

OPTIMIZATION OF ACTIVATED CARBON FOR NATURAL COLOR REMOVAL

By

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To my parents, and also to my roommates, Kyle and Chad, who helped me when I needed help

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## TABLE OF CONTENTS

	<u>page</u>
ACKNOWLEDGMENTS.....	4
LIST OF TABLES.....	6
LIST OF FIGURES .....	7
ABSTRACT .....	8
CHAPTER	
1 INTRODUCTION.....	9
2 ACTIVATED CARBON: A BRIEF OVERVIEW .....	11
Adsorption Process.....	11
Production Process .....	13
Physical Activation .....	14
Chemical Activation .....	15
Surface Chemistry .....	17
Apple Juice Decolorization .....	20
Sugar Decolorization.....	22
3 EXPERIMENTAL PROCEDURE .....	24
Raw Materials.....	24
Charring .....	24
Particle Processing .....	27
Activation .....	27
Carbon Characterization .....	30
4 RESULTS .....	31
Charring .....	31
Steam Activation .....	34
Chemical Activation .....	38
Carbon Dioxide Activation.....	44
Surface Charge Modification .....	45
Surface Area Assessment .....	46
5 CONCLUSIONS .....	51
LIST OF REFERENCES .....	53
BIOGRAPHICAL SKETCH .....	56

## LIST OF TABLES

<u>Table</u>		<u>page</u>
4-1	Rice husks activated with steam.....	38
4-2	Chemical activations of sawdust.....	43
4-3	Surface modification.....	46
4-4	CA-50 performance.....	47
4-5	BET characteristics of selected samples.....	48

## LIST OF FIGURES

<u>Figure</u>		<u>page</u>
2-1	Particle transport mechanism .....	12
2-2	Aromatic bonding.....	13
2-3	Acidic and basic functional groups.....	18
2-4	Determination of PZC.....	19
2-5	Polyphenols in apple juice .....	21
3-1	Furnace used for activated carbon production.....	26
4-1	Sawdust mass loss during the charring process.....	32
4-2	Congo red and methylene blue adsorption for sawdust chars .....	33
4-3	Mass loss of rice husks during the charring process.....	33
4-4	Steam activation of sawdust at 1.6 mL/min .....	35
4-5	Images of activated carbon at high magnifications.....	36
4-6	Steam activation of sawdust at 0.4 mL/min .....	37
4-7	Congo red and methylene blue adsorption for rice husks char .....	38
4-8	Solution concentrations used for activation.....	40
4-9	Potassium hydroxide to carbon ratios .....	40
4-10	The impact of char and activation characteristics on apple color removal.....	41
4-11	Selected chemical activations.....	42
4-12	Chemical activations using sawdust .....	43
4-13	Carbon dioxide activation of sawdust.....	44
4-14	Carbon dioxide activation of rice husk .....	45
4-15	BET adsorption/desorption plots (a) CA-50 (B) Sawdust activated with steam for 2 hours at 850 °C .....	47

Abstract of Thesis Presented to the Graduate School  
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This work focuses on the creation of powdered activated carbon (PAC) from sawdust and rice husks, two agricultural wastes, using both physical and chemical means. Physical means included a traditional charring stage using nitrogen followed by activation with either steam or carbon dioxide; chemical activation focused on the use of anhydrous potassium hydroxide as an activating agent. The performance of the activated carbon created was evaluated by its ability to decolorize commercially-available apple juice typically found at grocery stores, with an existing commercially-available PAC used as a control. The created activated carbon was tested for its ability to decolorize apple juice as well as Methylene Blue and Congo Red laboratory dyes, with selected samples analyzed for specific surface area, total pore volume, and average pore size using nitrogen adsorption. Generally, sawdust responded favorably to physical activation, with the rice husks responding more favorably to activation with potassium hydroxide. However, activation using raw precursors, which saves time and energy by avoiding the charring stage, proved unsuccessful.

## CHAPTER 1 INTRODUCTION

Activated carbon has long been used as a high-quality adsorbent for the removal of contaminants from the air and water phases, and is today used in a variety of settings. Activated carbon is typically manufactured from organic substrates in either a powder or granular form, used as an adsorbent for its intended purpose, and then disposed of or reclaimed using a regenerative process.

The primary goal of this research is to use a renewable biomass to create a quality powdered activated carbon (PAC), and to develop a consistent method for doing so in a laboratory setting, with the final hope of adopting it for a larger industrial batch process. The produced activated carbon will be analyzed using traditional activated carbon testing, with the results then used to optimize the PAC for the removal of natural color from commercial-grade apple juice in an effort to compete with commercially-available PAC currently on the market. Removal of apple juice color was chosen as an available substitute for the sugar decolorization industry; activated carbon was first used in an industrial setting as part of the process of converting brown sugar to white sugar, and it remains a vital part of that industry. If the process developed via this research proves to be economically viable, it could later be incorporated directly into the sugar decolorization industrial procedure.

For this project, two precursors were selected by the supplier: sawdust, which is a traditional precursor for activation, and rice husks, which are more novel. Rice husks are a by-product of the rice milling industry, and account for roughly 20% of the whole rice grain mass. The amount of rice husk waste produced in 1995 was approximately 500 million tons in developing countries, and this amount far exceeds any beneficial uses for the waste, thus posing a disposal problem (Guo et al., 2000). It was hoped that an activated carbon could be created

using the rice husks as a precursor, thereby finding a beneficial use for an overly abundant waste product. Sawdust was also studied as an alternative agricultural waste product.

The following chapters of this thesis provide an overview of activated carbon, including its structure and traditional methods of production, followed by an overview of the experimental procedure for this research, the findings, and finally, the conclusions that could be drawn.

## CHAPTER 2 ACTIVATED CARBON: A BRIEF OVERVIEW

Activated carbons are a family of adsorbents formed by the partial combustion and thermal decomposition of carbonaceous materials. Activated carbon is used for a wide variety of applications including water purification and decolorization, air purification, deodorants, and industrial usages, such as food processes and the manufacture of pharmaceuticals.

Activated carbon is prized for its high adsorptive capacity, due to its high surface area to mass ratio, extensive microporous pore structure, and potential for surface reactivity. The surface area for a gram of commercially-available activated carbon ranges from 800 to 1500 m<sup>2</sup>/g, with carbons in the laboratory reaching as high as 3000 m<sup>2</sup>/g (Bansal, 1988).

The first recorded use of activated carbon was by the Egyptians as early as 1500 B.C. It was later adapted for commercial use in 1900 for the sugar refining industry; however, wide-scale usage did not begin until after the First World War, when activated carbon was necessary for the construction of gas masks to prevent casualties due to poisonous gas. Today, activated carbon can be made from a number of carbonaceous materials, particularly bituminous coals, lignite, wood, and coconut shells, with a new emphasis on creating activated carbon from renewable biomasses, such as seed husks, olive stones, and bamboo in the interest of sustainability (Warhurst, González, Hameed).

### **Adsorption Process**

Activated carbon owes much of its adsorptive capacity to its extensive pore structure. Activated carbon is composed of a series of layers, with each layer constructed from a matrix of aromatic rings. However, unlike graphite or other carbon allotropes, the layers within carbon are not arranged orderly, with layers lying on different planes. This disorder results in spaces

between the carbon layers, causing the pores that make activated carbon so valuable (Marsh and Rodriguez-Reinoso, 2006).

Contaminant adsorption is composed of four stages: the bulk transport stage, the film transport stage, the interparticle transport stage, and the adsorption attachment stage. Contaminants, either in the air or water phase, come into contact with an activated carbon particle and enter one of its many pores. The pore structure of activated carbon is cavernous, and contaminants will move farther into the pore network until they find a place to adsorb to the carbon surface (Snoeyink and Jenkins, 1980).

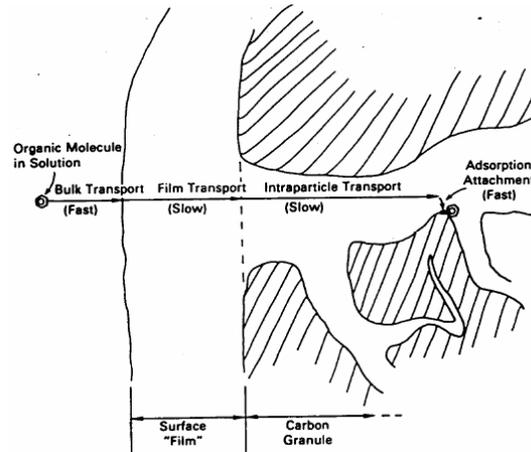


Figure 2-1. Particle transport mechanism (Chadik)

Adsorption occurs at the carbon surface in either a physical or chemical manner. Physical adsorption occurs when contaminants are attracted to the carbon surface without an actual chemical bond being formed, and as a result these physical intermolecular forces are weaker and can be reversed. Physical adsorption processes include weak intermolecular forces such as H-bonding, dipole-dipole forces, and van der Waal forces (Marsh and Rodriguez-Reinoso, 2006).

Chemical adsorption between the contaminants and the carbon surface occurs less often, but is stronger than physical adsorption and irreversible. The majority of bonds between contaminants and carbon fall into two categories: covalent bonds, which occur at the edges of the

carbon layers and result in a positive or negative surface charge, and aromatic bonding, which occurs on the sides of the carbon layer as aromatic molecules (Menendez et al., 1996). Aromatic bonding occurs when aromatic molecules, such as benzene or phenol, overlap aromatic molecules within the carbon matrix. As the molecules approach each other, the initial repulsion of their  $\pi$  electrons rings is overcome by an attraction between the  $\pi$  electron rings of one molecule and the  $\sigma$  electron rings of the other (Hunter and Sanders, 1990).

