The Mechanics Involved in Removing Copper Ions Using Hydrochars, Activated Carbons, and Resins

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Abstract

According to the World Health Organization around 785 million people do not have a good source for their drinking water. [1] The lack of clean water comes from a lack of access to proper water treatment methods, and the presence of heavy metals in rivers and coastal areas, due in a large part, to industrial run-off. Sorption techniques that use different materials including hydrochars, activated carbons, and resins can be used to clear heavy metals and organic compounds from water. Biomass is a cost effective supply due to its large abundance and when carbonized, yields chars that can be used as adsorbents. Hydrothermal carbonization (HTC) is the process where biomass is converted to hydrochar. In this work, hydrochars were compared to traditional adsorbents for the removal of copper ions in a copper nitrate solution. Incorporating acids such as acrylic acid and vinyl sulfonic acid into the HTC process was done to see how adding an acid affects the performance of the hydrochars ability to remove copper ions. These hydrochars were then activated with a base solution, which improved the hydrochar's ability to remove copper ions. Lastly, FTIR and titration of sorption materials was done to understand how adsorption of copper ions is related to the material's acid concentration. The results showed that hydrochars exhibit a strong intensity of carboxylic acids on their surface. In addition, activation helped to ionize the hydrochars' acid sites to give the char a more negatively charged surface to adsorb the positively charged copper ions. Overall, activated hydrochars have adsorption capacities that are comparable to traditional adsorption materials and that there is promise in exploring these materials as adsorbents in wastewater treatment.

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Table of Contents

Table of Figures

Table of Tables

Introduction

According to the World Health Organization, 785 million people do not have access to good drinking water. [1] The lack of clean water that exists is from the presence of heavy metals in rivers and coastal areas that is in large part due to industrial runoff. While the need for good drinking water has grown, "resources" remain "threatened in terms of quantity and quality." [2] This problem of poor drinking water was highlighted in recent years in the city of Flint, Michigan where a major health crisis occurred when approximately 100,000 people were exposed to the city's drinking water that had been contaminated with lead. The lead in the water came from the corrosive pipes that the city was using for its drinking water. The incident of poor drinking water in Flint, Michigan emphasizes the need to have a clean and healthy water supply. [3]

The water treatment industry has responded to the need for having a clean water supply by making it their priority to produce high quality water in a cost-efficient way. [2] This means focusing on eliminating the contaminants that exist in the water supply. The problem of having contaminants such as metals in the water supply has existed as far back as the time of the ancient Roman Empire. Some researchers have theorized that it was the water supply of ancient Rome, which had been contaminated with lead, that may have played a role in the downfall of the empire. The lead that seeped into the water supply came from the aqueducts that were built by the Romans to transport their water. [3]

Metal contaminants that are found in the water supply today continue to be a major issue in many countries worldwide. [3] The metal contaminant that this project focused on is copper, Cu^{+2}. Copper is a metal that is found in drinking water and can cause digestive illnesses such as

"nausea, abdominal pain, diarrhea, and vomiting," when the levels of "copper concentrations reach 4.0 [to] 6.0 milligrams per liter (mg/L)." [4] If a person ingests copper at high concentrations they can end up having copper toxicosis, which although rare, can cause a person to have major problems with their liver and kidneys. [4]

Currently there exist several methods that are used to remove heavy metals from contaminated water, these include: precipitation, membrane filtration, and the use of adsorption materials. [5] Precipitation is used when there is a large concentration of heavy metals in the water supply. However, one of the problems with this technique is that it is very expensive to implement and it is primarily used for the processing of industrial waste streams. [5] Membrane filtration is designed to remove both inorganic and organic contaminants based on the contaminants' size; these include membranes "such as ultrafiltration, nanofiltration, and reverse osmosis" ones. [5] One of the problems with membrane filtration is that it can be expensive to operate, and fouling can occur. [5] Sorption materials are used as a cost-effective alternative to the previously mentioned techniques and can absorb a variety of ions and compounds together. [5] While sorption materials have small adsorption capacities, the materials they are made from are in large supply. [6] In addition, sorption materials are capable of adsorbing metals in drinking water at low concentrations, which can make the water supply healthier for people and the habitats where they are used. [5]

There has been an "increase" interest to use carbon materials that are derived from renewable resources and are "environmentally friendly," cost effective, and quick to produce. [7] In the field of water purification, the carbon materials are used as adsorbents to remove organic compounds and heavy metal ions. It is ideal to have adsorbents that have good adsorption capacities as well as ones that are selective in what materials they remove. Good adsorbents must

have strong "kinetics" for the ions to be removed and must be "regenerab[le]" so metals can be removed continuously. [8] To remove metal ions, the adsorbent should have a high surface area along with a porous structure with the correct size pores that will enable metal ions to pass through its surface. [8] In industry, activated carbons are used to remove metal ions and organic compounds. Some of their promising attributes include the fact that they have high "surface area[s]," attractive "porous structure[s]," and excellent "oxygen functional groups." [9]

In this project, hydrochars were investigated as a sorption material to see how they perform in comparison to activated carbons and resins. As an adsorption material, hydrochars are more cost effective than activated carbons and resins since they do not require a pre-drying step when they are synthesized from biomass. [6] Hydrochars can also be produced from a vast variety of biomass materials, which are in large "abund[ance]" worldwide. [6] Therefore, the goal of this project is to show that hydrochars have comparable adsorption capacities to activated carbons and resins that are already used in many industries.

Background

Copper

A vast majority of the earth's natural water has a copper content that is only a "few milligrams per liter", however water from wells and water that flows through new copper pipes can yield high levels of copper. [4] Dr. Magdalena Araya, a scientific researcher who studied the effects of copper at the University of Chile's Institute of Nutrition and Food Technology, believes that copper found in food is less likely to lead to a person having gastrointestinal symptoms upon ingestion. [4] Instead, she concluded that it is the pH level of the water that promotes the "solubilization and absorption" of copper which can lead to a person to becoming ill. [4] Dr. Araya and her research team in Chile conducted a study and found that copper that had concentration levels of 4.0 milligrams per liter and 6.0 milligrams per liter, caused gastrointestinal problems in a significant percentage of people in the study. Their results from copper levels between <.01 milligrams per liter and 2.0 milligrams per liter were "not statistically significant" in the study. [4] They were able to conclude that the World Health Organization's "safe limit" of copper that exists of 2.0 milligrams per liter was an acceptable level for the water supply. [4] Keeping the concentration of copper low in the water supply is essential to the health of humans. It is very important that scientists investigate adsorption materials, like hydrochars, to see if they have the ability to absorb copper ions in order to make the water supply as safe as possible for humans.

Biomass

Researchers have looked to other sources of energy that can be renewable as well as sustainable. [6] Biomass has been found to be a good alternative energy source that has both of these factors. Biomass is referred to as a "lignocellulosic material" when it originates from

organic materials such as agricultural wastes and woods, and when it comes from city wastes as well as animal wastes it is referred to as a "non-lignocellulosic material." [6] Biomass is highly versatile in that it can be transformed into fuels that can be in a solid, liquid, or a gas phase. Biomass has been explored as a resource for energy production because it comes from a large variety of materials that are in large supply and additionally has the ability to grow on many kinds of terrain. [6] Biomass that comes from plants is made up of three parts: lignin, cellulose, and hemicellulose. These parts have "non-covalent" chemical bonds that exhibit "cross-linking" which helps to keep them together. Together they give the plant its firm structure. [6]

While biomass is used as an energy source, it is not considered to be a perfect fuel because some its drawbacks include the fact that it has an elevated moisture content," a small heating value", "a high number of volatile" parts, and a high content of "alkali and alkaline earth" metals. [6] Because of this, treatments have been developed to improve the properties of biomass in order to make it more energy efficient. Some of these pre-treatment methods include using pyrolysis and gasification, which are both thermochemical treatments that have "short reaction time[s]" and "high conversion efficienc[ies]." [6] The type of pre-treatment that is used is dependent on the state of the feedstock, whether it is wet or dry. Wet biomasses are feedstocks such as sludge or vegetable wastes that have a moisture content above 30%, while dry biomasses like crop residues have a moisture content below 30%. [6]

Aside from the heat aspect of biomass, "the ash content", the "percent of volatiles", and the "susceptibility to slagging and fouling" are the most important compositional properties of biomass. Ash content is the mass fraction of material that is not combustible and is usually higher in field crops and grasses than in wood. [10] Wood usually has an ash content below 2 percent, while bark's ash content is from 2 to 5 percent. [11] Ash can cause slagging and fouling

when it starts to melt. It is essential that ash remains in a powdery form, but if it melts, it leaves deposits on the surfaces of a combustor, which is known as fouling. [10] Melting ash also can form deposits of material in the combustion chamber's base, which is referred to as slagging. Fouling and slagging are dependent on the elevated "mineral content" that exists in field crops. This property can be impacted by the time that harvesting occurs, as lower ash content has been found in "late harvested crops." In addition, fuels that have dirt have higher mineral content, which leads to fouling issues and it means that fuel must be completely separate from soil. [10]

Having a low combustion temperature, that prevents the melting of ash, helps to decrease the amount of fouling and slagging. Percent volatiles, the fraction of fuel that volatizes easily and becomes gas when operating at increased temperatures, is an important component of biomass. High volatile fuels are inclined to vaporize before combusting, which makes them a less useful fuel to use for wastewater treatment. It is ideal to have fuels with low volatiles, which burn well as a "glowing char." [10] Wood and other kinds of biomass typically have a volatile percentage of 80 percent, which means that during combustion, 80 percent of the biomass is vaporized and light charcoal is left over. The elemental composition of wood-based biomass is "45 [to] 50" percent carbon, "40 [to] 45" percent oxygen, "4.5 [to] 6" percent hydrogen, and "0.3 [to] 3.5" percent nitrogen. [11]

Biochar

Biochar is a solid compound that is high in carbon and is made from the pyrolysis and the carbonization of biomass that comes from plants and animals. [12] A variety of biomasses including "wood, manure, or leaves" undergo a thermochemical process when heated in a closed container with a small amount of oxygen in order to yield biochar. The process results in a biochar that has a high content of carbon as well as having a porous structure. [12]

Biochar is synthesized through pyrolysis with a temperature range from 200°C to 900°C. [12] Three different kinds of pyrolysis are used to produce biochar. Each is based "on the residence time and temperature" of the process, which is either slow, intermediate, or fast pyrolysis. Fast pyrolysis has a small residence time of below two seconds, and largely results in the production of bio-oil. It is ideal to use slow or intermediate pyrolysis, which has residence times from a "few minutes" to multiple hours or days, in order to maximize the production of biochar. [12]

The production of biochar is dependent upon the pyrolysis temperature, the heating rate, and the feedstock type that is chosen. [12] For example, choosing feedstocks like solid waste and animal waste result in higher biochar yields than when the feedstock is chosen from waste from crops, because the crops have inorganic components that lead to a higher ash content in the biochar. [12] The heating rate has the smallest impact on the amount of biochar produced when one studies the three key parameters, as *Karaosmanoğlu et al.* found that when they increased the heating rate from 5 to 15°C/min. This resulted in only a small change in the biochar yield. [12] The pyrolysis temperature that is selected has a major impact in the biochar yield. For example, *Uchimiya et al.* pyrolyzed cottonseed hull at temperatures that went from 200°C to 800°C. The biochar yield was relatively low due to the removal of non-condensable gases like CO, H_2 and CO_2 that occurred. Increasing the pyrolysis temperature raised the carbon content of the biochar, while the contents of hydrogen and oxygen amounts were lowered. [12]

Biochars are very useful for the removal of metals found in wastewater. *Lima et al.* found that activated biochars derived from different kinds of biomass were good at adsorbing metals in water and soil. This is because biochars have "high surface area[s]" and their functional groups are very "accessi[ble]." Copper was shown to be a metal that is drawn to biochar, possibly due to

the attraction copper may have to the functional groups that are found on the biochar surface and include: "-COOH and -OH." [12]

Hydrochar

Hydrochar is a very good sorption material because of its special characteristics that include its excellent "thermal stability," its fairly good porosity, and its "high carbon content." [13] Hydrochar is similar to biochar, but differs in how it is synthesized. Biochar is made by processing biomass through dry carbonization, which includes using pyrolysis followed by the use of gasification steps. [12] Hydrochar, on the other hand, is synthesized using hydrothermal carbonization, where biomass is pressurized in water, which results in a slurry that includes both the process water and hydrochar. [6] In hydrothermal carbonization, (HTC), the feedstock is placed under pressure in water from 2 MPa to 6 MPa at temperatures that fall between "180[°C] and 260°C" for "5 to 240 min[utes]." [6] The HTC process takes place in water, so the moisture content of the feedstock is not a factor. With the pre-drying step eliminated, the cost of production is lowered as well as less energy consumed. The HTC process produces three products: a mixture of liquid bio-oil and water, gases that are mostly made up of CO_2, and the hydrochar itself that has a mass yield that ranges from approximately "40% to 70%." [6]

The HTC process helps to lower the ash content of the desired solid product by using water to "demineralize these inorganics" in the biomass and transfer them to the "liquid product stream." [6] Results from *Kambo et al*. show that the ash content of biochar that went through the slow-pyrolysis step was higher than that of the original biomass used for the feedstock. The products made using HTC had lower ash content as the process uses water to remove minerals from the solid product. [6] With water being present in the HTC process, hydrolysis occurs, which decreases the activation energy of cellulose and hemicellulose and results in very quick

"depolymerization of these polymers into water soluble products like oligomers and monomers."
[6] Water is also an attractive reaction medium since biomass has water as part of its composition and it is "non-toxic," and inexpensive. [6]

One problem, however, that exists with the HTC process when using it in a large-scale operation would be the amount of water that would be required to yield a solid product. The ratio of water to dry biomass is around a 3:1 ratio. For example, 12 metric tons of water would be needed to yield one metric ton of dry hydrochar from *Miscanthus* if the process occurred at 260° C. The large amount of water needed leads to high operational costs, which ends up being more than the potential revenues made by producing hydrochar on an industrial scale. One solution to this production issue would be to recirculate the water used in the HTC process, which would then reduce the operational costs and improve the "efficiency" of the process. [6] Extensive studies have been completed to maximize the properties of hydrochars, produced by HTC, so that they can be used in "the field of environmental remediation and agricultural land application." [13]

