run.<sup>26,27</sup>**

Char	Capacity (mg Cu/ g)
HP-120	17.5 ± 0.2
8 hour glucose	6.28 ± 5.2
16 hour glucose	1.1 ± 1
CELF Maplewood*	4.0 ± 0.4
CELF Bagasse*	3.9 ± 0.8
Pyrolysis Medium Mesh*	3.9 ± 6.4
Pyrolysis Small Mesh*	8.2 ± 0.1
Coffee Cake A**	-22.2
Coffee Cake B**	-11.0
Raw Coffee Material R2**	-25.3
Raw Coffee Material 2**	-11.5
Coffe batch**	-20.4

Depending on what chars are used, the absorption capacity varies. Commercial activated carbons such as HP-120 adsorb more than any other char, which is to be expected because of its high surface area. At the same time, synthesizing a same char can also influence its capacity. 8-hour glucose adsorb about six times on average more than the 16-hour glucose. This behavior is to be expected, as 16 hour synthesis time of glucose starts changing the oxygen groups that were present on the surface raw glucose char.<sup>28</sup> Pyrolysis medium mesh had a negative capacity, which contributed a lot in the error bar and average capacity. However, when comparing the other value for medium meshing, the capacity is actually greater than both of the small ones (from 10.3 mg/g to 8.2 mg/g). Overall, the best char disregarding the activated carbon is the Pyrolysis

<sup>26</sup> W.t Tsai et al., "Adsorption of Acid Dye onto Activated Carbons Prepared from Agricultural Waste Bagasse by ZnCl<sub>2</sub> Activation," Chemosphere

<sup>27</sup> Hans Darmstadt et al., "Co-pyrolysis under Vacuum of Sugar Cane Bagasse and Petroleum Residue," Carbon

<sup>28</sup> Brendan McKeogh. "Analysis of Furanic and Aromatic Structural Motifs in Hydrothermal Carbon." PhD diss., Worcester Polytechnic Institute, 2015.

Medium Mesh, however the 8 hour glucose char are also very close and further synthesis times between 8 and 16 hours should be studied.

Some of the solutions, when the char has added, changed color. Bagasse and Maplewood changed to a yellowish and red-like solution, however it didn't affect the reading of the spectrometer. For all the coffee related samples, the solution turned into a green-yellow solution. Contrary to Bagasse and Maplewood, the coffee samples had a higher absorbance than the initial concentration. This means that there is something that has dissociated from the coffee samples and that has the same absorbance wavelength as copper.

### *Surface area and adsorption for different materials*

*Table 9: Capacity for 0.2 g of different chars for a 0.04 M solution shaken for 96 hours. Chars with an Asterix have been run twice<sup>29</sup>*

Char	Capacity (mg Cu/ g)	Surface Area from literature (m <sup>2</sup> /g)	Capacity ( atom copper / aromatic ring)
HP-120	17.5 ± 0.2	2130	2.832-10 <sup>-5</sup>
8 hour glucose	6.28 ± 5.2	13.1	1.652 -10 <sup>-3</sup>
CELF Maplewood*	4.0 ± 0.4	340	6.49 - 10 <sup>-4</sup>
CELF Bagasse*	3.9 ± 0.8	529	2.54 - 10 <sup>-5</sup>

When knowing the capacity at steady state and the surface area, the surface of the chars at equilibrium can be sorted out. The values for surface area have been mostly retrieved from the literature, except for the glucose char which was determined by a member of the laboratory. The calculations assumed that the surface of the char was mostly dictated by aromatic rings.

What is interesting is that there has to be many aromatic rings in order for the copper to be adsorbed. Although the exact percentage of the surface covered by aromatic rings remains unknown, these results can have different interpretation. In this project, two of them are proposed, both of which can be simultaneous.