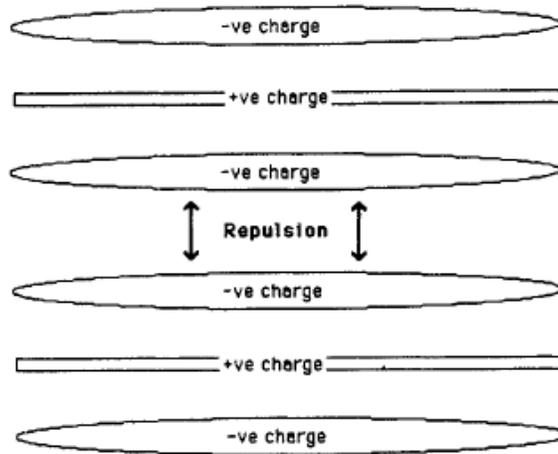


Figure 2-1. Aromatic bonding (Hunter and Sanders, 1990)

### Production Process

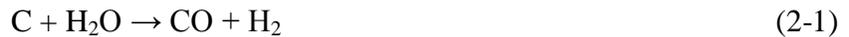
Production of activated carbon is essentially a two-step process. First, a carbonaceous material such as wood is heated under the absence of oxygen in a step referred to as carbonization or pyrolysis, as opposed to “burning” which implies the presence of oxygen. During the pyrolysis stage, volatile materials within the precursor are gasified and removed, leaving behind a porous carbon structure that can then be modified (Tennant, 2003). Carbonization usually occurs at temperatures less than 800 °C. During the activation phase some additional volatilization of the carbon precursor will occur independently of activation (Bansal et al., 1988). Concerning the rate of heating, Ferraz (1988) found that slowly increasing the

temperature of the furnace results in denser and harder chars, as gases created during volatilization have more time to escape the pore structure, allowing the precursor to shrink.

Next, the carbon is oxidized at high temperatures (750 to 850 °C) under a flow of steam and/or carbon dioxide. Because the structure of the carbon is irregular, some carbon atoms within the matrix will react chemically while others do not: this selective reaction allows the creation of a carbon with larger, more randomly distributed, pores that have a much greater adsorptive capacity (Bansal et al., 1988).

### **Physical Activation**

Once carbonization has taken place, the pores within the carbon matrix must be widened in order for them to prove useful; it is this widening of existing pores and the creation of new pores that is referred to as “activation”. Physical activation of carbon is typically done using either steam, carbon dioxide gas, or some mixture of the two. The mechanisms for the two processes are shown below (Bansal et al., 1988).



Some of the carbon monoxide created during the steam activation process will be further oxidized by excess steam. All carbon removed by the activation process will leave the furnace as either CO or CO<sub>2</sub>.



Both of the primary activation reactions are endothermic, meaning that a constant supply of energy must be provided by some sort of furnace or kiln. The reaction involving steam has a lower activation energy than the reaction involving carbon dioxide; as such, physical activation with steam occurs more quickly, widening existing pores and creating a wider pore size distribution throughout the carbon. Activation with carbon dioxide occurs more slowly, first

creating pores before widening them, limiting the carbon to mainly microporous pores that are more uniform in size (Bach, 2007).

Physical activations are typically performed at temperatures ranging from 800 to 1100 °C. Azargohar and Dalai (2008) used a furnace temperature ranging from 600 to 900 °C for a period of 0.9 to 4 hours for the physical activation of spruce char. For activations using rice husks as the precursor, Malik (2003) created char at a temperature of 400 °C and activated at a temperature of 600 °C for 1 hour. Flows vary; when using carbon dioxide, anywhere from 80 to 200 mL/min seems acceptable (Pastor-Villegas, Rodríguez-Reinoso). For steam, flow is either measured as the actual steam flow, the amount of water required to create this steam flow, or the steam-to-carbon ratio. Mazyck and Cannon (2000) used 1.6 mL/min of liquid water as steam for conventional activation (8 g H<sub>2</sub>O/g carbon), and 9.5 mL/min for “high” flows.

The most important point to gather from the literature concerning steam activation is that pore size generally increases with activation time, and this pore size has a direct relationship on adsorption capacity (Tennant, 2003). It has been proposed that organic contaminants will adsorb into pores that have an average pore diameter ranging from 1.5 to 2 times that of the contaminant. As steam exposure time increases and pores gradually widen, the surface area of the carbon as well as the adsorptive capacity of the carbon increases. However, at a certain point the carbon becomes overactivated; pore walls begin to collapse, and pore sizes exceed the desired size for adsorption (Bach, 2007).

### **Chemical Activation**

Chemical activation shares the same goals as physical activation but uses entirely different processes. The carbon precursor is mixed with a solution containing a chemical agent and then left to dry, impregnating the carbon with the chemical agent before being placed in a furnace or kiln to cause a chemical reaction. Traditionally, phosphoric acid or zinc chloride have been used

for the chemical activation of lignocellulosic materials, while metal compounds such as KOH were used for the activation of coal precursors or chars (Srinivasakannan and Bakar, 2004). Potassium hydroxide was chosen as the activating agent for this research because it is a relatively inexpensive chemical that is readily available in the laboratory, and because the small amount of literature regarding the chemical activation of rice husks using KOH had been promising (Malik, Guo).

Chemical activation is not nearly as well understood as physical activation, but it seems to work by dehydrating the carbon precursor and preventing the formation of tars during the activation process (Azargohar and Dalia, 2008). The chemical mechanism by which activation occurs using potassium hydroxide consists of several steps; however, they can be condensed into two main reactions.



The second reaction, in which potassium carbonate is converted to potassium oxide, occurs at a minimum temperature of 700 °C and usually requires a minimum of one hour for completion (El-Hendawy, 2009). For the production of activated carbon from fir wood, Wu et al. (2005) used a KOH to char ratio varying from 0.5 to 6, and then activated the carbons in a furnace at 780 °C for one hour. For rice husks, Gou et al. (2000) used a rice husk charred at a temperature of 400 °C for a KOH to char ratio of 4, and then activated the carbons at temperatures ranging from 650 to 800 °C for a period ranging from 0.5 to 2 hours. Both approaches created carbons that were either very microporous or at the divide between microporous and mesoporous carbons, defined as 20 Å.

Concerning the amount of water used to create the potassium hydroxide solutions, no definitive answer is given by the literature, as all of the water should evaporate before the carbon is ready for activation and therefore does not play a role in the chemical activation process. El-Hendawy (2009) suggests using “the least amount of water”; generally, as much water should be used to effectively mix the KOH solution and the carbon.

### **Surface Chemistry**

Activated carbon does not consist solely of carbon atoms; while the carbon matrix that makes up the graphite layers will be entirely carbon, atoms other than carbon will come to occupy edge sites. These atoms, referred to as heteroatoms, are typically oxygen, nitrogen, or sulfur (hydrogen is not included as its chemical bond energy is so low). These heteroatoms are responsible for giving the carbon a surface charge (Lei et al., 2002).

Heteroatoms on the edge sites of activated carbon will combine to form a variety of different molecular structures, typically referred to as surface functional groups. Pure carbon is naturally amphoteric; that is, in solution it can act as either an acid or a base (Marsh and Rodriguez-Reinoso, 2006). Electrons flow freely through the carbon matrix, giving regions of the matrix a momentarily net positive or negative charge depending on the electron density at that given instant. In regions where electrons have temporarily accumulated, the carbon will have a net negative charge. In response, this accumulation of electrons will produce a lack of electrons in the surrounding area, resulting in a net positive charge in those regions. In practice, however, because the vast majority of atoms that attach to carbon in solution are hydrogen, carbon is usually referred to in the literature as basic (Tennant, 2003).

Surface functional groups will give the edges of the carbon matrix a charge, and are grouped accordingly: acidic functional groups, such as carboxyl, lactone, hydroxyl, or carbonyl, will take hydrogen atoms from solution and give the carbon a positive charge. Basic functional

groups, such as pyrone, amides, amines, or nitriles, will give away protons in solution and result in a negative surface charge. When researchers refer to a carbon as being basic, they can either be trying to communicate that the carbon surface has basic surface functional groups, or that the carbon surface simply has a lack of functional groups.

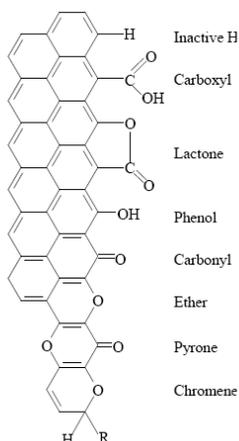


Figure 2-2. Acidic and basic functional groups (León and Radovic, 1994)

Determination of the surface charge of a carbon is typically done by using either titration with a base or potentiometric titration to calculate the point of zero charge (PZC) of the carbon. The PZC indicates the pH of the solution at which the surface charge of the carbon is negated. Figure 2-4 shows the relationship between the surface charge of the carbon and the pH of the solution: at different ionic strengths, the surface charge  $\sigma$  of the carbon will change as a result of changes in the pH. The PZC is defined as the pH at which the carbon has a neutral charge in solution; at a pH less than the PZC, the net surface charge of the carbon will be positive, while the carbon will have a negative net charge if the pH is greater than the PZC value.

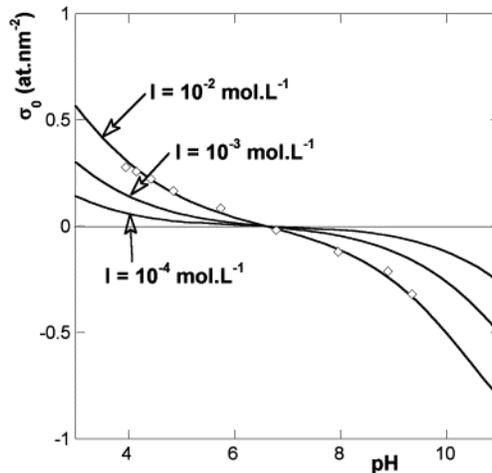


Figure 2-3. Determination of PZC (Barale et al., 2008)

Functional groups containing the oxygen atom are almost always acidic, and these surface groups are undoubtedly the most important concerning surface charge. Oxygen has a relatively high electronegativity, meaning that in a molecule it will pull electrons towards itself and give the molecule a dipole (polarity). More polarity within the functional groups results in a greater net surface charge.