Activated Carbons

Activated carbons have a variety of commercial uses from "food processing" to absorbing pollutants in the air or absorbing heavy metals that exist in the water. [14] Activated carbons exhibit high surface areas, high porosity and functional groups on their surfaces. The range of the surface area, however, can be found to be uncharacteristically low as 13 m^2/g, in the case of rice husks treated with $FeCl_3$ and water, to a high surface area of 2410 m^2/g, when rice straw was activated with KOH. [15] [16] Activated carbons are the most often used adsorbents when it comes to "remov[ing]" compounds from "air and water." Inexpensive materials that contain a large amount of carbon, along with a low amount of inorganics, are used to produce activated

carbons. [14] Agricultural wastes are commonly used as the feedstock for synthesizing activated carbons primarily because they are inexpensive. These raw materials will yield activated carbons that have the following properties: "high adsorption capacity, considerable mechanical strength, and low ash content." [14] Examples of raw materials used as the feedstock for activated carbons include grape seeds, nutshells, rice hulls, pecan shells, bagasse, and olive stones. [14]

The production of activated carbons involves two major steps in order to create the activated carbon's surface area and porous structure. The first step is carbonization, which involves slow pyrolysis. The second step is activation, which is done by either physical or chemical activation. [14] When physical activation is used the raw material is carbonized at a temperature that is lower than 700 °C. Then the material is gasified at a temperature above 700 °C with the presence of an "oxidizing gas" such as "steam, CO_2, air," or a combination of those three. [17] In chemical activation the raw material is mixed with water and an activating reagent including, K_2CO_3, Na_2CO_3, KOH, NaOH, $ZnCl_2$, or H_3PO_4. Afterwards, the mixture is "kneaded" and then dried at a low temperature of 110 °C. Then the mixture is heated in a furnace at the "carbonization temperature[s]" that "range from 500 ^{o}C to 900 ^{o}C." In the final steps, the mixture is washed multiple times to recover the reagent and dried to yield the activated carbon. [18]

Ion Exchange Resin

Ion exchange resins are sorption materials that are used in industry to remove metal ions. The resin is made up of organic polymers in which a hydrocarbon network is formed. Ion exchange sites are present in the polymer matrix where "functional groups" with positively or negatively charged ions are attached to the "polymer network." The functional groups will attract ions of the "opposite charge." Most resins are bead shaped with radii in the range of 0.25 to 1.25 mm. [19]

Adsorption Process

Copper ions in a copper nitrate solution have a +2 positive charge and have a relatively small diameter of 0.146 nm diameter. [20] It is ideal for a sorption material to have a negatively charged surface with a high surface area and a large amount of micropores. According to the International Union of Pure and Applied Chemistry (IUPAC), there are different pore sizes for sorption materials that fall "roughly" into three categories: micropores, mesopores, and macropores. Micropores have diameters that are below 2 nm. Mesopores have diameters that range from 2 to 50 nm. Lastly, macropores have diameters that are above 50 nm. [21] It is best for sorption materials to have a large percentage of micropores in its structure in order to adsorb and remove as many small copper ions as possible. In addition, a larger surface area helps to remove more copper ions. [22] Functional groups are very important for adsorption as they will react with the species of interest such as copper. The mechanism that explains the interactions between ions and the functional groups is still unknown, but it has been demonstrated that specific functional groups with high concentrations will lead to reactions with particular chemical species. For example, nitrogen containing functional groups tend to result in the adsorption of anions. [23] Oxygen containing functional groups such as alcohols, aldehydes, ketones, and carboxylic acids help to lead to the adsorption of heavy metal cations in phenols and aqueous solutions. [24] [25]

Sorption Materials Tested

The adsorption capacity of each sorption material was calculated in order to compare their effectiveness of removing copper ions in copper nitrate solution. The sorption materials that were used include activated carbons and glucose hydrochars. The following activated carbons were used in this project: Norit SX-1, Norit Darco SX Ultra, Norit Darco KB-G, Norit Darco KB-M,

Norit Darco KB-WJ, Norit Darco S-51, and Nuchar Activated Carbon. The hydrochar that was used in this project was derived from D-Glucose and underwent HTC for 8 hours.

Norit SX-1 and Norit SX Ultra are derived from peat through thermal activation. Norit KB-G and Norit Darco KB-M are synthesized form wood through chemical activation with the use of phosphoric acid. Norit Darco S-51 is produced when lignite coal undergoes physical activation by using steam. [9]

Methodology

Procedure to Synthesize Glucose Hydrochar

The first step in synthesizing glucose char was to mix 28.152 g of D-glucose with 100 mL of water in a beaker. After mixing the solution for an hour, 100 mL of the solution was placed into a 160 ml Teflon reactor that was then inserted into an autoclave, which was placed in an oven, set to 180 °C. The solution reacted in the oven for a holding time of 8 hours.

Figure 1: Autoclave in an oven that has Teflon reactor and glucose-water solution inside it

Then the oven was shut off and the autoclave was left in the oven to cool for 12 hours. Afterwards, the autoclave was taken out to obtain the vessel that had a char slurry product. The slurry was mixed with 200 mL of 50 % ethanol and 50 % water by volume for approximately an hour in order to remove any inorganics that were present on the char.
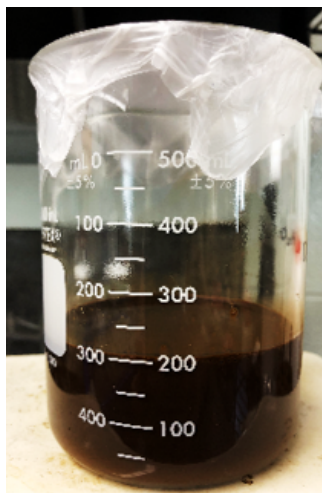
Figure 2: Glucose slurry mixed with 200 mL 50% ethanol, 50% water solution by volume

After mixing, the slurry was vacuum filtered with a Buchner funnel to separate the solid char product from the liquid product.

Figure 3: Vacuum filtering slurry and ethanol-water solution

The char was washed again two more times and vacuum filtered two more times.

Figure 4: Hydrochar on filter paper on top of Buchner funnel after vacuum filtering

The hydrochar was then placed in a crucible that went in an oven at 65 °C for 24 hours in order to remove any moisture that was present in the char.

Figure 5: Hydrochar in crucible after being in oven at 65°C for 24 hours

After this time, the char was removed from the oven and a mortar and pestle were used to grind up the char and make it into a powder.

Figure 6: Hydrochar grinded up with mortar and pestle

Having it in a powder form, made it easier for the hydrochar to have contact with the copper ions to remove them more easily. Lastly, the hydrochar was placed into vials for future use.

Activating Hydrochar Using Base Solutions

Hydrochar was activated by mixing 2 g of hydrochar with 500 mL of a 2N base solution for 1 hour. The base solutions used were sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide.

Figure 7: Hydrochar washed with potassium hydroxide solution

After mixing, the solution was vacuum filtered using a Buchner funnel, filter paper, and a flask. The residual char that was on the filter paper was then added to 50 mL of distilled water and mixed for 30 minutes. After mixing, the pH of the solution was measured, and the pH was adjusted by adding 1 N hydrochloric acid or 1 N sodium hydroxide solutions to achieve a pH that fell within a range of 5 to 7. After adding small volumes of 1 N NaOH or 1 N HCl, the solution was mixed for 30 minutes and the pH was measured to verify that the solution pH was between 5 and 7. Afterwards, the solution was vacuum filtered using a Buchner funnel, filter paper, and a flask. Then 50 mL of distilled water was added three times to the Buchner funnel with the residual char still on the filter paper while the vacuum remained on. The residual char was then transferred to a crucible. The mass of the wet char was recorded and the crucible with the wet char was placed into a 100 °C oven to dry for 24 hours. After drying, the crucible with the dry char was taken out of the oven and the mass of the dry char was recorded.
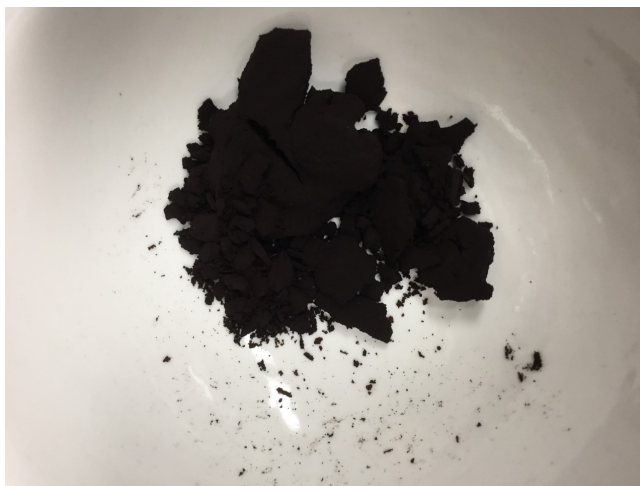
Figure 8: Activated hydrochar washed with KOH taken out of 100 °C oven

The char was grinded up to make the char into a powdery form, and then it was placed into a glass vial. [26]

Copper Adsorption

In order to analyze the adsorption capacity of different materials, copper nitrate was the solid compound that was used because it contains Cu^{2+} ions. The first step was to make a 0.08 M solution of copper nitrate solution in a plastic container. After mixing for 30 minutes, a mixture with a ratio of 10 mL of copper nitrate solution to 0.2 g of each sorption material was added to plastic centrifuge tubes. Three trials were completed for each sorption material and 20 mL of copper nitrate was added to a plastic centrifuge tube as a blank in order to find the exact concentration of the solution at a later time. The plastic tubes were put on the arms of a shaker where they were shaken for 24 hours.

Figure 9: Shaker that shakes the samples for 24 hours

After this time, the samples were taken off the shaker and vacuum filtered in order to separate the copper nitrate solution from the sorption material. Then the solution was syringe filtered in order to filter out any small solid particles that were left in the solution.
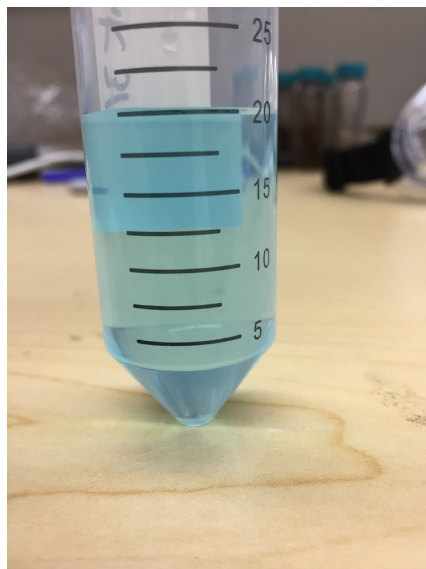
Figure 10: Copper nitrate solution

Inductively Coupled Plasma for Adsorption Calculations

To analyze the copper concentration after adding the sorption material, an Inductively Coupled Plasma (ICP) machine, *Perkin Elmer, Nexion 350x*, was used.

Figure 11: Inductively Couple Plasma to measure copper concentration of each sample

The concentration of the sample must be below 500 ppb for the ICP machine to analyze each sample's copper concentration. As a result, each sample was diluted multiple times in order to get the copper concentration to fall below 500 ppb. In addition, the ICP machine needed a copper calibration curve in order to measure each sample's copper concentration. Thus, a copper calibration solution was diluted into five tubes with concentrations of 10 ppb, 50 ppb, 100 ppb, 200 ppb, and 400 ppb. The ICP machine works by using argon plasma that is at a high temperature in order to "excite atoms into high-energy states." Light is emitted when these atoms subside at specific wavelengths. [27] The machine measured the concentration of the blank solution and the solutions that had samples added to them to get the concentrations before and after adding each sample. Knowing the concentrations of the samples and the blank solution helped to calculate the adsorption capacity for removing copper ions for each sorption material.

Synthesizing Acrylic Acid Char

Acrylic acid chars were synthesized to see how incorporating acrylic acid to the glucose-water solution would affect the char's ability to remove copper ions. To make the char, 80 g of water was mixed with 10 g of acrylic acid for 30 minutes. The solution was then mixed with D-(+)-glucose for 30 minutes and the final solution was placed in a 160 mL Teflon reactor and then placed into an autoclave. The autoclave was heated in an oven at 190 °C for 16 hours. After this time, the oven was turned off and cooled for 12 hours. After cooling, the autoclave was taken out of the oven and the slurry product was mixed with 100 mL of water for 30 minutes. The slurry was then vacuum filtered to separate the liquid product from the solid product.

Figure 12: Acrylic acid char after vacuum filtering

The solid hydrochar was recovered and placed in a crucible and the mass of the wet char was recorded. The hydrochar in the crucible was then put in a 65 °C oven for 12 hours. After drying, the sample was taken out of the oven and placed in a mortar. A pestle was then used to grind up the hydrochar to make it into a powder that was then placed in a glass vial. [28]

Synthesizing Vinyl Sulfonic Acid Char

Vinyl sulfonic acid was incorporated into the glucose-water solution to see how adding an acid to the solution would affect the hydrochar's ability to remove copper ions. To make the hydrochar, 150 mL of water was mixed with 7.22 g of vinyl sulfonic acid for 30 minutes. 36.1 g of D-(+)-glucose was added to the solution and mixed for 30 minutes. The solution was then added to a 160 mL Teflon reactor, which was then inserted into an autoclave. The autoclave was put in an oven and heated at 190 °C for 24 hours. After heating, the autoclave was immediately

taken out of the oven and put in a bucket in a sink. Water was added to the bucket from a faucet continuously for 30 minutes so that the autoclave could be cooled off by being completely submerged in water. Next, the slurry product was taken out of the autoclave and vacuum filtered to recover the solid hydrochar product. After the liquid product was filtered, 1 L of distilled water was added to the Buchner funnel with the hydrochar still on the filter paper while the vacuum was still running. The hydrochar was added to 750 mL of distilled water and stirred overnight. The next day, the distilled water was vacuum filtered off and the hydrochar was washed with 1L of ethanol while the vacuum was still on. The hydrochar was then added to 750 mL of ethanol and stirred for 2 hours. Afterwards, the ethanol was vacuum filtered off and the hydrochar was washed with 1 L of acetone while the vacuum was still on. The hydrochar was then added to 750 mL of acetone and stirred for 2 hours. Then the acetone was vacuum filtered off and the hydrochar was washed with 1 L of distilled water while the vacuum was still on. The hydrochar was then added to a crucible that was dried in an oven at 65 °C for 12 hours. Then, the hydrochar was taken out of the oven and mixed with 180 mL of 1 N hydrochloric acid overnight. The next day, the hydrochloric acid was filtered off using a vacuum filter and the hydrochar was then added to 750 mL of distilled water and stirred for 2 hours. Afterwards, the distilled water was filtered off using a vacuum filter and the hydrochar was washed with 1 L of ethanol while the vacuum was still on. The hydrochar was then added to 750 mL of ethanol and stirred overnight. The next day, the ethanol was filtered off using a vacuum filter and the hydrochar was washed with 1 L of water while the vacuum was still on. Then the hydrochar was added to a crucible that was dried in an oven at 65 °C for 12 hours.