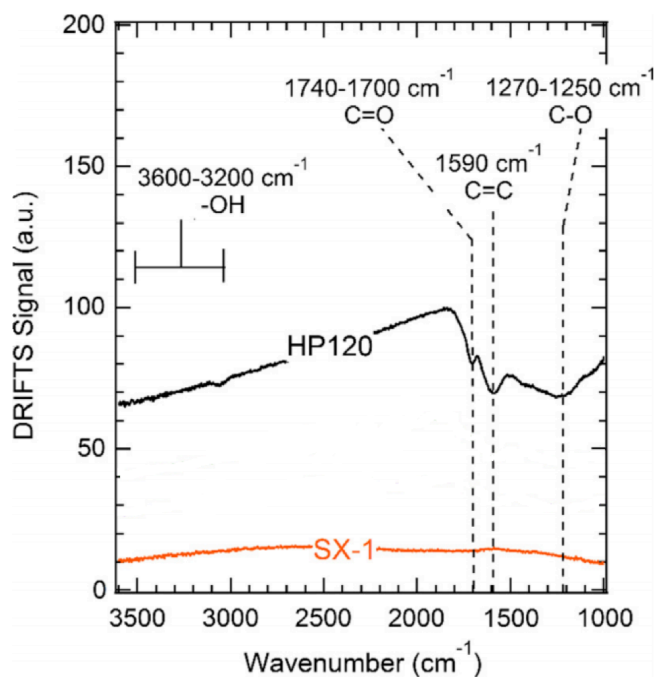
The first interpretation possible, the most likely, is that the surface area of a char is multiple different groups. Although this idea is not new, the data shows that the aromatic rings aren't the major structure that are found on the surface. As found in the literature, it is possible that pores

<sup>29</sup> Appendix A: Sample Calculations

(from meso to nano pores) are more predominant, which could translate into a variety of structures that would bend (recall that aromatic rings are 2D structures). Doing XRD imaging would help image and understand better the surface and see how predominant pores are.

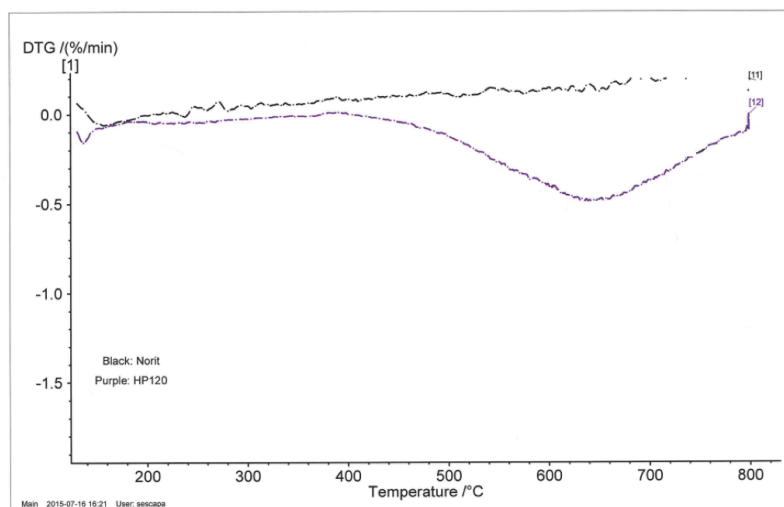
The second interpretation is that not aromatic rings are active sites for adsorption. This means that only a select amount of aromatic rings are able to bind with the copper (II) cation and adsorb it. This is possible because of how electrons keep moving at the surface of the char. Looking at an angstrom scale, alcohol groups can “jump” from one carbon to the other since the rings formed are constantly changing dipole moments. This could be an explanation on why only few functional groups are so important in the adsorption of copper: they allow aromatic rings to become active sites. This theory could be tested by testing the adsorption of copper onto benzene rings, and see if it varies when using phenol.

### *Activated Carbons characterization and first mechanism proposal*



**Figure 4: IR spectroscopy of the activated carbons<sup>30</sup>**

<sup>30</sup> Michael T. Timko et al., "Roles of Surface Chemistry and Structural Defects of Activated Carbons in the Oxidative Desulfurization of Benzothiophenes," Fuel



**Figure 5: TGA of the activated carbons**

As shown above, Norit has a lower capacity than HP-120. The surface area is different on the char ( $1173 \text{ m}^2/\text{g}^{31}$  to  $2130 \text{ m}^2/\text{g}^{32}$ ), however the main difference between both chars is the amount of functional groups that are present on HP-120. Recall that it was proposed earlier that there could be a second mechanism that is involved in the adsorption of copper when the vials is shaken for 12 hours. Knowing that there is close to no functional groups present (except alcohol), the adsorption in Norit can be attributed to the aromatic rings and to the alcohol group. Aromatic rings have electrons that changes positions constantly. Carbons changes dipole moments constantly, and makes the rings electronegative at times. By changing the pH, the aromatic rings would become less stable and more prone to react with other ions. Knowing this, it is possible that, because of the lack of functional groups, the copper interacts with the aromatic rings so that it stops creating a dipole moment with the carbons, and stabilize the structure. To compensate the charge of the solution, nearby alcohols will deprotonate and decrease the pH. This would be a form of ion exchange that is different from ion exchanges with resins for example. This mechanism, where the main driving force is static, will be the first mechanism that will be proposed: static adsorption.