Generally speaking, a basic carbon is preferred for the sake of adsorption performance (Tennant, 2003). Acidic functional groups, being polar, will attract other polar molecules, particularly water. This hydrophilic property of the surface of the carbon results in water molecules crowding around and within pore openings, blocking other molecules and preventing target adsorption. Basic functional groups not only help prevent acidic groups from forming on the carbon, but research has also shown that the presence of basic functional groups can aid in the adsorption of phenolic compounds, as the negative carbon surface charge will attract the positively charged aromatic ring portion of the phenols (Menendez et al., 1996). However, acidic functional groups can be beneficial for certain scenarios, specifically the removal of metals from solution (Monser and Adhoum, 2002).

The formation of surface functional groups is controlled primarily during activated carbon production by the maximum temperature of the activation furnace and the gases present during activation (Bach, 2007). During heating of the carbon in an inert environment using either nitrogen or hydrogen gas, nearly all of the acidic functional groups will break down at a temperature of less than 900 °C; phenolic and quinone at approximately 700 °C, and carbonide and lactone at 500 °C. At roughly 900 °C, oxygen on the surface of the carbon will bind into the aromatic matrix, forming the basic functional group pyrone (Vidic et al., 1997). All functional groups, acidic or basic, on the surface of the carbon will have been destroyed at a temperature of 1200 °C. Once the carbon has been cooled and reintroduced to ambient conditions, however, acidic functional groups may begin to reappear at room temperature; hence the need to create a lasting basicity. It is for this reason that, when only considering the surface charge of the carbon as a target parameter, hydrogen is preferred over nitrogen gas as the furnace atmosphere during heat treatment. While heat treatment using either gas produces a carbon without surface functionalization, use of hydrogen gas produces a carbon that will stay basic longer until ambient conditions due to the formation of more stable C-H bonds and the hydrogasification of loosely bound, highly reactive, carbon atoms (Menendez et al., 1996).

After activation has taken place, surface charge can be further modified using a variety of methods. At relatively low temperatures (400-700 °C), treatment of the activated carbon with ammonium gas can form basic functional groups such as amides or nitriles (Chen et al., 2005). For the creation of acidic groups, contact between the carbon and a nitric acid or hydrogen peroxide solution can catalyze surface oxidation (Pereira et al., 2003).

### **Apple Juice Decolorization**

The yellowish brown color of apple juice is caused by a number of different molecules that are collectively referred to as apple condensed tannins, phenolics, phenolic compounds,

antioxidants, flavonoids, apple peel powder, bioflavonoids, phytonutrients, and phytochemicals; in the context of this research, they will simply be referred to as apple polyphenols. For commercial reasons, the ability to remove these molecules from apple juice, thus making the juice more colorless, has been a particular goal of the juice industry for quite some time (Borneman et al., 1997).

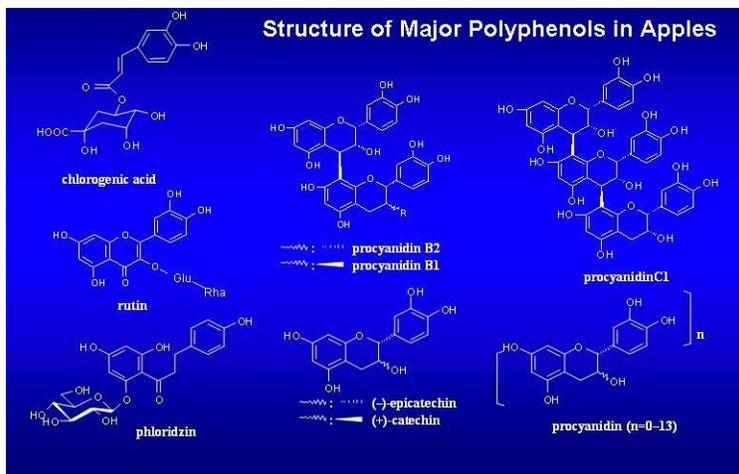


Figure 2-4. Polyphenols in apple juice (<http://www.applepolyphenols.com/>)

As seen in Figure 2-5, the molecular structure of these polyphenols is not so different from the natural organic matter that activated carbon is currently used to remove from municipal water sources: the molecules are a series of phenol and benzene aromatic rings, relatively large in size, with a number of protons that are likely to break off in solution, giving the molecules a slight negative charge.

For nearly the last decade, the vast majority of research concerning the removal of apple polyphenols has concentrated on ultrafiltration using polyethersulfone (PES), polyvinylpyrrolidone (PVP), or polyvinylpolyprrolidone (PVPP) membranes. Membrane technology has slowly begun to replace previous techniques, which relied on coagulants such as gelatins or bentonite and a settling stage (Borneman et al., 1997).

Very little literature exists concerning activated carbon and polyphenol removal in apple juice. However, Arslanog'lu et al. (2005) have shown mild success using powdered activated carbon to remove “dark colors” from peach pulps, reaching a color removal of nearly 40%.

### **Sugar Decolorization**

Although the juice industry does not currently use activated carbon as the primary tool for removing color from its juices, activated carbon has long been used as an adsorbent for the removal of color from the clarified juice in sugar refineries. In 1941, Hertzog and Broderick published a paper detailing the process of using steam-activated coal to remove the color from raw sugar solutions. At the time, the activation of carbon was not fully understood, and the sugar industry was using granulated bone char for the color removal process. The raw sugar, deep brown in color, was mixed into solution with powdered activated carbon and filter pressed. This process was repeated twice to remove nearly all of the color from the sugar, leaving it nearly white. The most important observation gathered from their work is that carbons with larger pore diameters were more effective in removing the sugar color, and that an increase in pore diameter resulted in a greater carbon mass loss overall (Hertzog and Broderick, 1941).

Today, activated carbon is routinely used in the sugar industry. During the sugar refining process, brown sugar is typically dissolved to make a syrup and then crystallized under vacuum to produce white sugar. Any remaining syrup that can no longer be economically converted back into sugar is referred to as molasses, and is a common waste product of the industry. Its color is due in large part to the presence of melanoidin, a brown polymer formed when amino acids react with sugar in a process referred to as the Maillard reaction. This colored polymer is considered a major pollutant; untreated wastewaters from sugar refineries are often so opaque that sunlight cannot reach aquatic vegetation beneath the surface of the water (Bernardo, 1997).

Because melanoidin and polyphenols are both responsible for the yellowish brown color of apple juice (polyphenols for the yellowish color, melanoidin for gradual browning), it was hoped that any research on the removal of polyphenols could also relate to the use of activated carbon in the sugar decolorization industry.

## CHAPTER 3 EXPERIMENTAL PROCEDURE

Activated carbon for this series of experiments was created using a traditional two-step approach, incorporating a pyrolysis stage followed by activation with either steam, potassium hydroxide, or carbon dioxide, with renewable biomasses chosen as the starting material.

### **Raw Materials**

Sawdust and rice husks, two waste products from the agricultural industry, arrived in two distinct conditions: one in a natural state, which will henceforth be regarded to by the term “raw”, and the other in a charred state, which will henceforth be regarded as “pre-char”. The samples were provided by an independent supplier operating out of China. The pre-char sawdust and rice husk samples were previously exposed to an inert high temperature environment by a third-party. Details such as the temperature of the furnace used in the charring process and the time spent in the furnace by the samples are unknown. Before any other preparation took place, the raw sawdust and rice husk samples were placed in an oven overnight at approximately 110° Celsius to remove any moisture; pre-charred samples were not placed in the oven as experiments had shown mass loss due to moisture loss to be less than 2% for these samples, and deemed inconsequential.

### **Charring**

After the initial drying process, the raw samples were placed in a vertical tube furnace for charring. Two methods were used to char the samples in the furnace. In the first, or traditional, method, the sample was placed on top of a frit in either a stainless steel or quartz tube and then placed in the furnace at room temperature (Figure 3-1). The clam-shell furnace was closed and then turned on; the temperature of the furnace rose gradually (about 20 °C per minute) to the desired temperature, remained at that temperature for the desired time, and then descended

gradually to room temperature once the desired time was reached and the furnace was turned off. This method, with some variations, seems to be preferred by the majority of activated carbon researchers (Bernardo, Bach, Wu). However, this method had the disadvantage of being very time-consuming: for higher temperatures, it can take several hours for the furnace to reach the desired temperature, and several more once the experiment has concluded. In an effort to be more efficient at charring samples, a new method was devised, which is henceforth referred to as the “bucket” method. For the bucket method, a stainless steel or quartz tube was placed in the furnace without the sample (i.e., activated carbon precursor) inside of it, and the furnace was turned on. Once the furnace reached the desired temperature, the sample was placed in a small, stainless steel “bucket”, 8” in length and  $\frac{3}{4}$ ” in diameter, and lowered into the tube with nickel-chromium wire. Wire mesh was placed at both the top and bottom of the bucket, allowing it to be porous while still prohibiting most of the activated carbon from escaping. The sample was suspended in the furnace for the allotted time and then removed from the furnace. It was beneficial to suspend the bucket near the top of the furnace tube before completely removing it in order to allow it to partially cool before exposure to air. Therefore, the heating and cooling times for samples activated using the bucket method are considerably lower, probably occurring within a matter of a few minutes as opposed to over an hour for samples activated using the traditional method. Although it is still not fully known how heating and cooling the samples so rapidly may have affected the results, results from using the traditional and bucket method were comparable. Herein, it will be noted whether the traditional or bucket method was used for a particular experiment.



Figure 3-1. Furnace used for activated carbon production

For the charring process, the raw samples were placed in a vertical tube furnace at varying temperatures, ranging from 350° to 850° Celsius, for times ranging from 30 to 120 minutes, under nitrogen gas (either High Purity or Ultra High Purity Nitrogen gas was used) at a flow rate of approximately 2500 mL/min. It is not expected that high purity or ultra high purity nitrogen would impact the results, for the objective was to maintain an inert environment. For the charring process, the bucket method was used, with approximately five grams of raw sample being charred during a single experiment. The pre-char samples were excluded from this step, as they had already been charred, albeit at unknown conditions. After charring, the sample was cooled and weighed to determine the mass loss.