Figure 13: Vinyl sulfonic acid char after taking it out of the 65°C oven

Then, the hydrochar was taken out of the oven and grinded up using a mortar and pestle and made into a powder. The hydrochar was then placed into glass vials and stored for future use.

Washing Ion Exchange Resins with Water

Before using the resins for copper adsorption, the materials were mixed with water for one hour. The water was then vacuum filtered, and the resins were recovered. The resins were put in a crucible that was placed in a 65 °C oven for 24 hours. Afterwards, the crucible was taken out of the oven and the resins were grinded up using a mortar and pestle. After grinding up the resins, the materials were placed in vials and stored.

Titration of Sorption Materials

Titration was done to the sorption materials to obtain their acid concentrations. The first step was to add 20 mL of 0.1 M sodium bicarbonate to 0.5 g of each sorption material in a plastic centrifuge tube. Then, the samples were put on the hands of a shaker where they were shaken for 48 hours. Afterwards, they were vacuum filtered to separate the sorption materials from the sodium bicarbonate solution. The sodium bicarbonate was then recovered and added to a new plastic centrifuge tube. Then the solution in the tube was centrifuged to get any remaining solid sorption material at the bottom of the tube to make it easier to recover the aliquot solution. The centrifuge was run for 10 minutes at 3,000 rpm. After centrifuging, the solution was syringed filtered to filter out any solid that remained in the solution. Then, 5 mL of water and 5 mL of 0.1 M hydrochloric acid were added to 5 mL of sodium bicarbonate solution to completely neutralize the base. [26] Then, the solution was sparged with nitrogen gas for 1 hour to remove any carbon dioxide that was present in the solution. Lastly, the pH of the solution was measured, and 0.1 M sodium hydroxide was added until the solution reached a neutral pH of 7. [29]
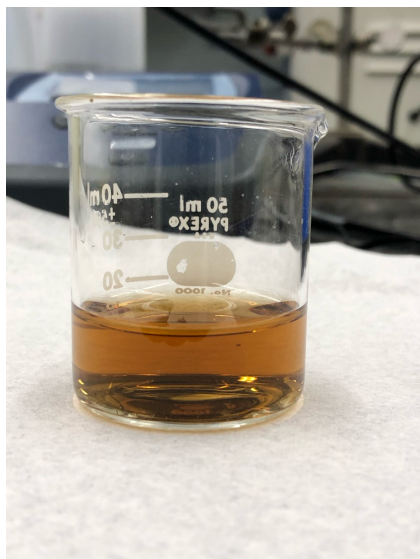
Figure 14: Titration of glucose hydrochar

FTIR of Hydrochars

Fourier transform infrared (FTIR) spectroscopy was used in order to obtain the functional groups on the surface of the hydrochars. The process works when IR radiation goes through a sample. A certain amount of radiation gets "absorbed by the sample" and some of the radiation goes through it. A spectrum resulted from the detector, which displayed the sample's "molecular 'fingerprint'." [30] Different peaks on the spectrum represent different functional groups of the sample.

Surface Area Measurements

Surface area measurements of sorption materials were done using nitrogen physisorption. The process works by using liquid nitrogen; since the surface area of the material is dependent on how much nitrogen is adsorbed onto the surface of the material. [31] The Dubinin–Radushkevich Method (DR) was used to obtain the micropore surface area of each material.

Results

Hypothesis of Mechanism for Adsorption of Copper Ions

The initial hypothesis for the hydrochar to adsorb copper ions was that functional groups like carboxylic acids are involved in removing the copper ions:
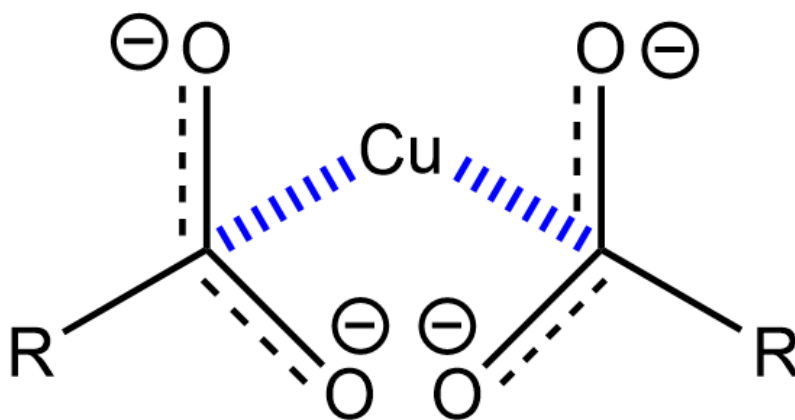
Figure 15: Hypothesis of mechanism for copper adsorption

The thought process for copper ion removal was that since the copper ion has a +2 charge, it would take two carboxylic acids to remove one copper ion.

Unactivated Hydrochar versus Activated Carbons

Hydrochar was added to a copper nitrate solution to analyze its ability to remove copper ions as compared to activated carbons. Activated carbons were used because they are used in industry as a cost-effective method for removing metals due to their high surface areas. [15]

Table 1: Surface area of activated carbons

Activated Carbons	Surface Area (m^2/g)
Norit SX-1	821.621
Norit SX Ultra	1165.606
Nuchar Activated Carbon	1657.757

The surface area results from nitrogen adsorption showed that activated carbons like Norit SX-1, Norit SX Ultra, and Nuchar Activated Carbon had relatively high surface areas. Other activated carbons were analyzed for copper ion removal such as Pica HP 120, Norit Darco KB-G, Norit Darco KB-M, Norit Darco KB-WJ, and Norit Darco S-51. The adsorption capacity of removing copper ions for hydrochars and activated carbons were calculated to see how effective hydrochar was at removing copper ions compared to different industrial activated carbons.
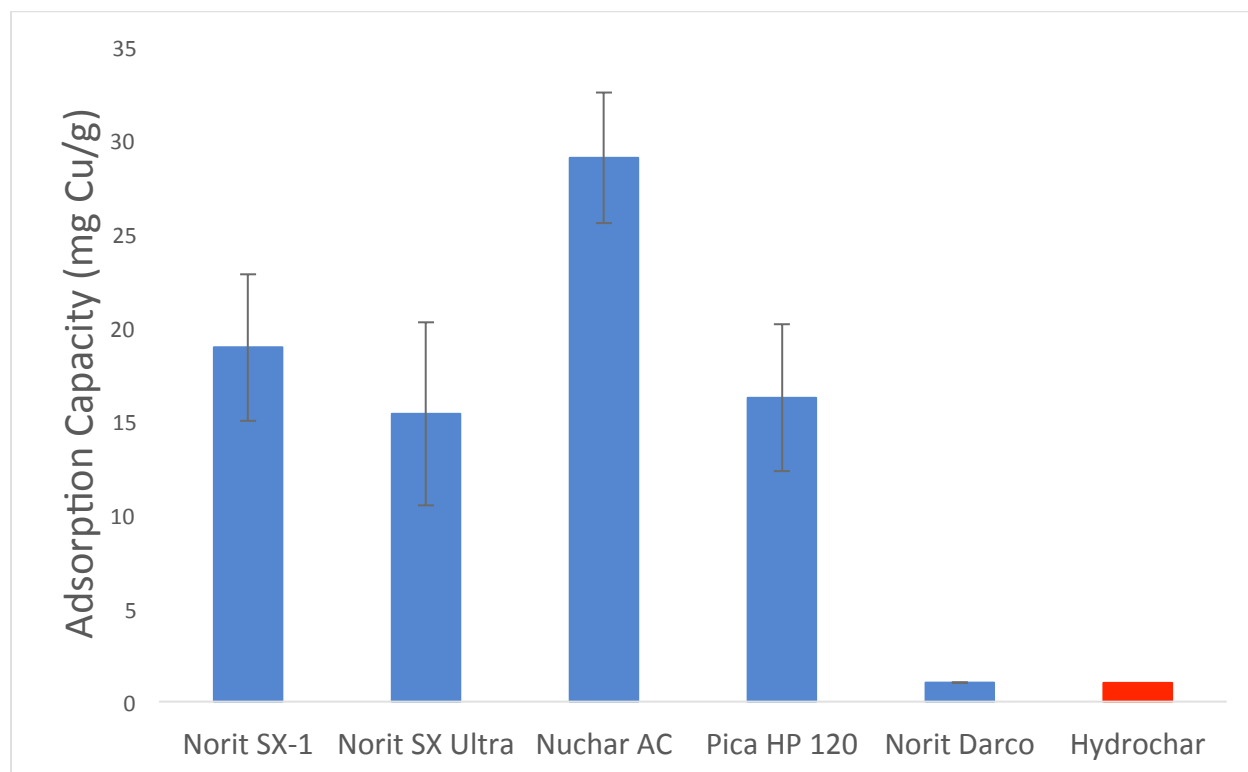
Figure 16: Adsorption capacity for activated carbons (blue) and hydrochar (red)

The results showed that the glucose hydrochar was ineffective at removing copper ions. Norit Darco represents the different Norit Darco activated carbons tested, and all of them had adsorption capacities that were relatively very low. Norit SX-1, Norit SX Ultra and Pica HP 120 were similar in their effectiveness in removing copper ions, while Nuchar Activated Carbon had the highest adsorption capacity for copper ion removal. The difference in performance for the hydrochar and the activated carbons showed that hydrochar must have a different surface chemistry when interacting with copper ions when compared to activated carbons. FTIR analysis was done in order to get a better understanding of the functional groups that were present on the hydrochar:
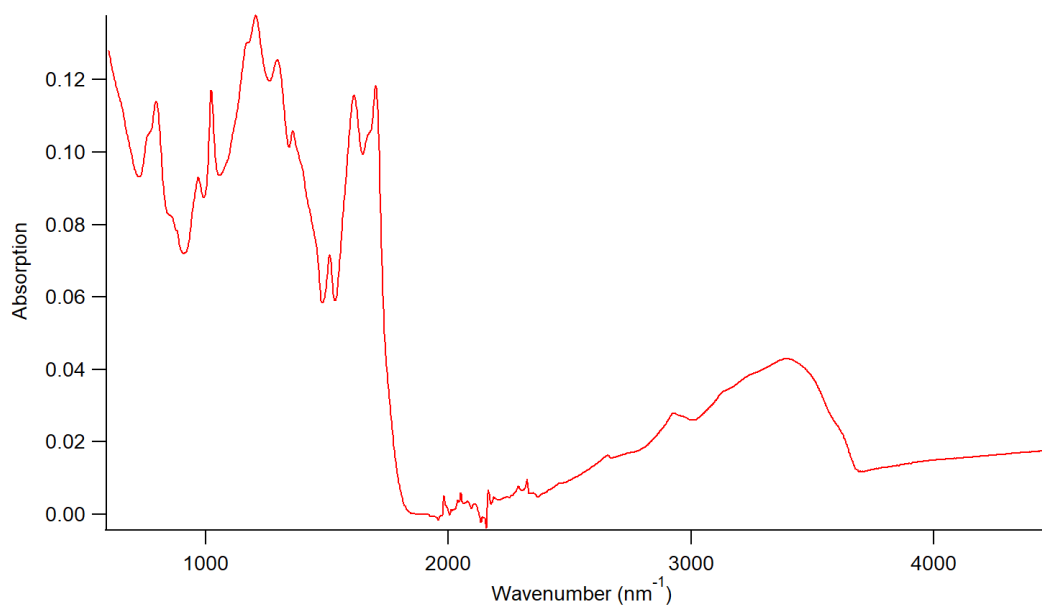
Figure 17: FTIR of hydrochar

The results showed a broad band around the 3200-3600 nm^{-1} range, which indicated the presence of OH functional groups. In addition, there was a peak in the 2800-3000 nm^{-1} range, which indicated the presence of alkanes. The most important band of interest was the band in the 1680-1750 nm^{-1} range, which represented the presence of carboxylic acids on the hydrochar's surface. This showed that the hydrochar had acid sites on its surface due to the presence of carboxylic acids.

Activating Glucose Hydrochar Using Base Solutions

Given the presence of carboxylic acids, the glucose hydrochar was washed with different base solutions such as, sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide, to see how chemical activation affected the hydrochar's ability to remove copper ions.
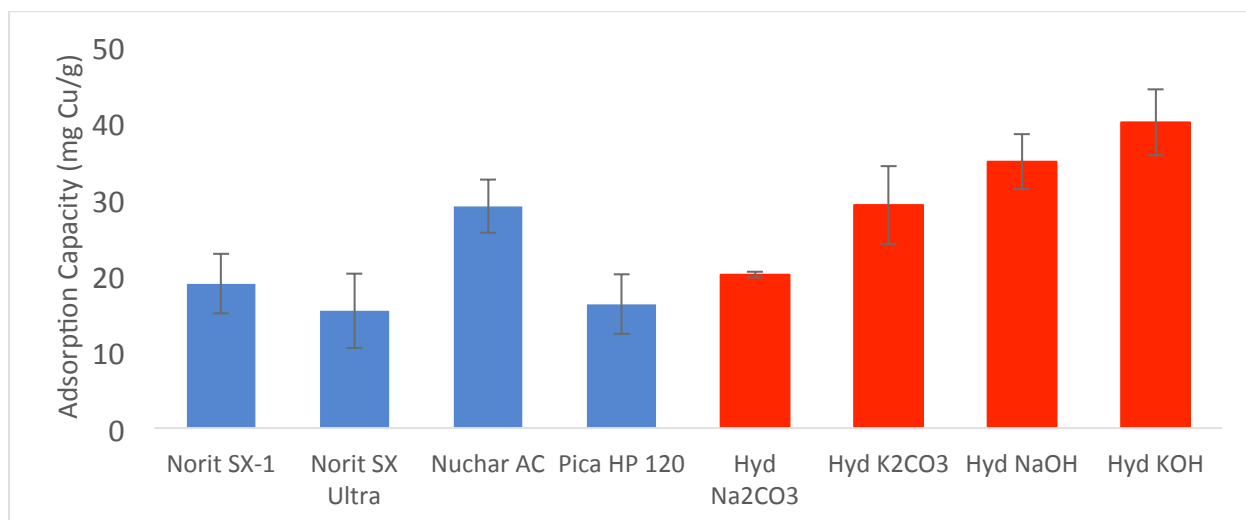
Figure 18: Adsorption capacity of activated carbons (blue) and activated hydrochars (red)