<sup>31</sup> Buyi Li et al., "Tailoring the Pore Size of Hypercrosslinked Polymers," *Soft Matter*

<sup>32</sup> Marina Mastragostino, Alessandra Missiroli, and Francesca Soavi, "Carbon Supports for Electrodeposited Pt-Ru Catalysts for DMFCs," *Journal of The Electrochemical Society*



Knowing that copper can easily interact with the aromatic rings through static forces, let's assume that HP-120 follows the same rule. If static energy is the governing force behind the adsorption of copper, the ratio between the copper adsorbed to the surface area should remain constant. For 12 hours, the adsorption to surface ratio would be approximately 34.3 mg/g.<sup>33</sup> This value is very close to the one that has been found experimentally (32.8 mg/g), and the difference can be attributed to the fact that there are multiple functional groups on the surface of HP-120 and changes the available surface area for adsorption. However, as mentioned before, HP-120 capacity peaks at 12 hours before decrease and remain constant. In this mechanism, when the copper attaches with the aromatic rings, protons are released from alcohol groups to compensate the charge left in the solution. However, in the process, the acidity of the solution increases and won't allow any other forms of copper ions to form.<sup>34</sup> By increasing the acidity, the pKa would decrease and large ether groups could start dissociating and break apart bonds that would maintain the char together.<sup>35</sup> Since Norit compounds doesn't contain a lot of functional groups, the structure maintains it's stability. However, since HP-120 contains multiple functional groups that have oxygens in them (ethers, carboxylic acids...), many of them start to break apart. In order to maintain the structure, the char reshapes, changing it's structure and, therefore it's capacity. This second mechanism will be proposed as surface reshaping. In order to see if how the structure is affected, IR and TGA for chars that have been tested for different hours should be analyzed. At the same time, the pH of the solution should also be tested at different times to see if the pH changes with time and how see what functional groups are still present.

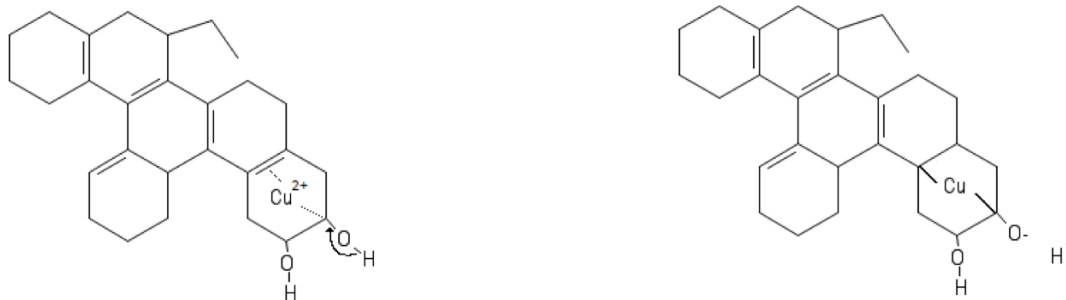
This two-step mechanism proposal involves under the assumption that the main driving force behind the adsorption mechanism is the alcohol and the presence of aromatic rings wanting to keep the char stable. Because of their electronegativity, they attract copper ions and start bonding with them. As a result, there is deprotonation of nearby alcohol groups, which increases the pH. If the material doesn't contain many oxygenated groups, the mechanism will reach equilibrium.