For these experiments, temperature readings were recorded by lowering a two-foot thermocouple into the tube furnace, with the temperature of the furnace adjusted manually. The thermocouple measured temperatures at its tip; however, for a tube furnace with an opening at the top, such as that used herein, temperature gradients on the inside of the furnace can be very high, ranging to as much as a 100° Celsius every few inches. When placing the sample inside the tube furnace, the tube was positioned such that the bottom of the sample coincided with the tip of

the thermocouple. Therefore, any temperature given in this paper should be considered as a *temperature range*, and not a precise temperature existing throughout the entire furnace.

### **Particle Processing**

After the charring process, samples were ground using a ceramic mortar and pestle and sieved through a 325-mesh sieve (45  $\mu\text{m}$ , U.S. STD/ASTM E11). They were then either subjected to dye testing or reserved for activation by being placed in glassware and kept in an oven at approximately 110° Celsius. For dye testing, 30 mg of sample was placed in a glass vial containing 100 mL of either Methylene Blue or Congo Red dye at a concentration of 10 mg/L. Samples were mixed using a rotating mixer for four hours and then filtered through a 0.45  $\mu\text{m}$  HAWP cellulose ester filter using a vacuum pump. Dye adsorption was assessed using a Hach 4000U Spectrophotometer at a wavelength of 650 nm and 487 nm for Methylene Blue and Congo Red, respectively. Results were calculated as a percentage removal of the dye, with nano-filtrated water used for calibration. The filtering process did not remove any appreciable concentration of either dye.

### **Activation**

After being charred, the samples not used for dye testing were activated using two distinct methods, one physical, using steam (and in very rare cases, carbon dioxide), and the other chemical, impregnating the char with an aqueous solution of potassium hydroxide (KOH) prior to heating. For physical activation, either the traditional or the bucket method was used, with the traditional method usually reserved for samples larger than five grams. The physical activation process was nearly identical to the charring process only that instead of using a nitrogen flow, steam was introduced through the furnace tube at a constant rate. Samples ranging from 1.0 to 5.0 grams were activated for varying furnace temperatures (typically greater than 750° C), varying times (30 minutes to 4 hours) in the furnace, and varying steam flows, with steam flows

(0.4 to 1.6 mL/min volumetric flow rate). Steam for the physical activation was created by using a 400 mL glass bottle, filled with distilled water, on top of a laboratory hot plate and connected to the lower end of the tube furnace. Laboratory heating tape was used at the top of the bottle to prevent steam from condensing before entering the furnace and returning to the bottle as liquid water. This system, although slightly unorthodox, created a consistent, measurable, flow of steam without the “flare-ups”, inconsistent flows, or unnecessary complexity observed with other methods. For physical activation using carbon dioxide, the bucket method was used, with carbon dioxide used in the tube furnace instead of steam. The flow rate for the carbon dioxide was approximately 200 mL/min. Once the samples were physically activated, they were removed from the oven and allowed to cool to room temperature under steam flow. After cooling, their mass was taken and they were placed in a glass vial and kept in a desiccator until being used for testing.

For chemical activation, samples were first mixed with an aqueous solution containing varying concentrations (15 to 50% by mass) of potassium hydroxide. Anhydrous potassium hydroxide (KOH) was mixed by hand with water in a glass beaker under a fume hood at a given ratio (0.25:1 to 6:1 KOH:C). Carbon that had been charred, ground, and sieved was then added to the solution; laboratory parafilm was used to cover the beakers to prevent loss and the beakers were then mixed from two to eight hours using a magnetic bar and mixing plate. After mixing for the allotted time, samples were dried in an oven at 110° Celsius until visibly dry. It is extremely important that the sample be completely dry before being placed in the furnace, for potassium can be combustible when allowed to react with water at high temperatures. After drying, the mass of the samples was taken and they were then lowered into the tube furnace under nitrogen gas flow using the bucket method in the same manner as the charring process, with a nitrogen

gas flow of approximately 2500 mL/min. After being chemically activated and allowed to cool to room temperature, the samples were ground using a ceramic mortar and pestle and sieved through a 325-mesh sieve (45  $\mu\text{m}$ , U.S. STD/ASTM E11). The sample passing the sieve was then washed in a 2500 mL glass beaker with distilled water to remove residual potassium and hydroxide molecules, and then filtered through a 0.45  $\mu\text{m}$  laboratory filter paper (cellulose ester paper should not be used if the sample is to be retained because it has a tendency to decompose upon repeated use) using a vacuum pump. After washing, the samples were placed in an oven overnight at 110° Celsius to dry. After physical and chemical activations, the mass of the sample was weighed to calculate the mass loss from activation.

Once samples were activated and washed (only for the chemical activations), they were subjected to Methylene Blue and Congo Red synthetic dye testing in the manner described above. Congo Red dye testing is typically a better indicator of apple juice testing success than Methylene Blue, as the Congo Red molecules are larger. Samples that performed exceptionally well in the synthetic dye testing (> 50% Congo Red removal) were then subjected to apple juice testing. For apple juice testing, 100 mg of sample was mixed with 20 mL of refrigerated Hannaford © Apple Juice, 100% juice, using a rotating mixer for four hours and then filtered through a 0.45  $\mu\text{m}$  HAWP cellulose ester filter using a vacuum pump. Apple juice color adsorption was assessed using a Hach 4000U Spectrophotometer at a wavelength of 330  $\mu\text{m}$ . As apple juice is not a simple solution containing only one solute, such as the Congo Red dye, it does not have a single spectrophotometer absorption peak that can be assessed for removal; as such, the 330 nm value used is somewhat arbitrary. Values as low as 270 nm could still be used for the spectrophotometer, with comparable results. Results were calculated as a percentage removal of the apple juice at 330 nm, with nano-filtrated water used for calibration.

## Carbon Characterization

Samples that performed particularly well in the apple juice color removal tests were analyzed using a NOVA 2200e, manufactured by Quantachrome Instruments, to determine the specific surface area ( $\text{m}^2/\text{g}$ ) and the pore size distribution of the PAC. Approximately 200 mg of activated carbon was outgassed overnight under vacuum at  $110^\circ$  Celsius, and then dosed with liquid nitrogen to determine the isotherm. The BJH method was used by the provided software to calculate pore size distribution.

For surface charge adjustment, selected samples were placed in a 250 mL glass beaker filled with 200 mL of a 5 M solution of nitric acid and mixed by hand. Samples were refluxed (boiled with no steam loss) for four hours, and then washed with distilled water until the wash water had a negligible pH change (for distilled water,  $\text{pH} = 5$ ). The samples were filtered through a  $0.45 \mu\text{m}$  laboratory filter paper using a vacuum pump, and then dried overnight in an oven at  $110^\circ$  Celsius. The samples were then tested for apple juice color removal, using the method described earlier.

## CHAPTER 4 RESULTS

### **Charring**

For the production of activated carbon, the first step was to create a charred material from the raw precursor by using heat in an inert environment. Some researchers skip this step and simultaneously char and activate the carbon in a single one-step process (Warhurst et al., 1996). However, this was avoided in order to gather information about the activation process and also to create as much charred carbon as possible for both the physical and chemical activations. As the raw carbon source was heated, volatile organic matter is gasified and removed, leaving behind a mostly carbon material that resembles what could be considered flaky charcoal. Any ash in the sample (i.e. charred carbon) is a sign that the carbon had exposure to oxygen at some point while the temperature was greater than about 400 °C and samples containing ash should be discarded.

Figure 4-1 shows mass loss for sawdust as it undergoes the charring process. Samples of raw sawdust were lowered into the furnace using the bucket method under nitrogen flow. The legend on the right of the graph shows the temperature of the furnace while charring was taking place; the x-axis shows what amount of time the sample was exposed to heat. Because the raw sawdust is dried in an oven overnight at 110 °C, the mass loss presented on this slide should not include mass loss due to moisture loss. Because samples charred at 550, 650, and 750 °C have approximately the same mass losses, the mass loss for the sawdust seems to occur in three distinct phases: one group of organic matter seems to volatilize at a temperature lower than 450 °C, another group at some temperature between 450 and 550 °C, and a third group at some temperature between 750 and 850 °C. Also, the graph shows that mass loss increases marginally with an increase in charring time.

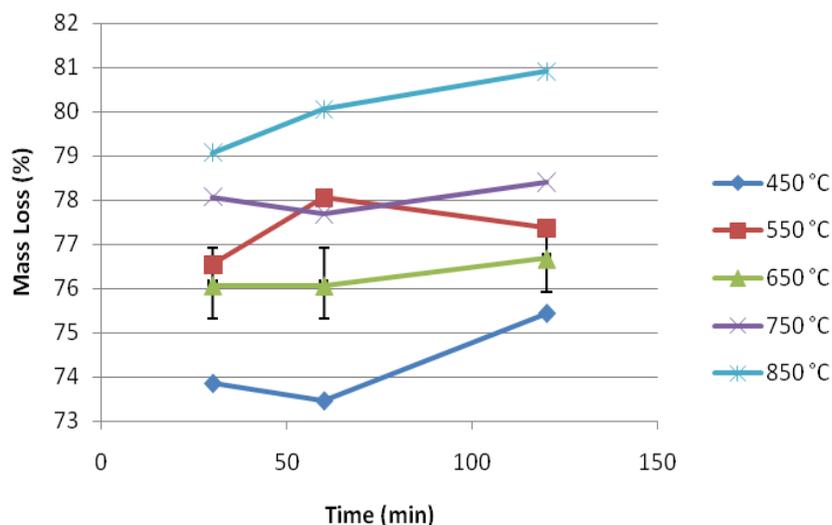


Figure 4-1. Sawdust mass loss during the charring process

After charring, dye adsorption tests were carried out (Figure 4-2). At this point, the carbon had a capacity to adsorb dye molecules from solution because of pores created in the carbon structure as volatile organic matter gasified; however, it has not yet been technically activated, as an activation step has not yet been completed. Figure 4-2 demonstrates a general relationship between charring temperature (and hence mass loss) and adsorptive capacity, with seemingly minor differences in mass loss resulting in very different dye removals: raw sawdust exposed to nitrogen at 850 °C for two hours loses only seven percent more mass than the same sawdust exposed to nitrogen at 450 °C for 30 minutes, and yet removes nearly 4.5 times the amount of methylene blue dye from solution. Also, as noted earlier, removal performances for the carbons are lower for the Congo Red dye as opposed to the Methylene Blue, as the Congo Red molecules are larger and require larger pores that would not be created during charring, but rather during activation. Because of the relatively low dye adsorption, it can be assumed that these charred sawdust samples would not remove much apple juice color, as the molecules that give apple juice its color tend to be larger and thus harder to remove.