The results showed that there was significant improvement in the hydrochar's performance in removing copper ions when it was activated with a base solution. In addition, the adsorption capacities of the activated hydrochar are comparable to the activated carbons. This was a significant breakthrough as these activated hydrochars could be used as an alternative for removing copper ions; since unlike activated carbons, they do not require a pre-drying step to synthesize them. Another observation made was that the hydrochars washed with stronger bases, such as potassium hydroxide and sodium hydroxide, had higher adsorption capacities than the hydrochars that were washed with weak bases, such as potassium carbonate and sodium carbonate. FTIR of the activated hydrochars was completed to see what functional groups were present on the activated hydrochars' surface:
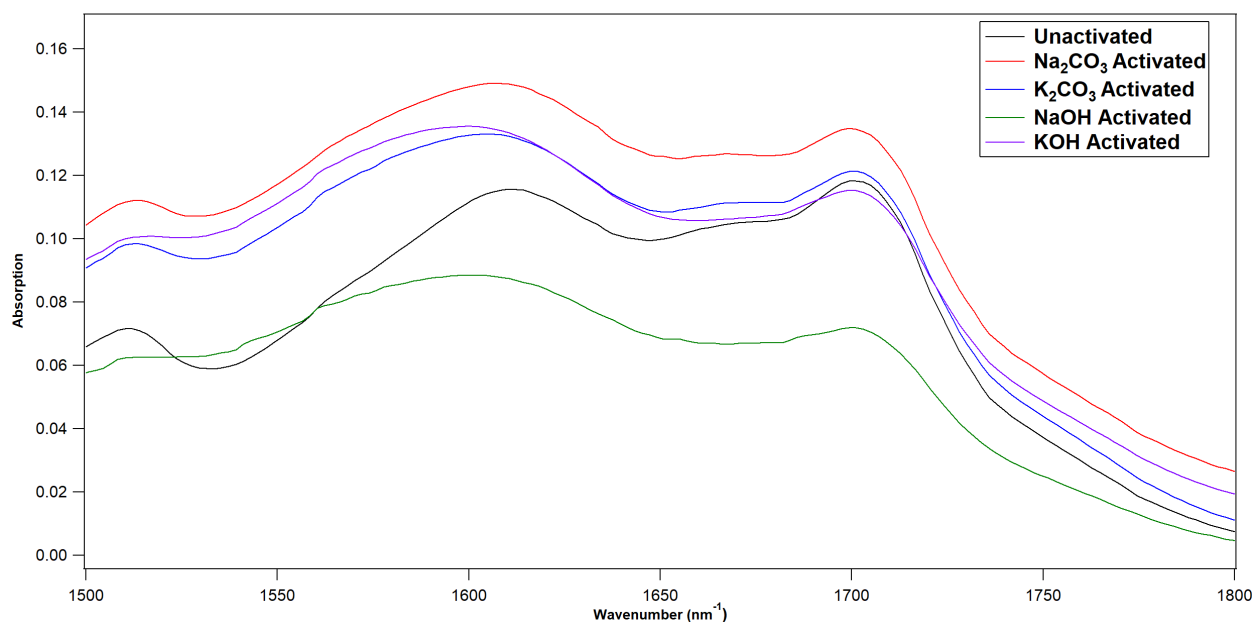
Figure 19: FTIR of unactivated and activated hydrochars

The results showed how both the unactivated and activated hydrochars had a band between 1680 and 1750 nm^{-1}, which represents the presence of carboxylates.

Mechanism for Copper Ion Removal

With a better understanding of the functional groups present on the hydrochar and activated hydrochars, density functional theory (DFT) was completed by Avery Brown, a graduate student at WPI, and Matthew Rando, an undergraduate student at WPI, to understand the behavior of the ion exchange between a copper ion and different functional groups.

Table 2: DFT for ion exchange between copper ion and different functional groups

	ΔH (kJ/mol)
R-OH	13.84
R-OK	-72.33
R-ONa	-71.65

The results showed that the ion exchange was unfavorable between the copper ion and the carboxylic acid, which helped to explain why the hydrochar was ineffective at removing copper. Given that the hydrochar had carboxylic acids on its surface, it did not achieve an ion exchange with the copper ion. The results did show that ion exchange was favorable between the carboxylate salts and the copper ion, which made sense given that the FTIR showed carboxylates on the surface of hydrochars that were washed with potassium hydroxide and sodium hydroxide. Those activated hydrochars were effective at removing copper ions. DFT also demonstrated that the reaction energy for ion exchange with the potassium carboxylate salt was slightly better than the reaction energy for ion exchange with the sodium carboxylate salt, which also made sense, given that the hydrochar that was washed with potassium hydroxide had a slightly higher adsorption capacity than the hydrochar that was washed with sodium hydroxide. Potassium hydroxide is a stronger base than sodium hydroxide, which means that it ionizes more easily and seemed to indicate that the potassium carboxylate salt would do an ion exchange with the copper ion more easily than a sodium carboxylate salt would. The results from DFT also helped to

demonstrate the mechanism for ion exchange reaction that occurs between the copper ion and the carboxylate salts:
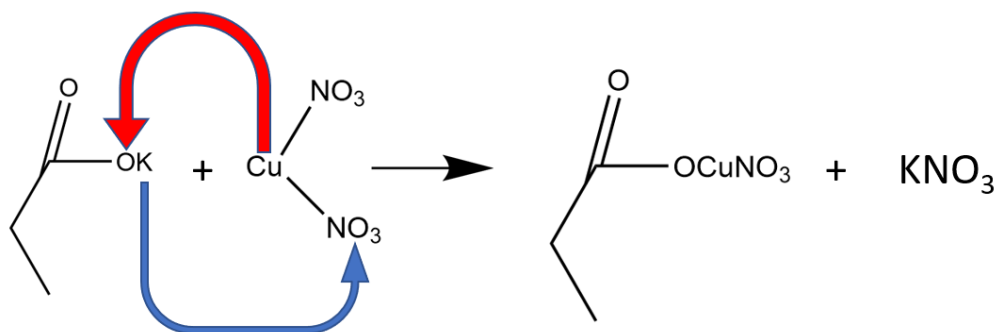
Figure 20: Schematic for ion exchange between carboxylate salt and copper nitrate
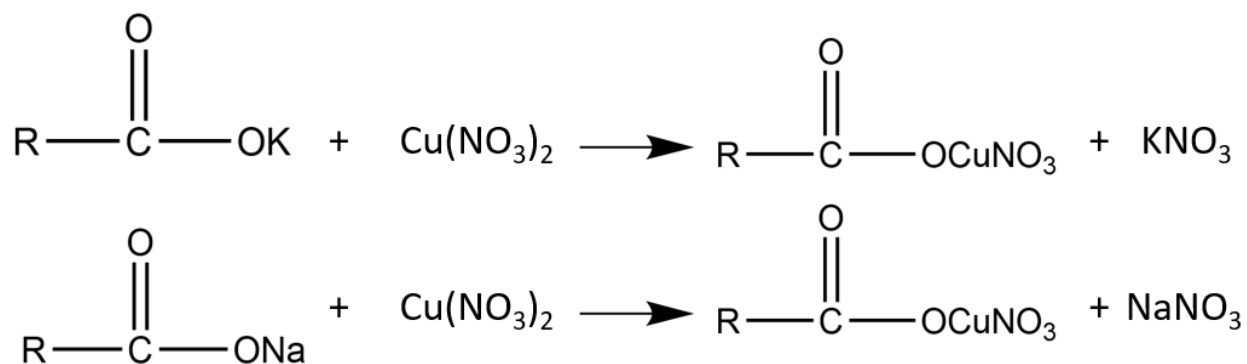
Figure 21: Mechanism for ion exchange between copper nitrate and carboxylate salts

Overall, DFT helped give a better understanding of how copper nitrate reacted with the carboxylate salts to remove copper from the copper nitrate solution.

Using Acrylic Acid Char for Copper Ion Removal

In order to further improve the removal of copper ions, acrylic acid was incorporated into the glucose-water solution for HTC to see how adding an acid would affect the hydrochar's ability to remove copper ions:
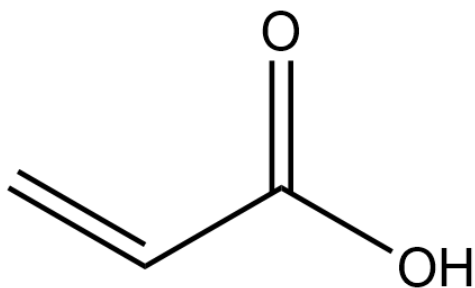
Figure 22: Acrylic acid molecule

The reason why acrylic acid was chosen was because the molecule has an OH group. It was hypothesized that the OH group would help to add additional acid sites on the hydrochar's surface during HTC and that additional acid sites would help to add more carboxylate salts after the hydrochar was washed with a base solution. After the acrylic acid hydrochar was synthesized, FTIR analysis was done to see what the intensity of the carboxylic acids would be for this hydrochar:
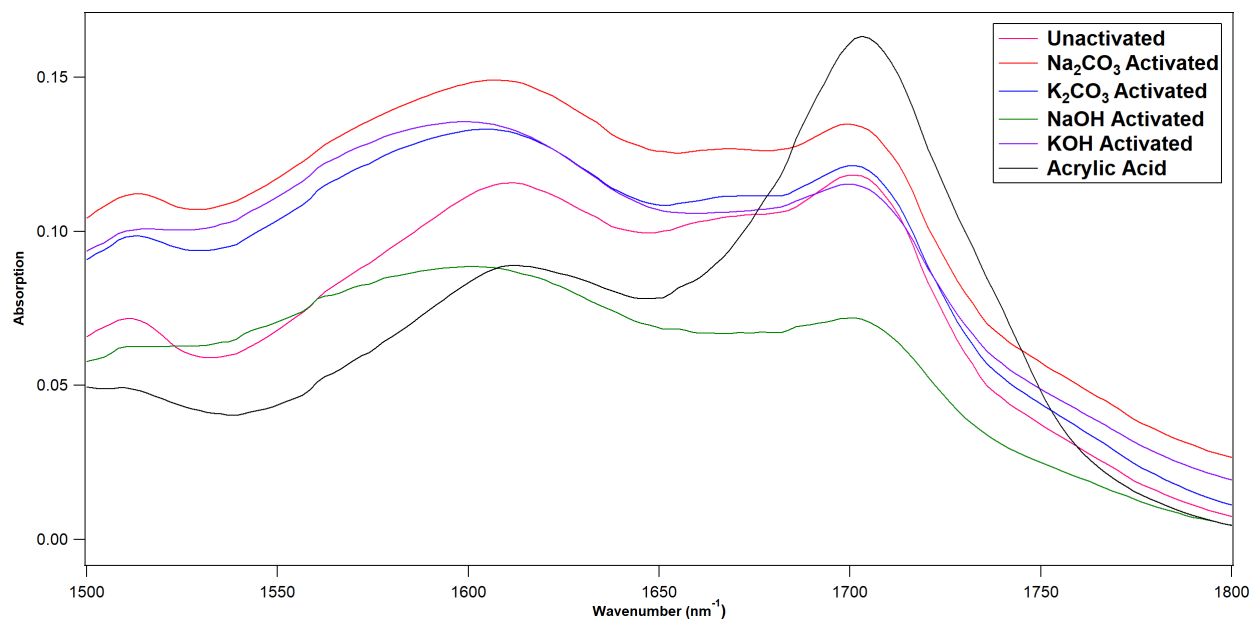
Figure 23: FTIR of acrylic acid char, unactivated, and activated hydrochars

The results showed the acrylic acid char's carboxylic acid band was greater in intensity than both the unactivated and activated hydrochars. This was significant because it confirmed how the addition of acrylic acid helped to add more acid sites to the hydrochar. In the next step, acrylic acid chars were washed with base solutions to see if the addition of acrylic acid helped to improve the hydrochar's effectiveness to remove copper ions:
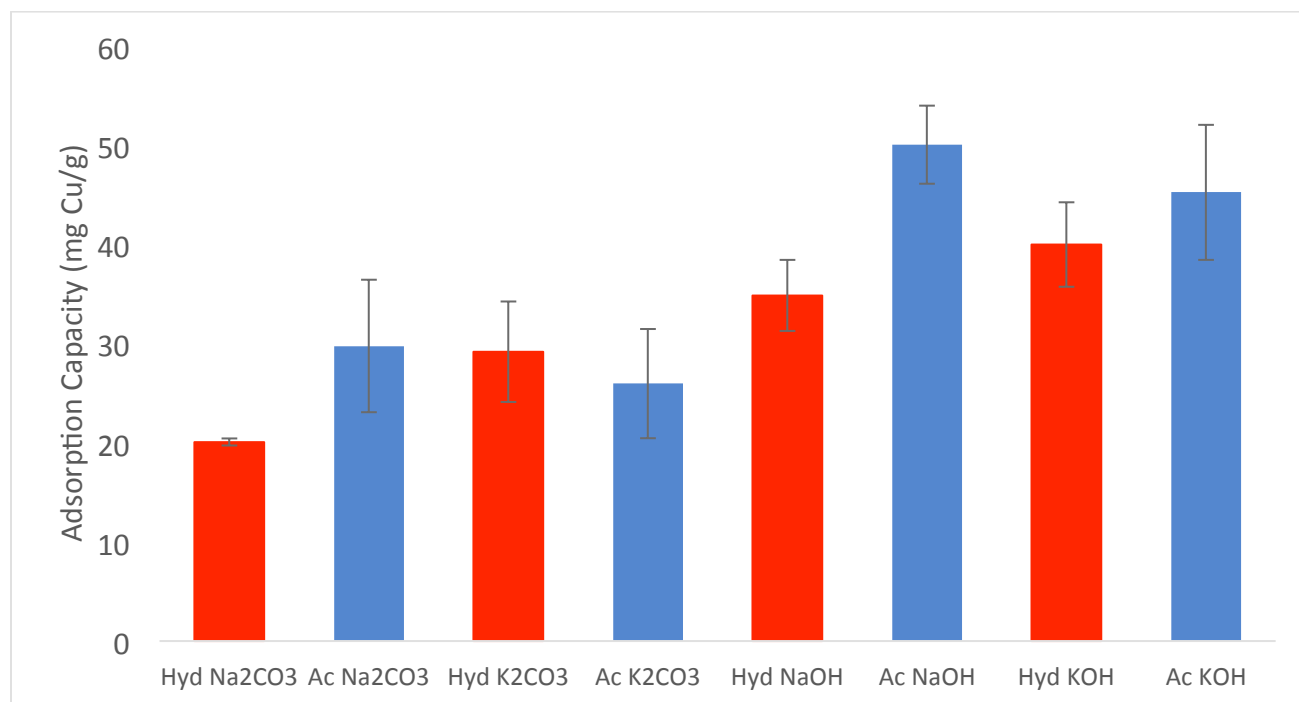
Figure 24: Adsorption capacities of activated hydrochars (red) and activated acrylic acid chars (blue)

The results showed how there was improvement in the removal of copper ions for the acrylic acid char that was activated with different base solutions, except in the case of sodium carbonate, when compared to the regular activated hydrochars. This was a significant finding because it demonstrated how incorporating an acid during the HTC process helped to improve the ability of the activated hydrochars to remove copper ions. FTIR analysis was also done on the activated acrylic acid chars to observe what functional groups were present on the chars:

43
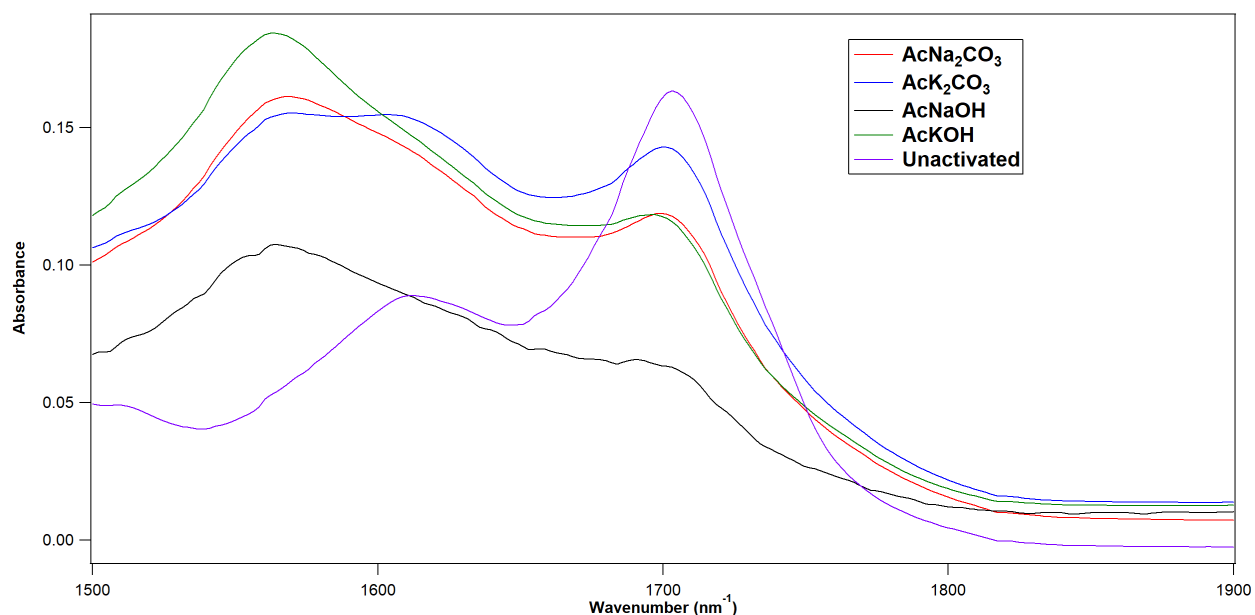
Figure 25: FTIR of unactivated and activated acrylic acid chars

The results also revealed the presence of a band in the range of 1680 to 1750 nm^{-1}, which indicated the presence of carboxylates. This helped to explain how important the carboxylates were in terms of the adsorption of copper ions and that carboxylate salts helped to remove copper ions through the process of ion exchange.

Using Vinyl Sulfonic Acid Char for Copper Ion Removal

Vinyl sulfonic acid was tested and incorporated into the glucose-water solution for HTC to see if this acid could add additional acid sites and give the activated char more carboxylate salts to remove more copper ions.
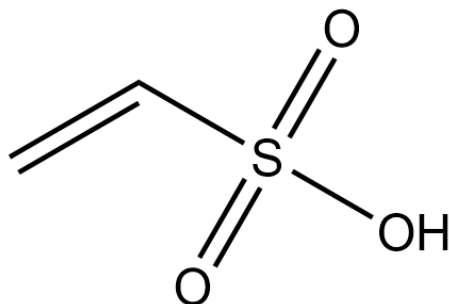
Figure 26: Vinyl sulfonic acid molecule

The reason why vinyl sulfonic acid was chosen was because of the presence of the OH functional group on the molecule, and it was hypothesized that the OH group on the acid would help to add acid sites onto the hydrochar after HTC. The acid also has a sulfur atom and it was also hypothesized that the sulfur atom could be added to the hydrochar after HTC to add even more acid sites. After the vinyl sulfonic acid char was synthesized, it was activated with different base solutions and analyzed in copper nitrate solutions to calculate their adsorption capacities:
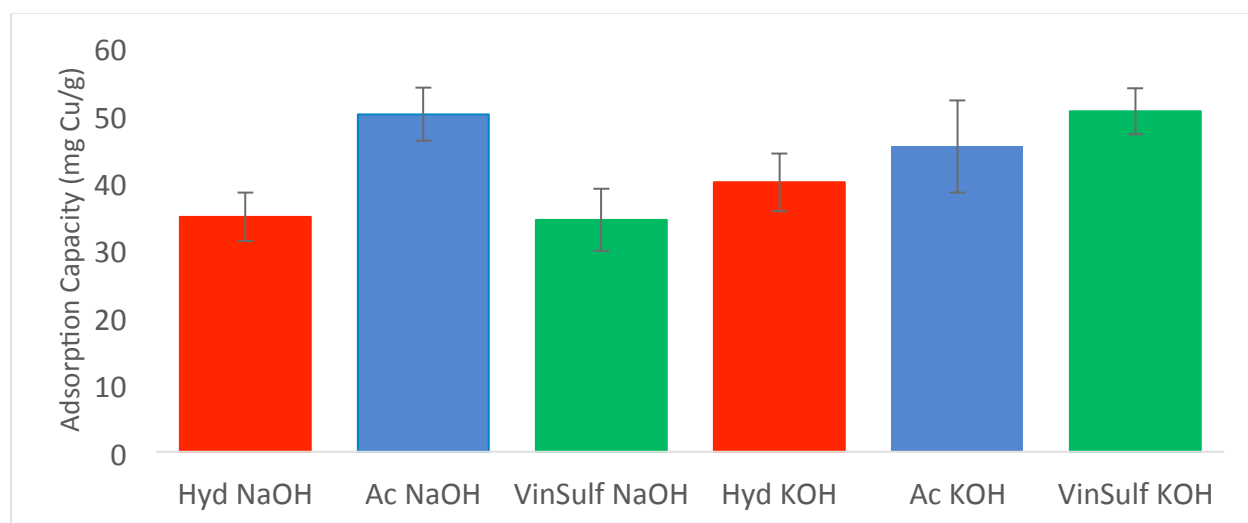
Figure 27: Adsorption capacities of activated hydrochars (red), activated acrylic acid chars (blue), and activated vinyl sulfonic acid chars (green)

The results showed that vinyl sulfonic acid seemed to help improve the adsorption capacity of the hydrochar when activated with the strong base, potassium hydroxide. This was a significant finding because it demonstrated how incorporating an acid to the HTC process, followed by activation with a base solution, helped to remove copper ions after activation. The vinyl sulfonic acid char that was washed with sodium hydroxide was not better at removing copper ions when compared to the regular hydrochar that was washed with sodium hydroxide. This could have been because only one batch of activated vinyl sulfonic acid char was analyzed, whereas two batches of the activated hydrochar were analyzed. In the future, more trials can be done to get more adsorption capacity data.

Washing Activated Carbons with Base Solutions

Activated carbons were washed with potassium hydroxide to see how adding a base would affect the activated carbons' ability to adsorb copper ions.
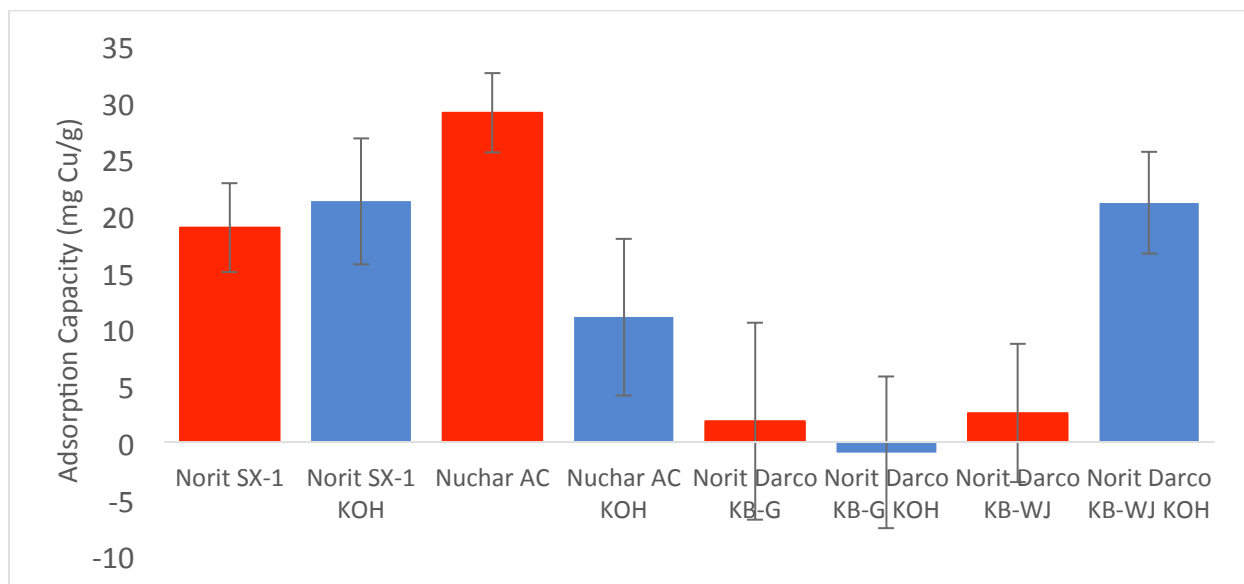
Figure 28: Adsorption results of activated carbons before (red) and after (blue) mixing with

KOH

The results showed that there was no significant change in the adsorption of copper ions for Norit SX-1 even after mixing it with potassium hydroxide. For Nuchar activated carbon, the adsorption capacity to remove copper decreased after washing with potassium hydroxide. For Norit Darco KB-G, there was no improvement in the removal of copper ions when it was mixed with potassium hydroxide. For Norit Darco KB-WJ, the adsorption of copper ions actually improved when it was washed with potassium hydroxide. These results revealed how the mechanism that exists for activated carbons for removing copper ions, seemed to be different from the one used by activated hydrochars. For hydrochars, the theory was that the base solutions add carboxylate salts to the hydrochar surface to do ion exchange with the copper ions for copper removal. However, when the base solution was added to the activated carbons, it did not seem like carboxylate salts were added to these materials, which was why most of the activated carbons did not improve in their adsorption of copper ions. This appeared to indicate that there were not a lot of acid sites on most of the activated carbons, so that carboxylate salts would be added to the materials after activation with a base solution. Further analysis needs to be done to further understand the activated carbons' mechanism for copper ion removal.

Using Ion Exchange Resins for Copper Ion Removal

Resins were also analyzed to see how effective they would be at removing copper ions.
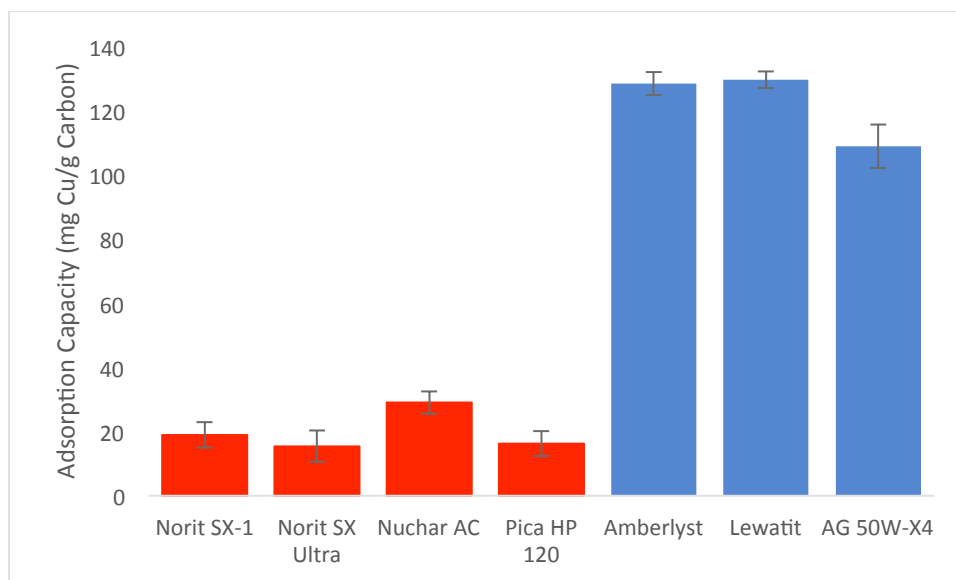
Figure 29: Adsorption capacities of activated carbons (red) and resins (blue)

The results showed that the resins had much higher adsorption capacities than the activated carbons did. This was a significant finding because this meant that the resins must have some kind of mechanism for them to be able to adsorb a relatively high amount of copper ions. The thought process in choosing the resins was that the resins' acid concentrations affected the adsorption of copper ions.

Adsorption of Sorption Materials Related to Acid Concentrations

Titration was done on the sorption materials to get their acid concentrations and was then plotted with adsorption to see the relationship between acid concentration and removal of copper ions.
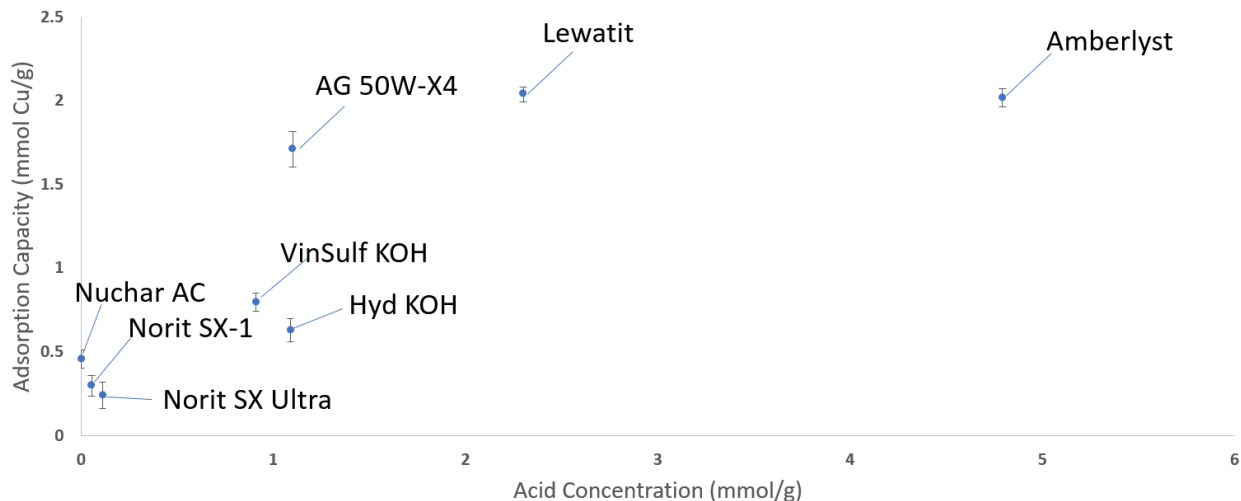
Figure 30: Copper adsorption (mmol Cu/g) versus acid concentration (mmol acid/g) [32] [33]

The acid concentration of Amberlyst was measured by Maksim Tyufekchiev, a WPI graduate student, using sodium hydroxide solution instead of sodium bicarbonate. The results showed that the activated carbons had relatively low acid concentrations. These results made sense, given that washing with potassium hydroxide did not improve the adsorption of most of the activated carbons. This meant that the addition of carboxylate salts did not occur on the surface of the activated carbons. In addition, both hydrochar and vinyl sulfonic acid char had much higher acid concentrations than the activated carbons had, which also made sense because these chars were effective at removing copper after washing with base solutions. This also meant that the base solutions added carboxylate salts to the chars' surface given that they have acid sites. The resins also had relatively very high adsorption capacities, while also having relatively high acid concentrations. This revealed how important acid concentration was for the resins to be effective at removing copper ions.