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<sup>33</sup>Appendix A: Sample Calculations

<sup>34</sup> Shunsuke Yagi, "Potential-pH Diagrams for Oxidation-State Control of Nanoparticles Synthesized via Chemical Reduction," *Thermodynamics - Physical Chemistry of Aqueous Systems*

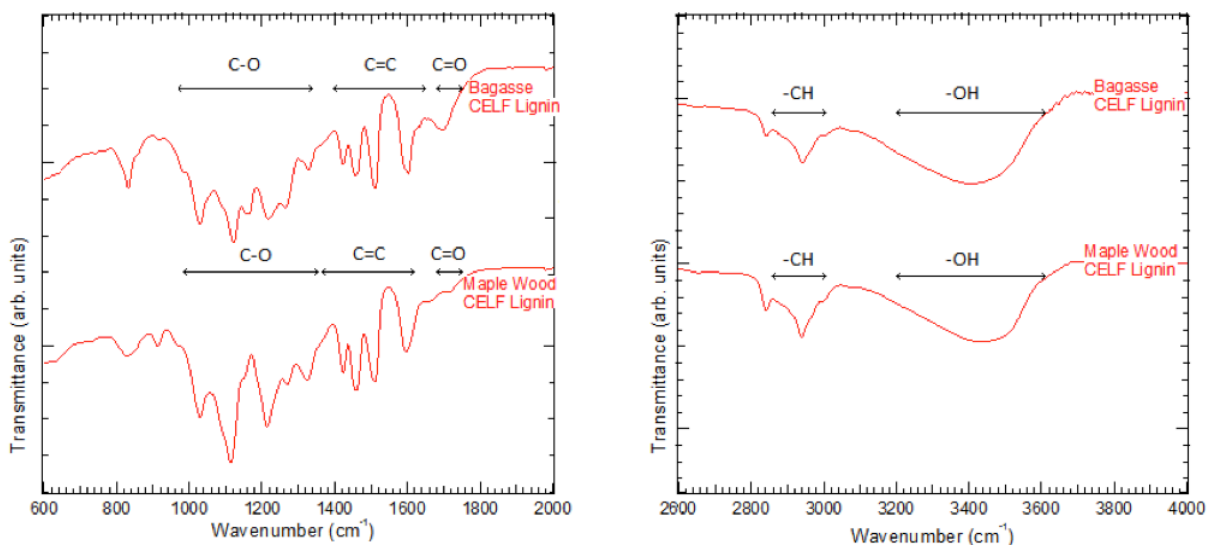
<sup>35</sup> John A. Dean, *LANGE'S HANDBOOK OF CHEMISTRY*, Fifteenth ed. (New York, NY: McGraw-Hill, 1999).



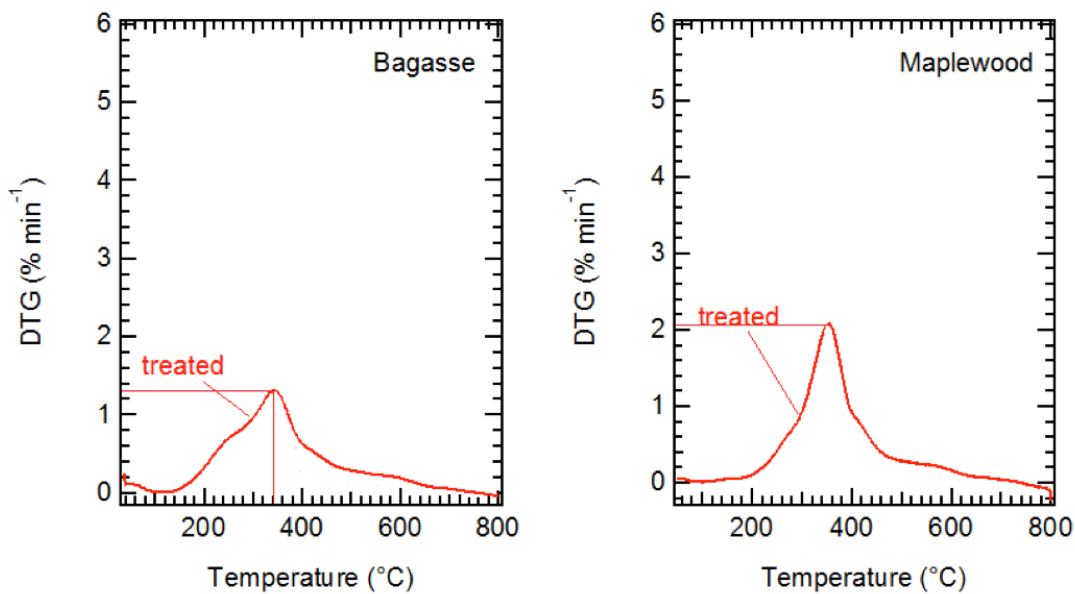
**Figure 4: Simplified first mechanism. The alcohol deprotonates (left) so that the oxygenated carbon forms a bond with copper (right).**