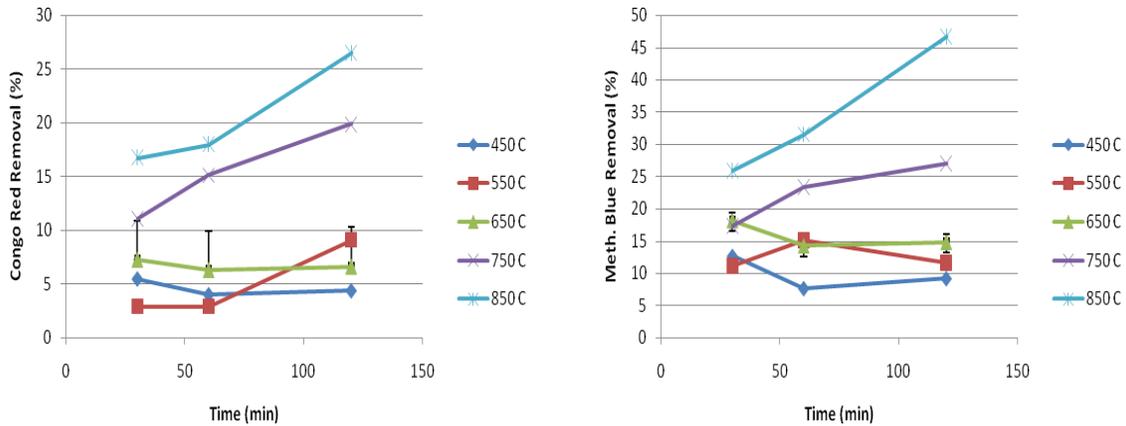


Figure 4-2. Congo red and methylene blue adsorption for sawdust chars

(Figure 4-3) is a similar graph for the mass loss of raw rice husks during the charring process, which were performed in the same manner as the sawdust samples. The primary difference between the rice husks and the sawdust during the charring process is that mass loss for the rice husks is far less dependent on time; as opposed to the sawdust, mass loss for the rice husks occurs within the first thirty minutes of charring. It seems that the rice husks, being less dense, lose their volatile organic matter much faster than the sawdust. As another consequence of their lower density, the rice husks lose less mass overall, losing roughly 62% of their mass after 30 minutes at 450 °C, as opposed to 74% for the sawdust under the same conditions.

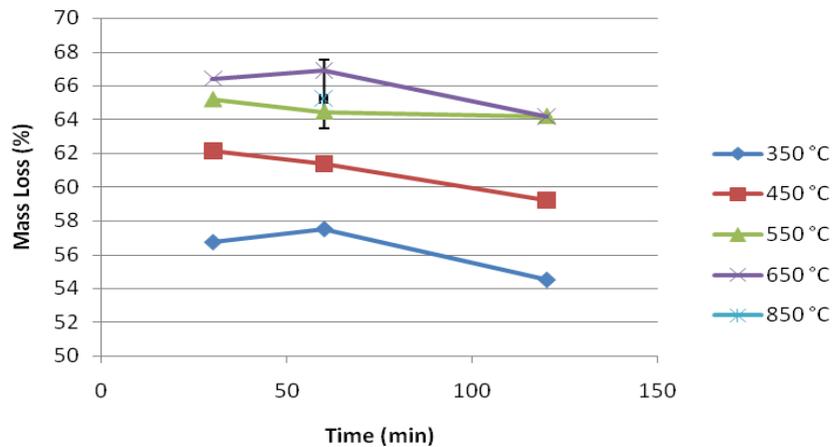


Figure 4-3. Mass loss of rice husks during the charring process

## Steam Activation

Once the raw sawdust and rice husks have been charred, activation is necessary to widen pores in the carbon structure to increase the adsorptive capacity of the carbon; it is during this step that the raw material becomes “activated”. Concerning physical activation, nearly all of the research concentrated on physical activation using steam as opposed to carbon dioxide (which is covered later). For steam activation, the sample was exposed to a steam flow (0.4 to 1.6 mL/min) while at temperatures greater than 750 °C.

The graph below (Figure 4-4) provides data for charred sawdust samples that were activated using steam. For this group of data, the bucket method was used, with a relatively high flow rate of approximately 1.6 mL/min (steam) to ensure that steam would have the velocity to enter the bucket, as opposed to circumventing it. All of these activations occur at a furnace temperature of 850 °C. It should be noted that apple color removal performance must be used as an indicator of success for these tests; all of the samples below had a Congo Red and Methylene Blue synthetic dye adsorption of over 99%. The graph below demonstrates two important points regarding steam activation of charred sawdust: one, that all the samples subjected to steam for two hours performed worse than the samples subjected to steam for only one hour, and two, that the char times of the samples before being activated is largely irrelevant. For example, the sample that had been charred for two hours and then subjected to steam for one hour performed roughly as well as the sample that had been charred for only 30 minutes before being subjected to steam for one hour.

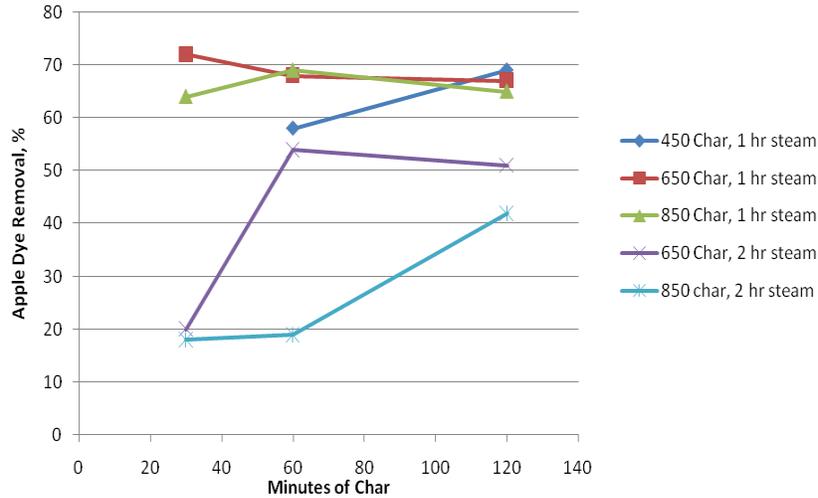


Figure 4-4. Steam activation of sawdust at 1.6 mL/min

The fact that all of the samples subjected to steam for two hours performed worse than their counterparts subjected to steam for only one hour proves that, for activation using steam, there is an optimum activation time for specific steam flows at specific temperatures (and for specific materials). As the charred sample is heated under steam, pores within the carbon structure widen as select carbon molecules oxidize; however, the pores can only widen so much before the pore walls break down and the pores collapse, lowering adsorption potential.

Figure 4-5 is comprised of two images taken of an activated carbon created during this project using steam activation of sawdust. The images, which were taken using a Field Emission Scanning Electron Microscope (SEM) at magnifications of 43,000X (left) and 80,000X (right), show the cavernous pore structure that develops on the surface and within the activated carbon, giving it its large surface area and adsorptive capacity.

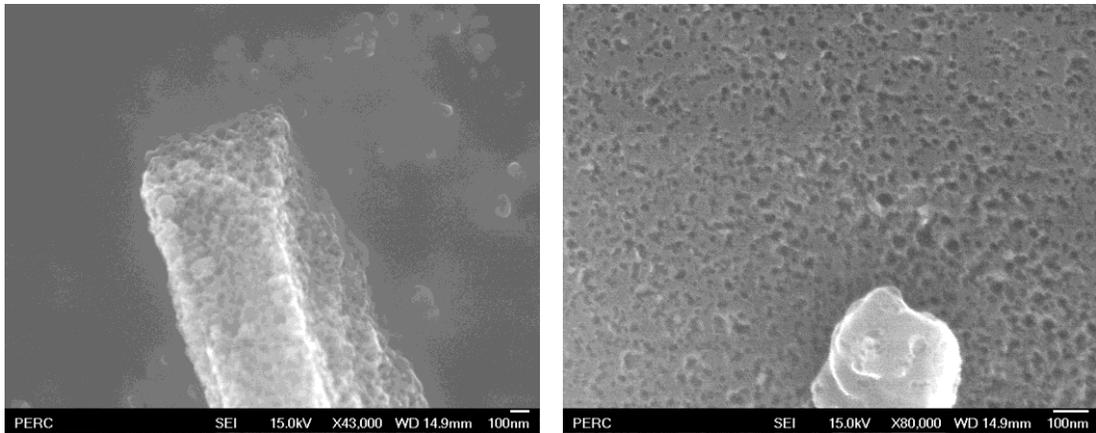


Figure 4-5. Images of activated carbon at high magnifications

To activate larger samples of sawdust char, the bucket method was abandoned in favor of the traditional method, as it was feared using large samples in the bucket would encourage flow to circumvent the bucket altogether. To keep sawdust char from exiting the vertical tube furnace, a lower steam flow rate was adopted, that of approximately 0.4 mL/min. Lower steam rates will change the steam to carbon ratio during activation and have an impact on the results. Samples sizes for this set of experiments were approximately 10 grams, as opposed to approximately one gram for the bucket method. Three of the samples were mixed approximately every 15 minutes by lowering a twisted nickel-chromium wire into the tube furnace; as shown, mixing has no noticeable effect on the performance of the activated carbon created. The graph (Figure 4-6) shows that, as opposed to having an optimum activation time of roughly one hour for higher steam flows, a lower steam flow shifts the optimum steam time to approximately two to three hours and allows for slightly greater adsorptive performance. The fact that the adsorptive capacity of the carbons did not increase dramatically when the activation time was increased from 2 to 3.5 hours tends to favor the hypothesis that sawdust may have an adsorptive limit of approximately 90% or less. Also, there seems to be no observable peak followed by a decrease in

adsorptive capacity for this lower flow rate; it would be interesting to see if pore breakdown occurred with activation times of four hours or more.