Adsorption Capacity versus Acid Concentration Based on Surface Area

The micropore surface area was obtained for the hydrochars and activated carbons to better understand how surface area relates to the adsorption of copper ions.

Table 3: Surface area of sorption materials

Sorption Material	Micropore Surface Area (m^2/g)
Hydrochar	4.269
Vinyl Sulfonic Acid Char	0.545
Nuchar Activated Carbon	1657.757
Norit SX-1	821.621
Norit SX Ultra	1165.606
Amberlyst 15 Hydrogen Form	53 [34]
AG 50W-X4	0.657

The Brunauer-Emmett-Teller method (BET) was used to get the surface area of the vinyl sulfonic acid char, as the DR method could not measure the char's surface area because it was very low. The results showed that the activated carbons had a significantly higher surface area than the glucose hydrochars and the ion exchange resins. This is validated by scientific research, which points out that hydrochars exhibit low surface areas, while activated carbons have high surface areas. [6] [15] The next step was to plot the adsorption of the sorption materials against their acid concentration on a surface area basis.
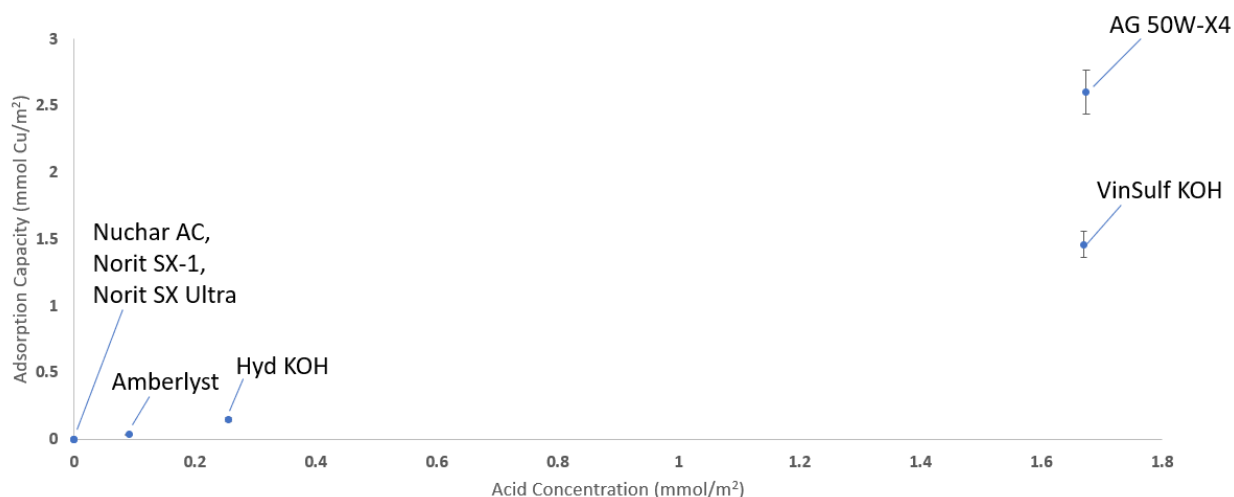
Figure 31: Adsorption capacity (mmol Cu/m^2) versus acid concentration (mmol acid/m^2)

On a surface area basis, the adsorption capacity of the activated vinyl sulfonic acid char was relatively high compared to the other sorption materials, except in the case of AG 50W-X4. The glucose hydrochars also had a higher adsorption capacity than the activated carbons surface area basis. Amberlyst, on a surface area basis, had lower adsorption capacity compared to the hydrochars, which made sense since its surface area was much higher than that of the hydrochars'. These results were significant, because the vinyl sulfonic acid chars were successful at removing copper ions, even though they had relatively low surface areas. These could be useful sorption materials going forward. The results also demonstrated that the activated carbons relied upon having relatively very high surface areas in order to be effective at removing copper ions.

Analysis of Copper Adsorption Based on Micropore Volume

The micropore volume of sorption materials was measured to see if there was a relationship between adsorption and the materials' micropore volume. Having a large amount of micropores can help copper ions have access to the very small internal pores of the materials. [35]

Table 4: Micropore volume of sorption materials

	Micropore Volume (cm^3/g)
Glucose Hydrochar	0.002
AG 50W-X4 Hydrogen Form	0
Norit SX-1	0.292
Norit SX Ultra	0.414
Nuchar Activated Carbon	0.589
Norit Darco KB-M	0.4117
Norit Darco S-51	0.2602

The adsorption capacities of the sorption materials were plotted with their micropore volumes to see if adsorption could be related to micropore volume.
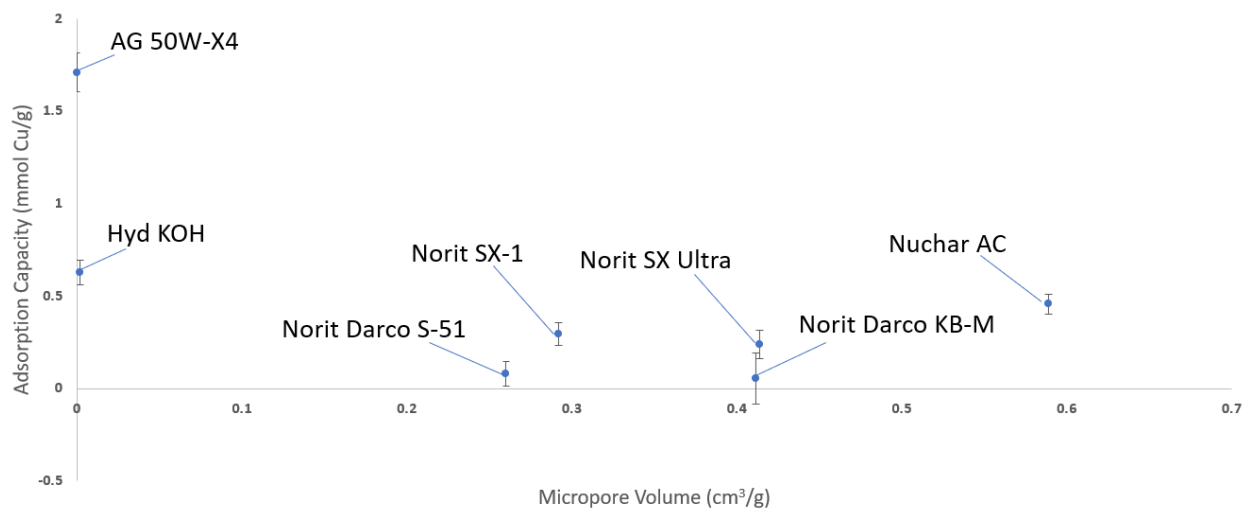
Figure 32: Adsorption capacity (mmol/g) vs micropore volume (cm^3/g)

Norit Darco S-51 and Norit SX-1 had micropore volumes that were close in value, but Norit Darco S-51's adsorption capacity was much lower. Norit Darco KB-M and Norit SX Ultra had similar micropore volumes, but Norit Darco KB-M's adsorption capacity was much lower. Nuchar Activated Carbon did have the highest micropore volume of the sorption materials that were measured and did have a higher adsorption capacity than Norit SX-1 and Norit SX Ultra. However, the hydrochar that was washed with potassium hydroxide had a slightly higher adsorption capacity than Nuchar Activated Carbon, even while having a very low micropore volume. In addition, AG 50W-X4 had the lowest micropore volume of all the sorption materials measured, even though it had a much higher adsorption capacity. While it is important for copper ions to have access to the sorption materials' internal pores, a relationship between adsorption capacity and micropore volume could not be determined from the data.

Error Analysis

One issue when synthesizing the vinyl sulfonic acid char was that there were some specs from the Teflon reactor that may have gotten into the slurry after HTC as well as maybe a tiny bit of filter paper during vacuum filtering. This could have been the reason why the microporous surface area could not be obtained. Therefore, the BET surface area for the vinyl sulfonic acid char was used whereas the micropore surface area for the other materials was used. There was also a lot of noise with the FTIR results for the vinyl sulfonic acid char, which could have been the result of the tiny specs of Teflon reactor and/or filter paper getting into the material.
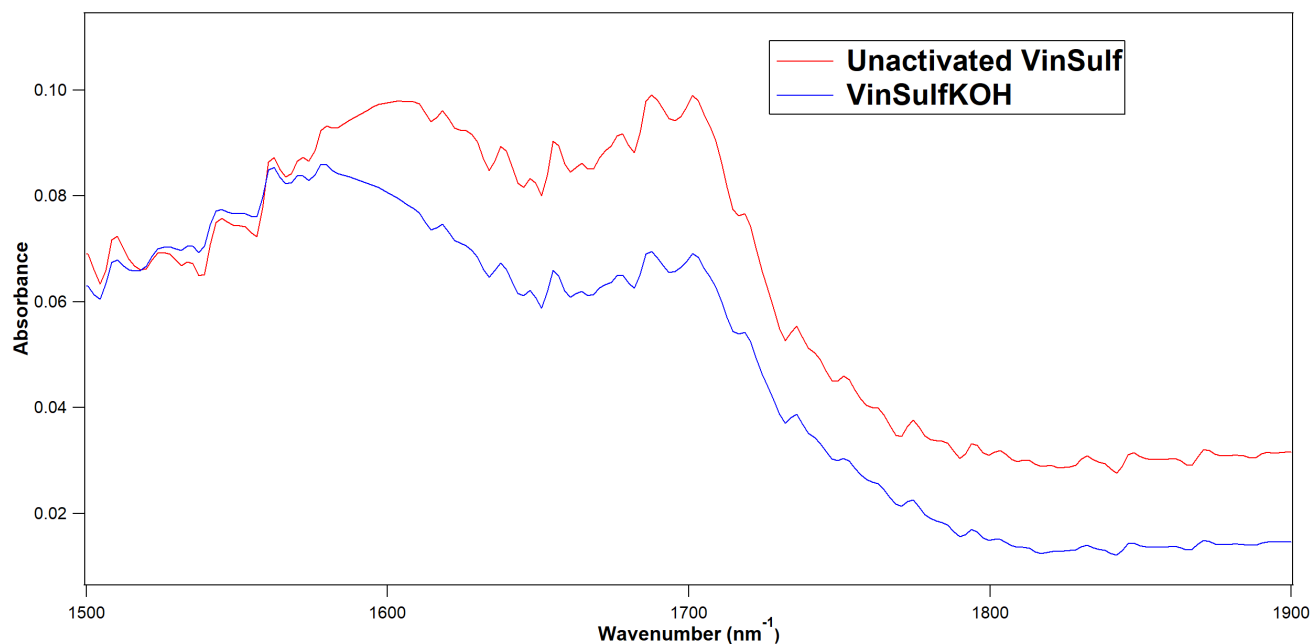
Figure 33: FTIR of unactivated and activated vinyl sulfonic acid chars

The results showed what appeared to be a carboxylate band in the 1690-1750 nm [1], the noise made it difficult to see.

While there were some issues with collecting analytical results for the vinyl sulfonic acid char, it was still effective at removing copper ions after washing with a base solution and the titration showed the presence of acid sites on the char.

When doing the titration for the glucose hydrochar, the aliquot solution, after shaking for 48 hours, was an orange color. When 5 mL was added to a beaker, some tiny amounts of the aliquot solution became stuck in the pipette tip and it was difficult to remove all of it. The aliquot solutions for the other materials did not have this issue with the pipette tip. Even with this small release issue, the results showed there were acid sites on the regular hydrochar, and its acid concentration was close to the vinyl sulfonic acid char's acid concentration.

Each time a copper nitrate solution was made, the solution's copper concentration was slightly different from one another:

Table 5: Concentration of copper for all the solutions used

Solution Number	Concentration (M)	% Error
1	0.0726	9.24
2	0.0822	2.81
3	0.0878	9.72
4	0.0861	7.60
5	0.0793	0.93
6	0.0726	9.28
7	0.0804	0.56
8	0.0846	5.72
9	0.0723	9.61

10	0.0796	0.50
11	0.0840	5.03
12	0.0826	3.20
13	0.0751	6.09
14	0.0818	2.28
15	0.0673	15.88
16	0.0731	8.67
17	0.0755	5.60
18	0.0771	3.57
19	0.0809	1.13
20	0.0691	13.63
21	0.0641	19.81

Most of the copper nitrate solutions used had concentrations within 10% of the targeted concentration of 0.08 M. Solution 15's concentration was relatively low, which could have been a result of an older plastic container being used. When the stir bar was used, tiny specs from the container spread into the solution and there were tiny specs of the container that got in the solution. Solutions 20 and 21 had percent errors above 10% possibly due to being over exposed to air since there were odd yellow bubbles in the solution. However, concentrations were high enough to show the effectiveness the sorption materials were at removing copper ions.

Conclusion

    Activated hydrochars have the potential to be effective sorption materials for the removal of copper ions. Initially, the unactivated hydrochars were unable to remove copper ions in a copper nitrate solution. However, when the hydrochar was washed with base solutions, it became effective in copper ion removal and had similar adsorption capacities to industrial activated carbons. The use of FTIR helped to show how hydrochars have carboxylic groups and that activated hydrochars have carboxylates on its surface. DFT helped to show how the carboxylate salts did ion exchange with copper, which explained why the hydrochars were effective sorption materials. Incorporating different base solutions such as acrylic acid and vinyl sulfonic acid also helped to better understand how adding acid sites to the hydrochars lead to more carboxylate salts on the activated hydrochars for the additional removal of copper ions. Washing different activated carbons with potassium hydroxide did not improve most of the activated carbons' ability to remove activated carbons, which showed how the activated carbons had a different mechanism for copper ion removal compared to hydrochars. The titration experiments further helped to explain how hydrochars, activated carbons, and resins have different mechanisms for removing copper ions. The resins and hydrochars had much higher acid concentrations than the activated carbons as the activated carbons had relatively very low acid concentrations. This helped to demonstrate how both resins and hydrochars were effective at removing copper ions due to the presence of acid sites. Adsorption on a surface area basis showed how there was a relationship between the activated carbons' adsorption of copper ions and their high surface area. Overall, hydrochars are a promising sorption material for the removal of copper ions and could be used as a cost-effective alternative compared to activated carbons or resins.