However, if the material is very oxygenated, the bonds will break apart and destabilize the structure. As a result, the char breaks apart and reshapes. This decreases the copper capacity, reshape functional groups on the char into a more stable. This systematically happens until the char reaches a stable form and reaches equilibrium

### **CELf Chars characterization and second mechanism proposal**



**Figure 5: IR spectroscopy for CELf Maplewood and CELf Bagasse**



**Figure 6: TGA of CELF Maplewood and CELF Bagasse**

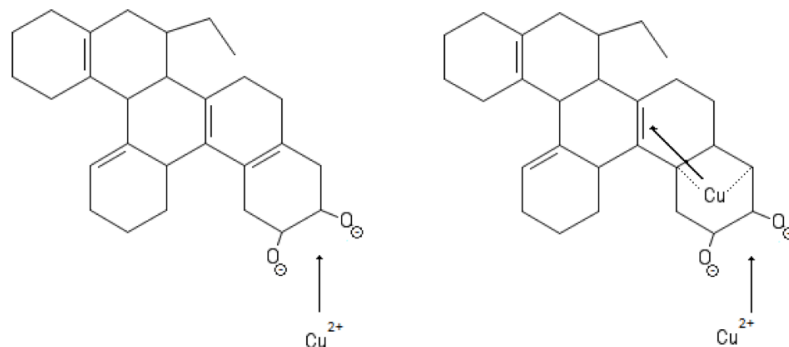
Looking at the IR of CELF Maplewood and Bagasse, both of them have a similar composition. They both have long broad ether, carbonyl, alcohol and aromatic groups that are attached to it. From literature, these are the main functional groups that are responsible for copper adsorption.<sup>36</sup> It is important to note that for IR, unlike UV, having less transmittance doesn't equate to having less of a certain functional group. At the same time, IR is heavily reliant on dipole moments, which changes constantly to aromatic compounds. Hence, identifying to carbonyl groups these peak have, a Raman Spectroscopy needs to be performed.

Using TGA, it is possible to see the alcohol content of the chars because of a specific peak. Alcohol dissociates at temperatures close to 573 K, which is a fairly similar peak that is seen on this TGA.<sup>37</sup> From TGA, about 1.3% and 2.1% of the weight of Maplewood and of the Bagasse chars are from alcohol groups. Knowing the initial mass added in the TGA (5.8mg and 5.3 mg), the mols of alcohols can be calculated, and found to be  $4.45 \cdot 10^{-6}$  and  $6.45 \cdot 10^{-6}$  mols for bagasse and maplewood respectively. This is persistent with the idea that having more electronegative

<sup>36</sup> J.I Figueiredo et al., "Modification of the Surface Chemistry of Activated Carbons," Carbon

<sup>37</sup> Liqing Li et al., "Thermal Stability of Oxygen-Containing Functional Groups on Activated Carbon Surfaces in a Thermal Oxidative Environment," Journal Of Chemical Engineering Of Japan

functional groups are present in the char allows more adsorption. This is what the second mechanism is going to be based on.



**Figure 7: Simplified second mechanism. The alcohol groups deprotonate because of pH, and allows the copper to adhere to the surface (left) and move in the rings (right)**

As mentioned above, the solution is acidic, which makes electronegative bonds unstable. Unlike the static mechanism that was mentioned above, the copper atoms would form bonds with the alcohol group first before moving towards the aromatic rings where it will rest. Because of the pH, copper oxide cannot be formed.<sup>38</sup> Now, this mechanism would repeat itself with another copper atom, and push the copper atom towards another ring. This will happen until the char become stable enough that it doesn't need to absorb more copper atoms.