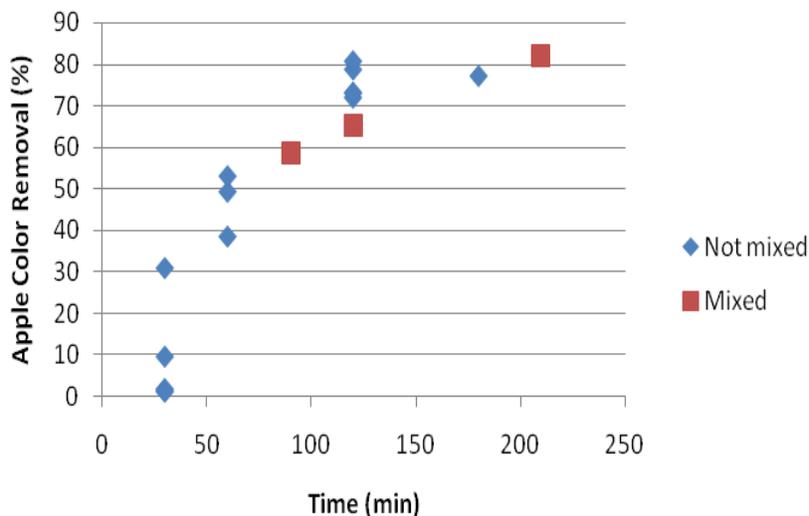


Figure 4-6. Steam activation of sawdust at 0.4 mL/min

Steam activation of charred rice husks is very similar to that of charred sawdust. The key difference between the two is that, while the optimum amount of steaming time for charred sawdust at a flow of 1.6 mL/min is approximately one hour, charred rice husks activated with steam at the same flow rate seemed to perform best when exposed to steam for less than 30 minutes. Figure 4-7 shows Congo Red and Methylene Blue dye adsorptions for the rice husks activated with steam; as expected, adsorption removal percentages for Congo Red are lower compared to that of Methylene Blue.

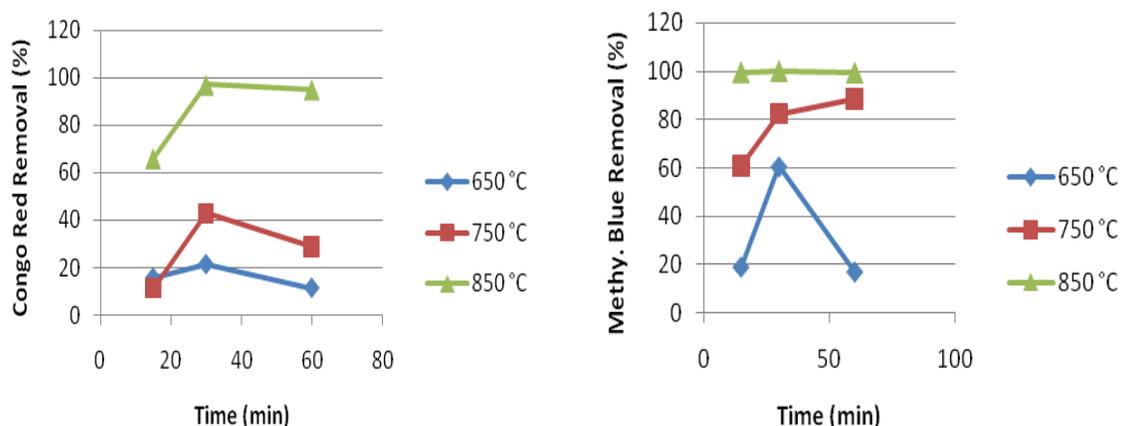


Figure 4-7. Congo red and methylene blue adsorption for rice husks char

Further experiments showed that the optimum way to create activated carbon from rice husks using steam at a flow rate of 1.6 mL/min was to char the sample for 20 minutes and then expose the sample to steam for 20 minutes. It seems that longer exposure to steam lowers the adsorptive capacity of the carbon, probably due to pore breakdown as a result of excessive widening. The sample below (Table 4-1) that achieved a 91.2% removal of Congo Red dye also achieved an apple juice color removal of nearly 82%.

Table 4-1. Rice husks activated with steam

Charring Time (min)	Activation Time (min)	Meth. Blue % Rem.	Congo Red % Rem.
	20	20	91.2
	30	30	30.9
	30	30	25.3

### Chemical Activation

From very early on in the research, it was decided that chemical activation would be achieved using potassium hydroxide (KOH), as potassium hydroxide is a relatively inexpensive strong base, and because there is a strong record in the literature of researchers achieving promising results with its usage (Azargohar, Malik). It was also decided very early that the majority of the chemical activation research would concentrate on using rice husks as a

precursor, both because this was the expressed intent of the supplier and because early studies using sawdust as a precursor for chemical activation were not very promising.

The primary problem associated with chemical activation is the large number of variables that play a role in the activated carbon's eventual performance as an adsorbent. Not only must the characteristics of the char material be considered, but also the concentration of the potassium hydroxide solution used, the ratio of KOH to carbon once the charred material is mixed with the solution, the temperature of the furnace used for activation, and the time allotted for activation. As such, it was decided early in the research to isolate certain variables to assess their impact. Once an optimum value for a variable was chosen, this value was used for all future experiments.

Figure 4-8 was used to determine the optimum solution concentration for activating rice husk char. Rice husks were charred for 30 minutes at a temperature of either 450 °C or 650 °C and then mixed with various solutions of aqueous potassium hydroxide. All of the samples have a ratio of anhydrous KOH to carbon of 3:1 by mass. For example, a 15% solution with a 3:1 KOH to carbon ratio would contain 1 gram of charred carbon, 3 grams of potassium hydroxide, (measured by mass in the solid state), and 17 mL of distilled water. The samples were mixed, allowed to dry overnight in an oven, and then activated in a furnace at 800 °C for three hours. Higher temperatures were chosen for the chemical activation studies because important reactions occur between the potassium and carbon atoms at temperatures above 700 °C, namely the conversion of potassium carbonate to potassium oxide and carbon dioxide.

As Figure 4-8 shows, a 15% solution concentration is optimum. It is assumed that, with more water available, a greater degree of mixing occurs once the carbon comes in contact with the potassium hydroxide solution.

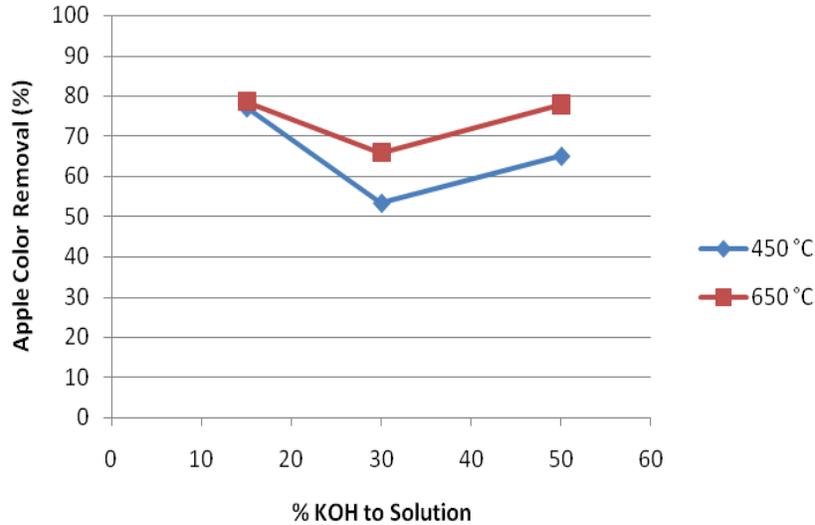


Figure 4-8. Solution concentrations used for activation

A 3:1 ratio of KOH to carbon by mass was initially chosen due to the supporting literature (Gou). Figure 4-9 below supports the decision. For the set of data below, pre-charred rice husks were mixed with two potassium hydroxide solutions, one at 15% and the other at 50%, at KOH to carbon ratios of 2:1, 3:1, and 4:1. The samples were allowed to dry overnight in an oven and then activated in a furnace at 800 °C for three hours. It seems that, at a 3:1 ratio of KOH to carbon, there is enough potassium available to create a porosity in the carbon without overactivation occurring.

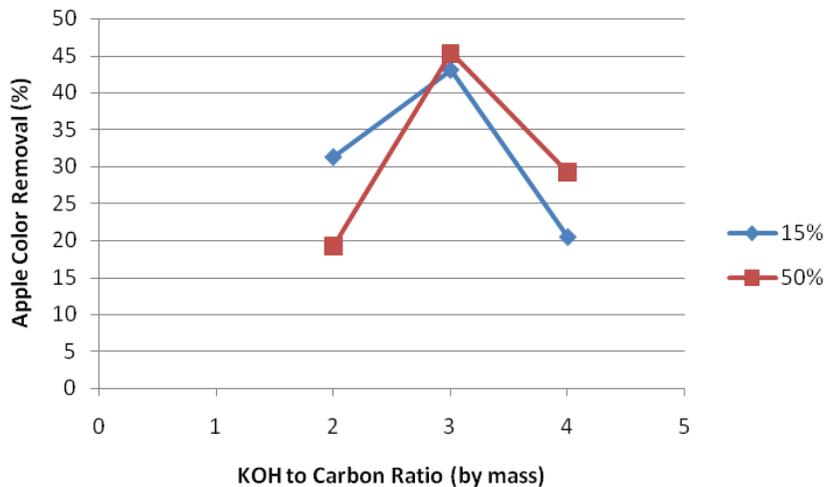


Figure 4-9. Potassium hydroxide to carbon ratios

Once it was decided that a 15% solution strength would be used in conjunction with a 3:1 KOH to carbon ratio, the optimum charring temperature and time, as well as the optimum activation temperature and time, had to be determined. In contrast to solution strength and the carbon to KOH ratio, the impact of changes in furnace temperatures and the time spent in the furnace are less definitive.