Recommendations

    For future research, pyrolysis could be used on the hydrochars and analyzed to see what effect pyrolysis had on removing copper ions. Pyrolysis could help to remove volatile groups on the hydrochars and allow the copper ions to have better access to the internal pores of the char for better adsorption. Another recommendation is to do more trials of the activated acrylic acid chars, especially the acrylic acid chars washed with sodium hydroxide and potassium hydroxide, to have more data as only one batch was made for each activated acrylic acid char. Making more batches of the vinyl sulfonic acid chars that were washed with sodium hydroxide and potassium hydroxide would be a good idea to collect more data as only one batch of each vinyl sulfonic acid char that was washed with a strong base was made. Another recommendation would be to increase the concentration of vinyl sulfonic acid in the glucose-water solution and then wash the hydrochar with potassium hydroxide to see what effect adding more acid would have on the activated hydrochar. It is also recommended for the titration experiments to use sodium hydroxide as the base solution to mix with each sorption material in a centrifuge tube and shaken for 48 hours in order to obtain the total acid concentration of each material and see how it relates to each material's adsorption capacity for removing copper ions. In addition, more nitrogen adsorption tests should be done on the other materials that were not tested to obtain their surface areas and see how they relate to their adsorption for copper removal. It is also recommended to analyze each sorption material with different metal solutions such as lead to see how effective they are at removing lead ions since lead has a +2 charge as copper has. Lastly, it is also recommended to analyze each sorption material with an organic compound like methylene blue to see how effective each material is at removing the organic compounds.

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Appendix

Appendix A: Sample Calculations

Calculate Adsorption Capacity

$m := 0.1999$ g

$conc1 := 390.064$ ppb

$dH2O := 1.0058$ g/ml

$MWCu := 63.546$ g/mol

$Coppersoln1 := 490.536$ ppb

$Coppersoln2 := 481.448$ ppb

$w1 := 35.7779$ g of H2O

$v1 := 0.4$ ml of sample

$$conc2 := conc1 \cdot \frac{\left(\frac{w1}{dH2O}\right) + v1}{v1} = 3.508 \times 10^4$$

$w2 := 35.2001$ g

$v2 := 0.3$ ml of sample

$$conc3 := conc2 \cdot \frac{\left(\frac{w2}{dH2O}\right) + v2}{v2} = 4.127 \times 10^6 \quad \text{ppb}$$

$$ConcFinal := \frac{conc3}{1000000 \cdot MWCu} = 0.065 \quad M$$

$$Coppersolnconc12 := Coppersoln1 \cdot \left[\frac{\left(\frac{35.7695}{dH2O}\right) + v1}{v1}\right] = 4.41 \times 10^4 \quad \text{ppb}$$

$$\text{Coppersolnconc13} := \text{Coppersolnconc12} \cdot \left[\frac{\left(\frac{35.2003}{dH2O} \right) + v2}{v2} \right] = 5.189 \times 10^6 \quad \text{ppb}$$

$$\text{Coppersolnconc22} := \text{Coppersoln2} \cdot \left[\frac{\left(\frac{35.7695}{dH2O} \right) + v1}{v1} \right] = 4.329 \times 10^4 \quad \text{ppb}$$

$$\text{Coppersolnconc23} := \text{Coppersolnconc22} \cdot \left[\frac{\left(\frac{35.2003}{dH2O} \right) + v2}{v2} \right] = 5.093 \times 10^6 \quad \text{ppb}$$

- -

$$\text{CopperFinal1} := \frac{\text{Coppersolnconc13}}{MWCu \cdot 1000000} = 0.082 \quad \text{M}$$

$$\text{CopperFinal2} := \frac{\text{Coppersolnconc23}}{MWCu \cdot 1000000} = 0.08 \quad \text{M}$$

$$\text{AverageCopperFinal} := \frac{(\text{CopperFinal1} + \text{CopperFinal2})}{2} = 0.081 \quad \text{M}$$

$$\text{Coppermassinitial} := \text{AverageCopperFinal} \cdot MWCu \cdot \frac{10}{1000} = 0.051 \quad \text{g}$$

$$\text{Coppermassfinal} := \text{ConcFinal} \cdot MWCu \cdot \frac{10}{1000} = 0.041 \quad \text{g}$$

$$\text{Ads} := \frac{(\text{Coppermassinitial} - \text{Coppermassfinal}) \cdot 1000}{m} = 50.717 \quad \text{mg Cu/g}$$

$$\text{Adsmol} := \frac{\text{Ads}}{\text{MWCu}} = 0.798 \quad \text{mmol Cu/g}$$

Adsorption Surface Area Basis

$$\text{SA} := 0.545 \quad \text{m\textasciicircum2/g}$$

$$\text{AdsmolSA} := \frac{\text{Adsmol}}{\text{SA}} = 1.464 \quad \text{mmol Cu/m\textasciicircum2}$$

Titration Calculation for Acid Concentration

Volume of base in 48 hour solution $\quad$ VB := 0.02 $\quad$ L

ConcB := 0.1 $\quad$ M $\qquad$ mt := 0.4999 g

Volume of base solution added to acid solution $\quad$ Va := 0.005 $\quad$ L

Volume of acid solution and water $\qquad$ VHCl := 0.01 $\quad$ L

ConcHCl := 0.05 $\quad$ M

VNaOH1 := 1.1 mL $\qquad$ pH1 := 5.22

VNaOH2 := 1.2 $\quad$ mL $\qquad$ pH2 := 10

$$\text{VNaOHf} := \text{VNaOH1} + \left[(7 - \text{pH1}) \cdot \frac{(\text{VNaOH2} - \text{VNaOH1})}{(\text{pH2} - \text{pH1})} \right] = 1.137$$

Volume of NaOH added $\qquad$ $\text{VNaOH} := \dfrac{\text{VNaOHf}}{1000} = 1.137 \times 10^{-3}$ $\quad$ L

ConcNaOH := 0.1 $\quad$ M

- -

Moles of carbon surface functionalities

$$\text{ncsf} := (\text{VB} \cdot \text{ConcB}) - \frac{\text{VB}}{\text{Va}} \cdot [(\text{VHCl} \cdot \text{ConcHCl}) - (\text{VNaOH} \cdot \text{ConcNaOH})] = 4.549 \times 10^{-4} \quad \text{mol acid}$$

$$\text{Acidconc} := \text{ncsf} \cdot \frac{1000}{\text{mt}} = 0.91 \quad \text{mmol acid/g}$$

Surface area basis

$$\text{AcidconcSA} := \frac{\text{Acidconc}}{\text{SA}} = 1.67 \quad \text{mmol acid/m^2}$$

Appendix B: Adsorption Results of Sorption Materials

Table 6: Adsorption capacities of sorption materials

Sorption Material	Adsorption Capacity (mg Cu/g)
Norit SX-1	18.90 ± 3.91
Norit SX-1 KOH	21.22 ± 5.56
Norit SX Ultra	15.36 ± 4.88
Norit Darco KB-G	1.83 ± 8.68
Norit Darco KB-G KOH	-0.91 ± 6.70
Norit Darco KB-M	3.43 ± 8.87
Norit Darco KB-WJ	2.54 ± 6.10
Norit Darco KB-WJ KOH	21.10 ± 4.49
Norit Darco S-51	5.14 ± 4.34
Nuchar Activated Carbon	29.03 ± 3.49
Nuchar Activated Carbon KOH	11.01 ± 6.91
Pica HP 120	16.22 ± 3.92
Glucose Hydrochar	-6.09 ± 8.82
Hyd Na_2CO_3	20.06 ± 0.35
Hyd K_2CO_3	29.18 ± 5.09
Hyd NaOH	34.85 ± 3.58
Hyd KOH	39.99 ± 4.29
Acrylic Acid Char	-10.52 ± 8.28
Ac Na_2CO_3	29.76 ± 6.70

Ac K$_2$CO$_3$	25.96 ± 5.50
Ac NaOH	50.05 ± 3.93
Ac KOH	45.27 ± 6.82
Vinyl Sulfonic Acid Char	-7.38 ± 7.26
VinSulf NaOH	34.40 ± 4.60
VinSulf KOH	50.52 ± 3.43
Amberlyst 15 Hydrogen Form	128.26 ± 3.54
AG 50W-X4 Hydrogen Form	108.72 ± 6.79
Lewatit TP 260 Disodium Form	129.47 ± 2.67

Appendix C: Adsorption Results and Acid Concentrations of Sorption Materials

Table 7: Adsorption capacity and acid concentration of sorption materials

Sorption Material	Adsorption Capacity (mmol Cu/g)	Acid Concentration (mmol acid/g)
Norit SX-1	0.30 ± 0.06	0.05
Norit SX Ultra	0.24 ± 0.08	0.11
Nuchar Activated Carbon	0.46 ± 0.05	0
Hyd KOH	0.63 ± 0.07	1.09
VinSulf KOH	0.80 ± 0.05	0.91
Amberlyst 15 Hydrogen Form	2.02 ± 0.06	4.79 ± 0.01
AG 50W-X4 Hydrogen Form	1.71 ± 0.11	1.1
Lewatit TP 260 Disodium Form	2.04 ± 0.04	2.3

Appendix D: Adsorption Results and Acid Concentrations of Sorption Materials on Surface Area

Basis

Table 8: Adsorption capacity and acid concentration of sorption materials on surface area basis

Sorption Material	Adsorption Capacity (mmol Cu/m^2)	Acid Concentration (mmol acid/m^2)
Norit SX-1	$3.62*10^{-4} \pm 7.50*10^{-5}$	$6.65*10^{-5}$
Norit SX Ultra	$2.07*10^{-4} \pm 6.59*10^{-5}$	$9.63*10^{-5}$
Nuchar Activated Carbon	$2.76*10^{-4} \pm 3.31*10^{-5}$	0
Hyd KOH	0.15 ± 0.02	0.26
VinSulf KOH	1.46 ± 0.10	1.67
Amberlyst 15 Hydrogen Form	$0.04 \pm 1.05*10^{-3}$	$0.09 \pm 2.19*10^{-4}$
AG 50W-X4 Hydrogen Form	2.60 ± 0.16	1.67
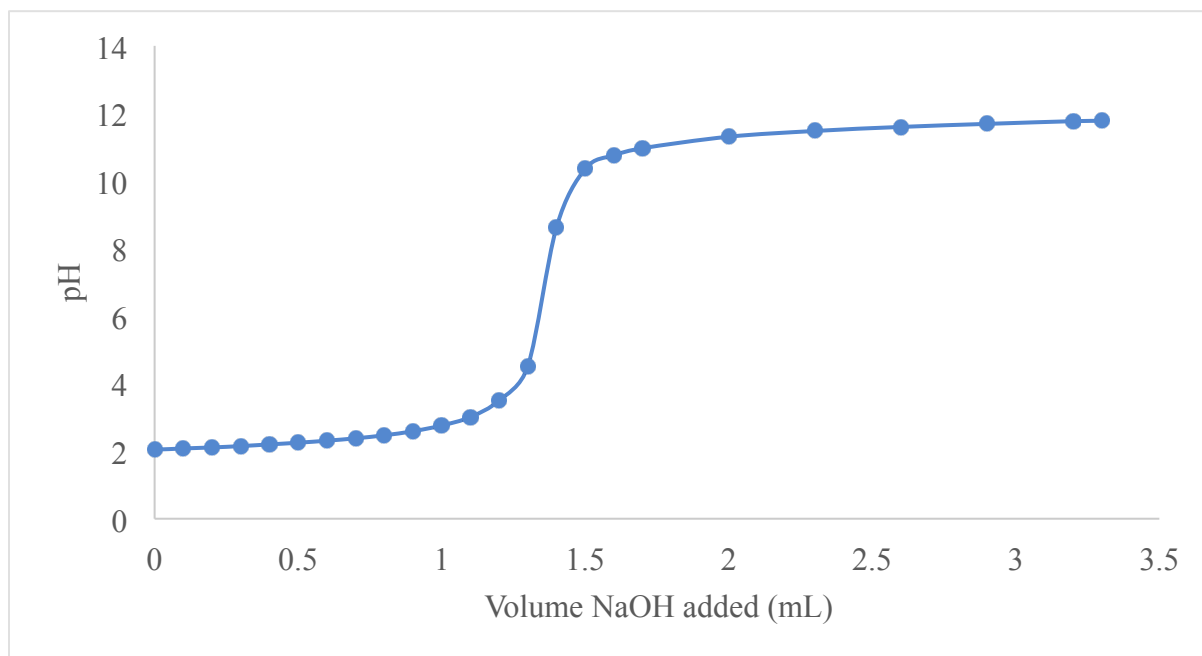
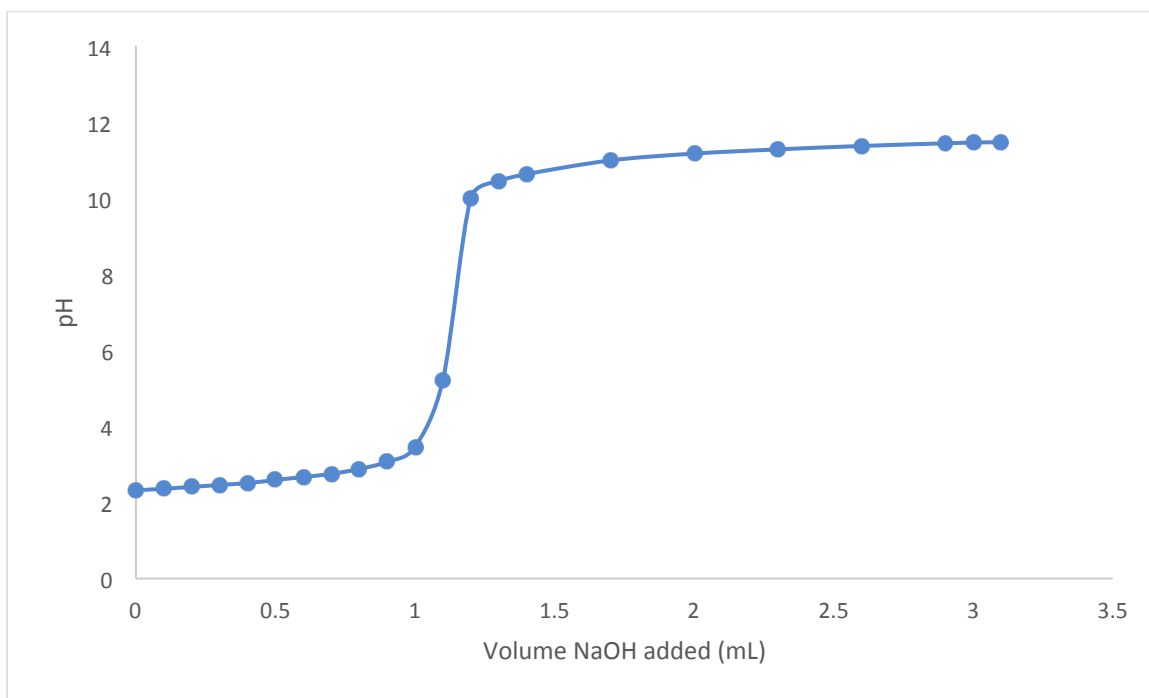*Figure 34: Titration of hydrochar of pH versus volume of NaOH added (mL)*