Considering symmetry, there is a point in time where the coppers won't be able to advance anymore. This would be represented as the peak at an hour. However, once it can't advance anymore, the char starts to expand to relieve some of the additional energy that has been accumulation because of copper atoms. When the char expands, the oxygenated functional groups such as ethers and carboxylic acids that hold the char together, start to elongate and react with the protons present in the already-acidic solution. These bonds break, changing the structure of the chars, and hence release more copper. This process starts again, until it reaches equilibrium. From a thermodynamic point, this could be possible if the nitrate ions help keep the copper on the surface of the char. By doing this, the char would be able to adsorb more char than the true equilibrium value. However, once it reaches a certain threshold, the interaction

<sup>38</sup> pH diagram

between carbon start to break down because of the charges, and hence disrupt the structure of the char. This could be another explanation for the vibrational-like behavior of the adsorption over time for several chars.

The second mechanism revolves around the idea that the nitrate ions help in the mechanism of adsorption. The copper ions enter the surface through the electronegative functional groups located at the surface and start to crowd the surface. Once it reaches a certain threshold, the char starts to break and release copper ions. The process repeats until the char remain stable and reaches equilibrium. In order to test the influence of the nitrate ions, another source of copper (copper hydroxide, copper sulfate...) could be used and run under the same conditions. If the adsorption behavior changes, it means that the ion that comes with the copper ion is actually involved in the mechanism.

## ***Conclusion And Recommendation***

Overall, electronegative functional groups do influence on the capacity of any char to adsorb copper, and affects it more than the surface area. By having more functional groups that contain alcohols, carboxylic or ether groups among others, the copper will be attracted to the negative poles on the char. The behavior of highly oxygenated HP-120 is very atypical of any regular equilibrium, as it peaks then decreases before reaching equilibrium. Two different two path mechanism were proposed for this particular behavior. Both of the mechanism involve stabilizing the multiple electronegative sites that are present on the surface and that highly oxygenated chars change composition.

The first mechanism involves around the properties of Norit. By having very few oxygenated functional groups except for alcohols, the copper would attach itself to an olefin through a static force, which would change the configuration of bonds in it's surroundings. This would release protons from the alcohols, making the solution more acidic. By increasing the acidity, oxygenated functional groups such as ethers and carboxylic acids start to break, and the structure of the char breaks down. From a thermodynamic view, this mechanism could be

possible without the help of the nitrate ion. The pH and the temperature of the solution should be recorded to see if the char releases energy abruptly or not.

The second mechanism involves around the ion. The electronegative functional groups would attract copper(II) cations and bond with them. Because of the aromatic rings, the copper (II) cations would then move towards rings, and start stabilizing the rings. As the copper start populating the surface, the char starts becoming slightly positive and the anions present in the solution would stabilize the char. However, once it passes a threshold, the char expands to release the excess energy. This char expansion would allow functional groups, such as ethers, to react with protons present in the solution. This will break the char, changing it. This process repeats itself until it reaches equilibrium. To test whether or not one of the mechanisms works, another copper mineral, such as Copper Sulfate, could be studied to see if the anion interact with the surface of the char.

Several different experiments could be done to validate either theory, however both of them revolve around a structural change in the char. To test how the structure changes, the char needs to run IR and TGA on those samples that are on the second mechanism and analyze them. If they differ from the original char, this indicates that the structure of the char has changed. The char needs to be well characterized before and after runs in order to validating any theory behind the adsorption mechanisms of copper.

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## Appendix A: Sample Calculations

### Sample calculations to find the amount of DI needed

Want a 180 mL solution of 0.04 M of  $\text{Cu}(\text{NO}_3)_2$

$$M := 0.04$$
$$V := 0.180 \text{ L}$$

$$\text{Amount of moles needed: } n := M \cdot V = 7.2 \times 10^{-3} \text{ mol}$$

We are given Copper Nitrate Hemipentahydrate

$$M_{\text{CopperNitratehemi}} := 232.59 \frac{\text{g}}{\text{mol}}$$

$$m_{\text{CopperNitrate}} := M_{\text{CopperNitratehemi}} \cdot n = 1.675 \text{ g}$$