For Figure 4-10, rice husks charred at various temperatures and for various times were mixed with a 15% KOH solution at a carbon to KOH ratio of 1:3, allowed to dry overnight in an oven, and activated in a furnace at various temperatures and for various times. When reading the legend, “30, 800 °C, 100” with a x-axis value of 450 should be interpreted as a rice husk sample charred for 30 minutes at a temperature of 450 °C, mixed with a potassium hydroxide solution, dried, and activated at 800 °C for 100 minutes.

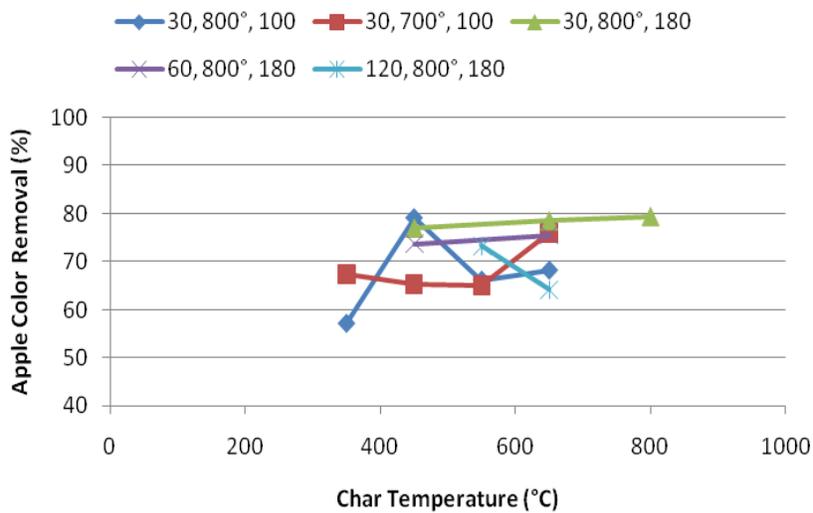


Figure 4-10. The impact of char and activation characteristics on apple color removal

As the Figure 4-10 shows, there is very little statistical difference in apple juice color removal performance between samples charred for 30 minutes as opposed to 60 minutes, with samples charred for 120 minutes actually performing marginally worse. This coincides with data presented earlier in this paper showing that rice husks lose the vast majority of their volatile mass

within the first 30 minutes of charring. As for charring temperature, the data shows a very slight increase in performance with an increase in charring temperature after 450 °C. It was decided that a charring temperature of 450 °C would be used in the interest of energy consumption, with future research divided between samples charred at 450 °C and those charred at 650 °C. Concerning activation, a minimum activation temperature of 800 °C was selected, as well as an activation time of three hours.

Once optimum variable values were selected, several exceptional samples were created using chemical activation of rice husks, with apple juice color removal percentages approaching 90%. For Figure 4-11, (450 °C, 30, 800 °C, 180) should be interpreted as rice husk charred at 450 °C for 30 minutes, mixed with a 15% potassium hydroxide solution at a 1:3 carbon to KOH ratio, and activated at 800 °C for 180 minutes.

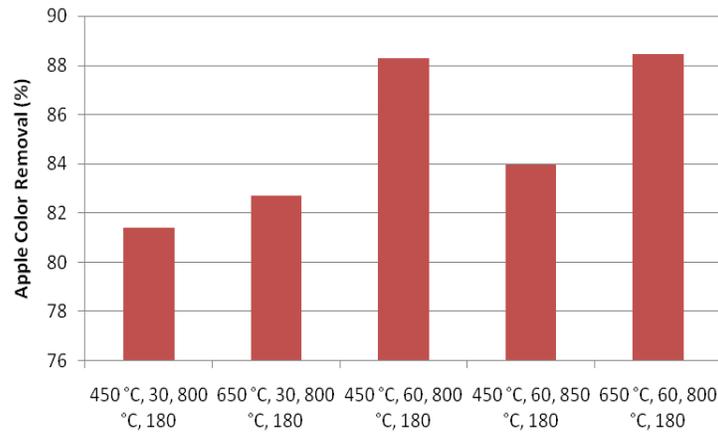


Figure 4-11. Selected chemical activations

Production of activated carbon using potassium hydroxide and sawdust was done in the same fashion as the chemical activation of rice husks. As stated earlier, only a small portion of this project was devoted to the chemical activation of sawdust due to a pre-determined emphasis on rice husks. Unfortunately, our laboratory has had little success achieving significant results using the chemical activation of sawdust. Figure 4-12 shows the Congo Red and Methylene Blue

dye adsorption values for a few of the samples created using chemical activation of sawdust. As expected, Congo Red dye removal is lower than the corresponding Methylene Blue removal, suggesting the activated carbons created are microporous. For these experiments, an emphasis was put on activating the sawdust and KOH mixtures at relatively low temperatures (< 800 °C) in an effort to develop a procedure that would minimize energy costs.

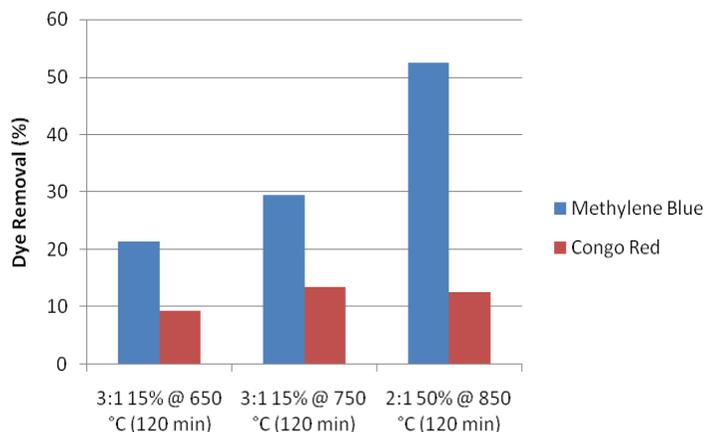


Figure 4-12. Chemical activations using sawdust

Later, towards the end of the project, chemical activation of sawdust was briefly revisited, this time using much higher carbon to KOH ratios as well as higher activation temperatures, both of which are suggested by the literature. For the samples below, sawdust char was created at a temperature of 450 °C for one hour and mixed at three distinct carbon to KOH ratios: 1:0.25, 1:0.5, and 1:1. For these particular experiments, the amount of water calculated for the 1:1 ratio sample was used for all three samples in an effort to maintain similar mixing and drying. As shown in Table 4-2, these samples also performed unfavorably.

Table 4-2. Chemical activations of sawdust

Carbon to KOH Ratio	Solution Strength	Apple Color Removal
1:0.25	3.7%	32.1%
1:0.5	7.5%	36.2%
1:1	15%	24.5%

## Carbon Dioxide Activation

Carbon dioxide was used as a replacement for steam in an effort to learn more about the process for future research. For these activations, pre-charred sawdust from our supplier was sieved through a 325-mesh sieve and activated under carbon dioxide flow at approximately 200 mL/min using the bucket method. Unlike steam activation, in which it can be assumed that a significant portion of the sample is being lost during the process, the carbon dioxide flow is not great enough to physically “blow” the sample out of the furnace; therefore, a correlation between mass loss during activation and adsorptive capacity can be created. All of the samples were activated at a temperature of 850 °C; Rodríguez-Reinoso (1995) have shown a minimum temperature of 800 °C to be necessary.

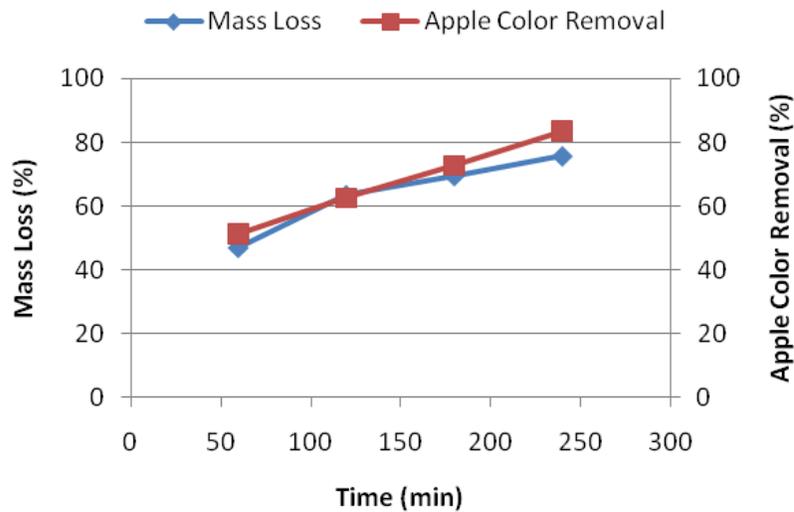


Figure 4-13. Carbon dioxide activation of sawdust

Figure 4-13 demonstrates a direct relationship between mass loss during carbon dioxide activation and resulting adsorptive capacity. It also shows that carbon dioxide activation is promising for mesoporic pore creation, at least for sawdust. Concerning rice husks, Figure 4-14 demonstrates a peak color removal of 70% after an activation period of roughly two hours, with pore breakdown occurring afterward.