Figure 35: Titration of vinyl sulfonic acid char of pH versus volume of NaOH added (mL)
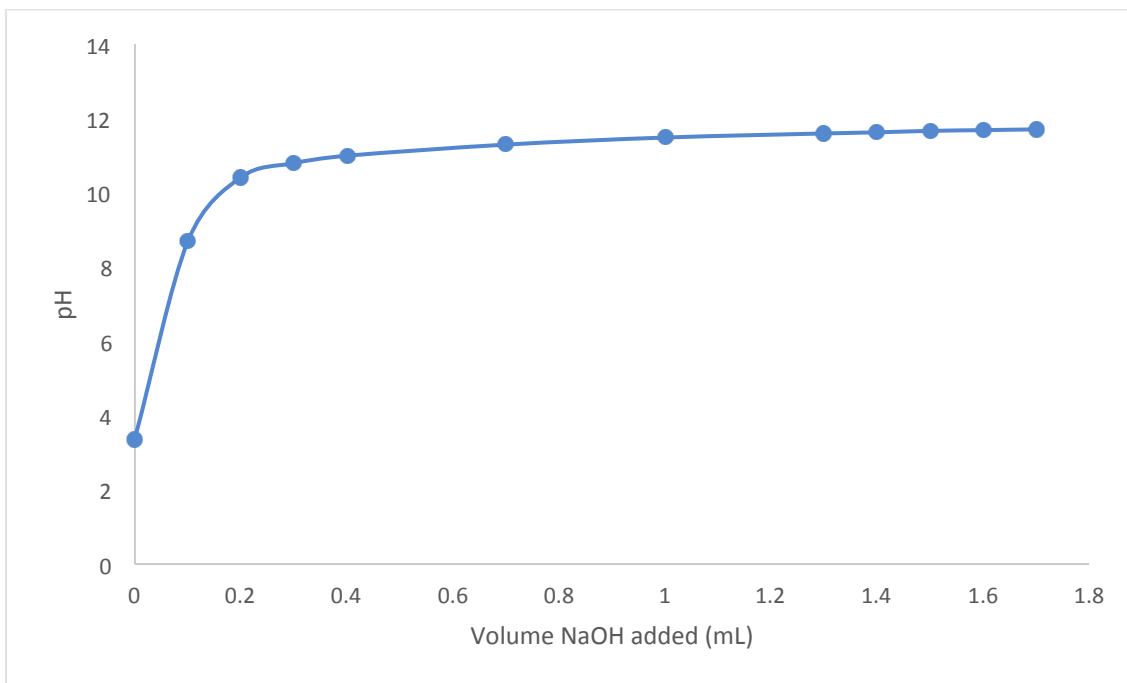
Figure 36: Titration of Norit SX-1 of pH versus volume of NaOH added (mL)
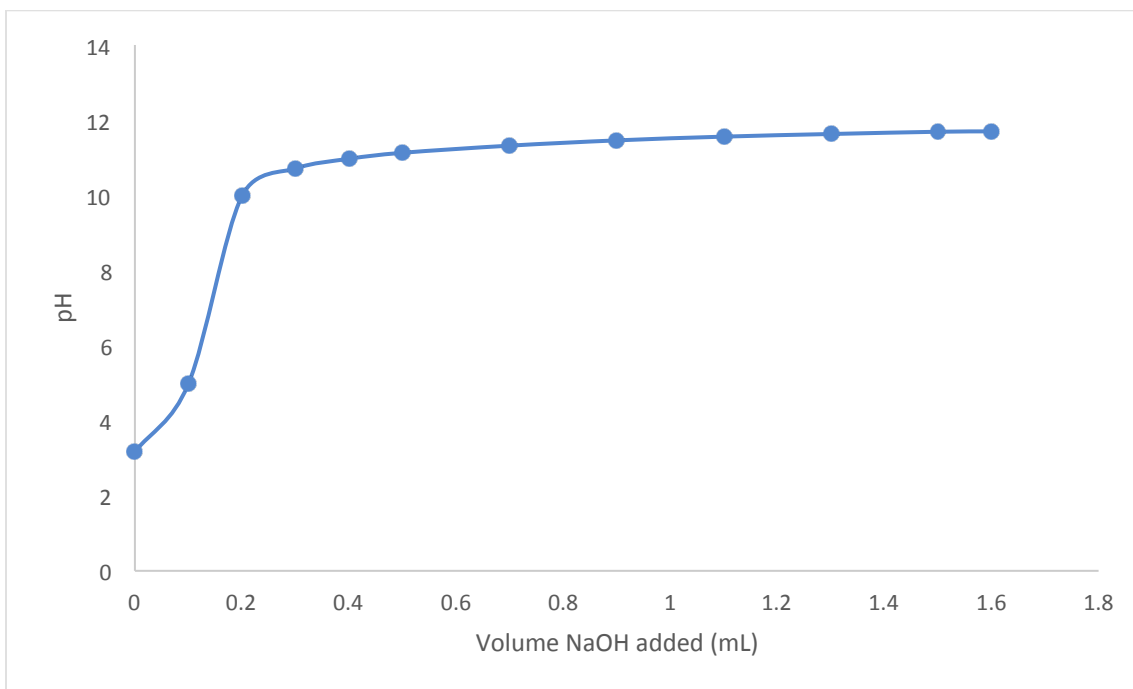

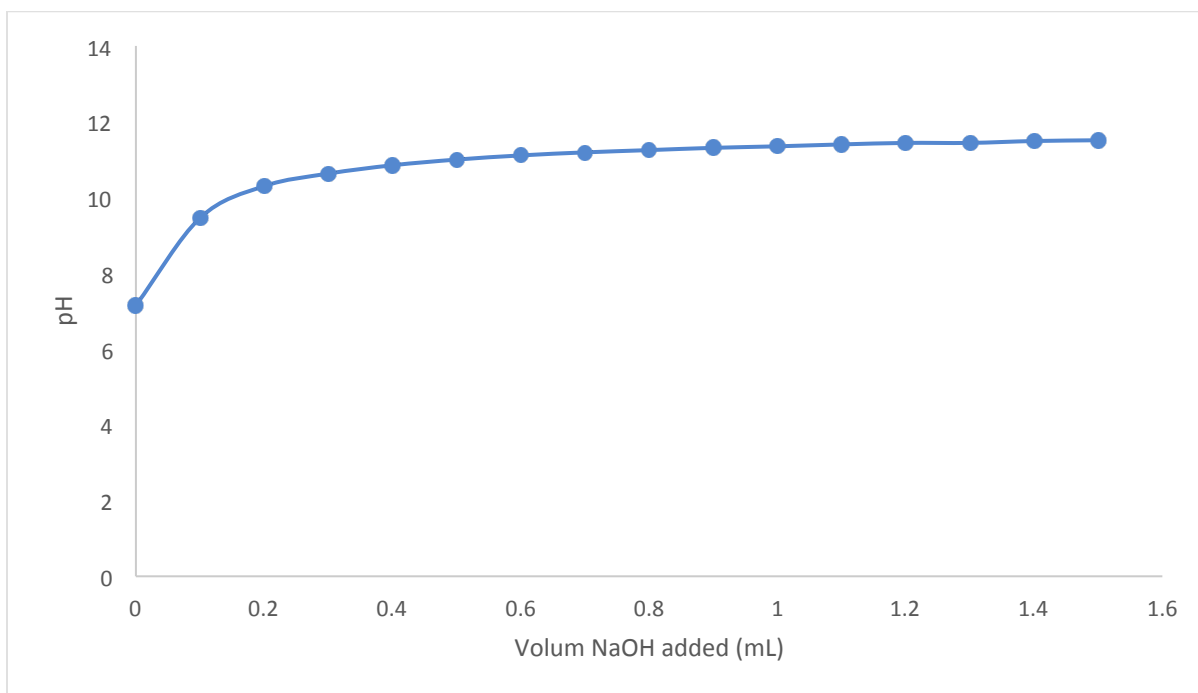*Figure 37: Titration of Norit SX Ultra of pH versus volume of NaOH added (mL)*

Figure 38: Titration of Nuchar Activated Carbon of pH versus volume of NaOH added (mL)
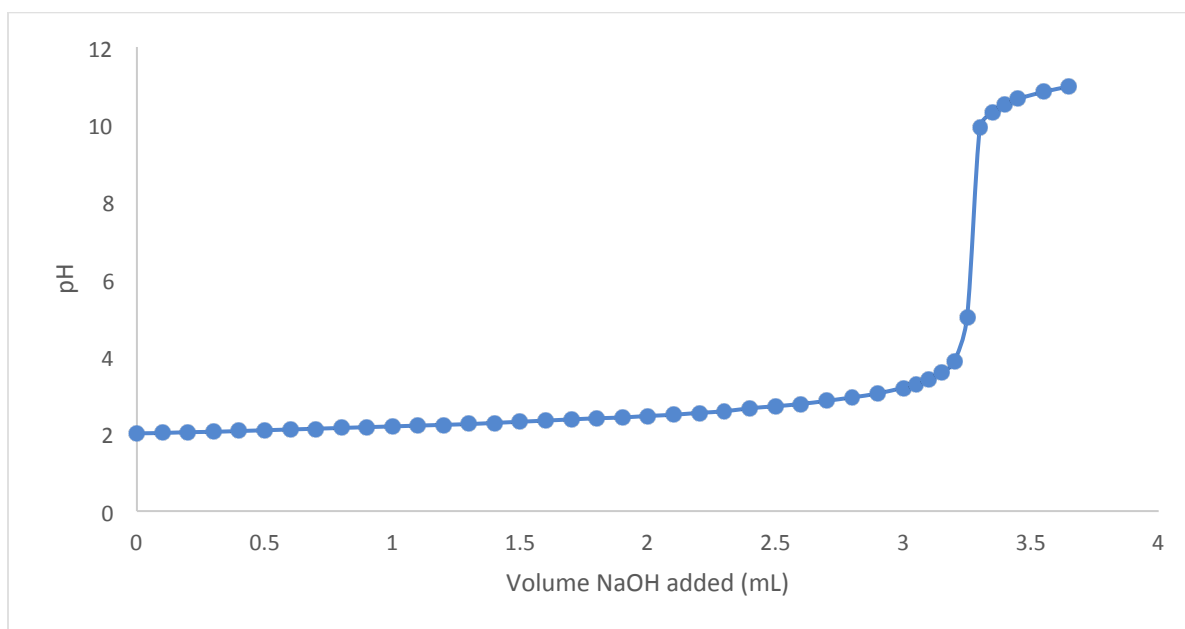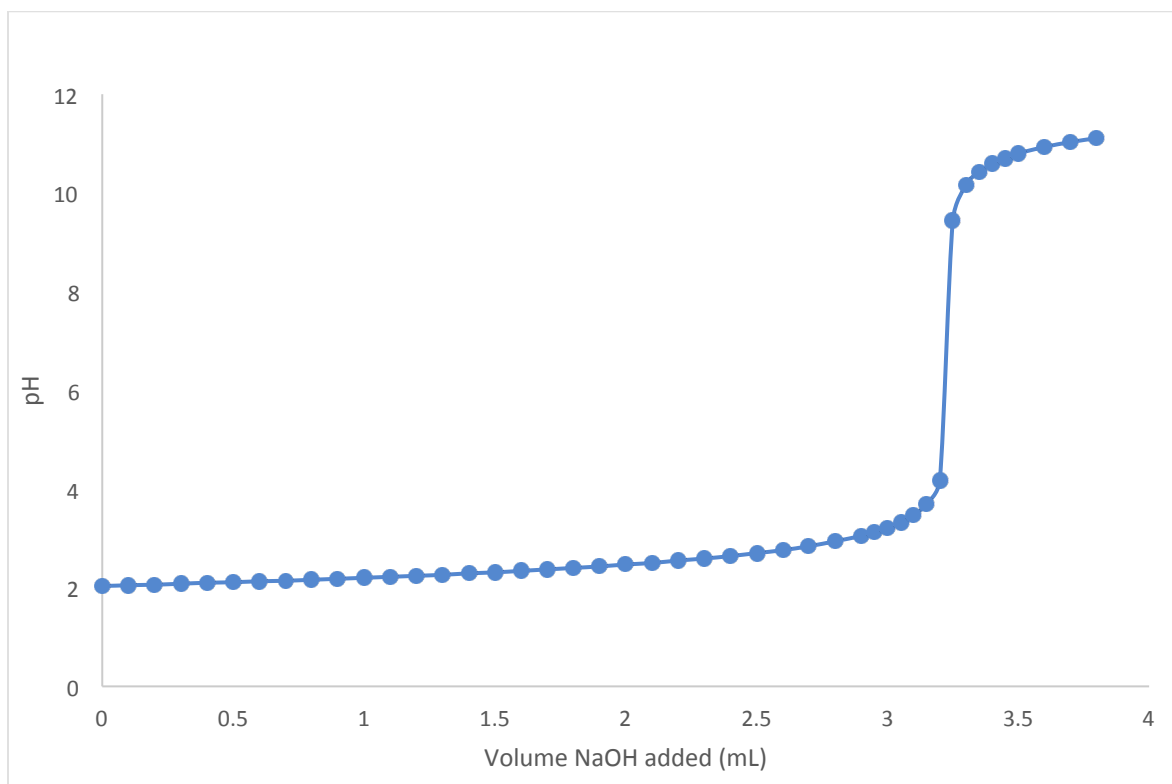

Figure 39: Titration of Amberlyst 15 of pH versus volume of NaOH added (mL), first run (from

Maksim Tyufekchiev)

Figure 40: Titration of Amberlyst 15 of pH versus volume of NaOH added (mL), second run

(from Maksim Tyufekchiev)