1.675 g of  $\text{Cu}(\text{NO}_3)_2 + 2.5 \text{ H}_2\text{O}$  is needed

$$n_{\text{water}} := \frac{2m_{\text{CopperNitrate}}}{M_{\text{CopperNitratehemi}}} = 0.014 \text{ mol}$$

$$\text{density}_{\text{water}} := 1 \frac{\text{g}}{\text{mL}}$$

$$M_{\text{water}} := 18.015 \frac{\text{g}}{\text{mol}}$$

$$V_{\text{water}} := n_{\text{water}} \cdot \text{density}_{\text{water}} \cdot M_{\text{water}} = 0.259 \text{ mL}$$

$$V_{\text{add}} := 180 - V_{\text{water}} = 179.741 \text{ mL}$$

For 180 mL, need to add 179.74 mL of DI

### *Sample calculations to find Capacitance*

$$V := 10 \text{ mL} \qquad M_{\text{Cu}} := 63.5 \frac{\text{g}}{\text{mol}}$$

$$\text{mass}_{\text{char}} := 0.2003 \text{ g}$$

$$\text{initial}_{\text{abs}} := 0.69001 \quad \text{final}_{\text{abs1}} := 0.650865 \quad \text{final}_{\text{abs2}} := 0.658558$$

$$\text{final}_{\text{average}} := \frac{\text{final}_{\text{abs1}} + \text{final}_{\text{abs2}}}{2} = 0.655$$

Recall the calibration curve is  $\text{Abs} = 11.334 [\text{concentration}] + 0.0119$

$$\text{initial}_{\text{concentration}} := \frac{(\text{initial}_{\text{abs}} - 0.0119)}{11.334} = 0.06$$

$$\text{final}_{\text{concentration}} := \frac{(\text{final}_{\text{average}} - 0.0119)}{11.334} = 0.057$$

$$\text{initial}_{\text{copper}} := \text{initial}_{\text{concentration}} \cdot \frac{V}{1000} \cdot M_{\text{Cu}} = 0.038 \text{ g}$$

$$\text{final}_{\text{copper}} := \text{final}_{\text{concentration}} \cdot \frac{V}{1000} \cdot M_{\text{Cu}} = 0.036 \text{ g}$$

$$\text{Capacitance} := \frac{(\text{initial}_{\text{copper}} - \text{final}_{\text{copper}})}{\text{mass}_{\text{char}}} \cdot 1000 = 9.873$$

*Sample calculation to find the capacity per aromatic ring*

$$M_{\text{Cu}} := 63.546 \frac{\text{g}}{\text{mol}}$$

$$\text{Capacity}_1 := 17.5 \frac{\text{mg} \cdot \text{Cu}}{\text{g} \cdot \text{char}}$$

$$\text{Surface}_{\text{area}} := 2130 \frac{\text{g} \cdot \text{char}}{\text{m}^2}$$

$$\text{Capacity}_2 := \frac{\text{Capacity}_1}{\text{Surface}_{\text{area}}} \cdot \frac{6.022 \cdot 10^{23}}{1000 \cdot M_{\text{Cu}}} = 7.786 \times 10^{16} \frac{\text{atom}}{\text{m}^2}$$

$$\text{Capacity} := \text{Capacity}_2 \cdot \frac{1}{10^{24}} = 7.786 \times 10^{-8} \frac{\text{atom}}{\text{pm}^2}$$

$$\text{Ring}_{\text{hexagonlength}} := 140 \text{ pm}$$

$$\text{Area}_{\text{ring}} := \frac{3 \cdot \sqrt{3} \cdot \text{Ring}_{\text{hexagonlength}}^2}{2} = 363.731 \text{ pm}^2 \quad \text{This is the area of an aromatic ring}$$

$$\text{Capacity}_{\text{end}} := \text{Capacity} \cdot 363.731 = 2.832 \times 10^{-5} \frac{\text{atom}}{\text{ring}}$$

## *Appendix B: Raw Data*

### *Raw data for the Glucose 8 hours*

Glucose 8 hr	mass AC (g)	initial abs	Average final absorption	mg Cu/ g AC
Vial A	0.4	0.3918	0.3864	1.52
Vial C	0.4	0.3918	0.3683	6.58
Vial D	0.2	0.4007	0.3706	8.4
Vial E	0.2	0.4007	0.3676	9.28
Vial F	0.2	0.4007	0.3965	1.18

### *Raw data for Coffee samples*

	mass A (g)	initial ab	Average final absorption	mg Cu/ g A
Cake	0.199	0.4674	0.5465	-22.1
Cake	0.200	0.4674	0.5067	-10.9
RMR	0.200	0.4674	0.5582	-25.3
Coffe	0.200	0.4674	0.50868	-11.5
RM2	0.200	0.4674	0.54051	-20.3