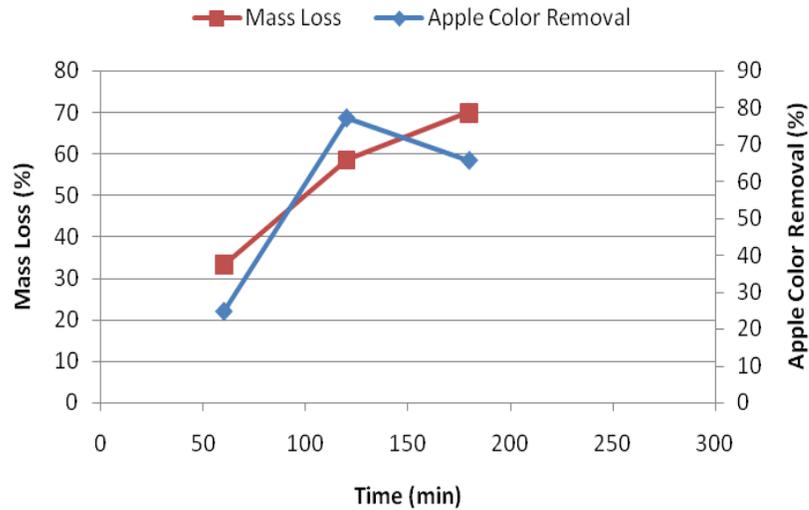


Figure 4-14. Carbon dioxide activation of rice husk

A key issue needs to be addressed before carbon dioxide is used as a replacement for steam for physical activations. First and foremost, carbon dioxide activation seems, at least in the context of this research, extremely volatile; not shown in Figure 4-14 is that several samples were completely gasified entirely and without explanation during the process, including numerous samples activated for over 4 hours that would have expanded the graphs. Secondly, when activating rice husks with carbon dioxide, there were several instances where the apple juice samples were visibly clear, yet performed poorly when analyzed with the photospectrometer. This underperformance did not occur with rice husks activated with steam or sawdust in general, and is presently unexplained. For these reasons, further research was not conducted.

### Surface Charge Modification

Lastly, an effort was made to modify the surface charge of an activated carbon sample in an attempt to further improve adsorption. As stated earlier, the surface of the PAC created using the standard two-step steam method is basic in nature and has relatively little surface functionalization. It was hoped that by creating acidic functional groups on the surface of the

PAC, a net positive charge could be produced, thereby attracting the negatively-charged color molecules in the apple juice and increasing adsorption. For this experiment, a sample of PAC that had been produced using steam was allowed to boil in a nitric acid solution for four hours. After washing and drying to remove the nitric acid, the apple juice color removal test was repeated. The results shown in Table 4-3 indicate that surface modification with nitric acid can improve the adsorptive capacity of the activated carbon to some degree.

Table 4-3. Surface modification

Removal before acid treatment	71%
Removal after acid treatment	84%

Although further research obviously needs to be done, especially on higher-performing samples and on samples created using chemical activation, it seems that treatment with nitric acid may give the carbon surface a positive net surface charge, which could contribute to the adsorption of the negatively-charged polyphenol molecules.

### **Surface Area Assessment**

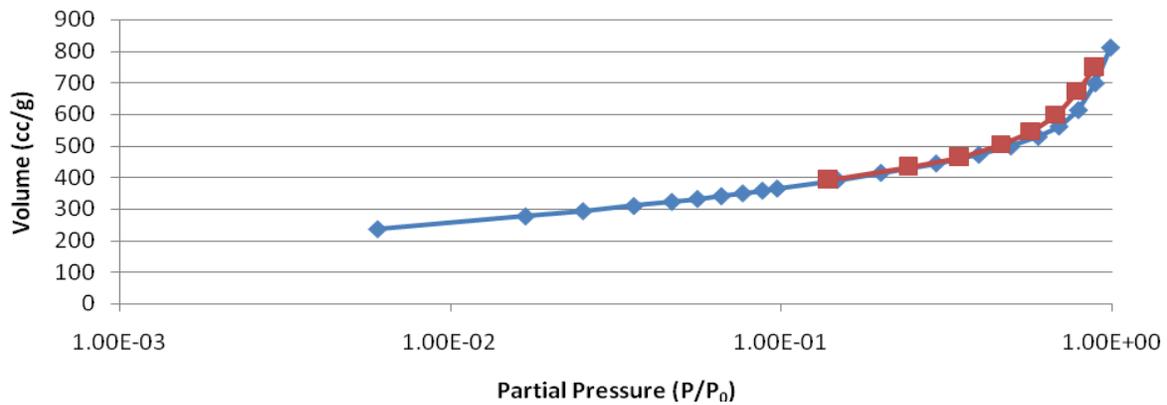
Selected samples were chosen to be analyzed by the NOVA Surface Analyzer in order to determine their specific surface areas and pore size distributions. The NOVA uses nitrogen gas at a temperature of 77 K as an adsorbate, and uses the amount of nitrogen gas adsorbed onto the carbon at various pressures to calculate the specific surface area, total pore volume, and average pore volume of the activated carbon sample.

For surface area assessment, two samples were chosen: CA-50, a commercially-available carbon created using chemical activation of sawdust with phosphoric acid, and a physically activated carbon derived from sawdust that performed very well. Dye and apple color removal performance for CA-50 is provided in Table 4-4; its exceptional performance was the basis for it being chosen as a test control for this research

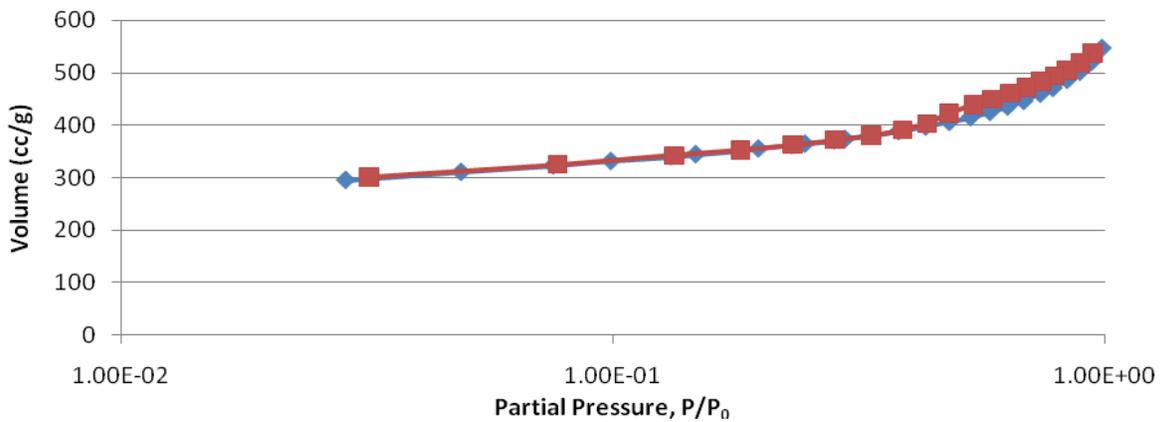
Table 4-4. CA-50 performance

Congo Red Removal (%)	98
Methylene Blue Removal (%)	100
Apple Color Removal (%)	92

Figure 4-15 shows the actual data points that the NOVA machine uses to calculate the values in the tables above. Adsorption points, which are taken as nitrogen gas molecules, attach themselves to the carbon surface, are colored blue, with desorption points, taken as the nitrogen is detaching, are colored red. While the two curves have roughly the same shape, CA-50 has a sharper curve in the high pressure range, which can be attributed to its larger average pore diameter, as well as a greater pore volume overall.



A



B

Figure 4-15. BET adsorption/desorption plots (a) CA-50 (B) Sawdust activated with steam for 2 hours at 850 °C

Data for five samples is shown below in Table 4-5. The five samples include: two samples created using steam activation of sawdust, one sample created using chemical activation of rice husks, one sample created using carbon dioxide activation of sawdust, and CA-50, a commercially-available powdered activated carbon. The key point to be gained from the BET data is that there is a direct correlation between the average pore size of the PAC and its adsorptive capacity; this conclusion has been previously expressed (Tennant, 2003). It could be said that the pore size of the PAC is the defining factor when relating its molecular structure to adsorption. This statement holds especially true for larger adsorbate molecules, as is the case with this research. Samples 1 and 2 were both created using identical procedures; the only difference between the two is the amount of time that the samples were exposed to steam flow. As Sample 1 had a longer exposure to steam, it had more time for its pore structures to widen, creating larger pores and thus a higher capacity for adsorption. Also, Sample 3, which was created using chemical activation, is similar to Sample 1 in every parameter, showing that physical activation and chemical activation of two different organic precursors can achieve similar results..

Table 4-5. BET characteristics of selected samples

Sample 1: Charred Sawdust with Steam, 2 hr		
Apple Color Removal	79	%
Specific Surface Area	1331	m <sup>2</sup> /g
Total Pore Volume	0.848	cc/g
Average Pore Volume	25.5	Å

Table 4-5. Continued

Sample 2: Charred Sawdust with Steam, 1 hr		
Apple Color Removal	31	%
Specific Surface Area	520.2	m <sup>2</sup> /g
Total Pore Volume	0.519	cc/g
Average Pore Volume	20.6	Å

Sample 3: Rice at 450 °C, 60 min, 15%, 850 °C, 180 min		
Apple Color Removal	84	%
Specific Surface Area	1487	m <sup>2</sup> /g
Total Pore Volume	0.946	cc/g
Average Pore Volume	25.5	Å

Sample 4: Sawdust with Carbon Dioxide, 4 hr		
Apple Color Removal	84	%
Specific Surface Area	1096	m <sup>2</sup> /g
Total Pore Volume	0.621	cc/g
Average Pore Volume	22.7	Å

Table 4-5. Continued

Sample 5: CA-50		
Apple Color Removal	92	%
Specific Surface Area	1489	m <sup>2</sup> /g
Total Pore Volume	1.255	cc/g
Average Pore Volume	33.7	Å

## CHAPTER 5 CONCLUSIONS

The goal of this research was to create a method by which sawdust or rice husks, two agricultural waste products, could be used to create a powdered activated carbon by either physical or chemical means, with the latter concentrating on the use of potassium hydroxide in solution. The litmus test for this research would be the optimization of the activated carbon created for the removal of natural color from commercially-available apple juice, a task that would provide a unique set of challenges.

Physical activation of charred sawdust, either by using steam or carbon dioxide, can consistently create a PAC that will remove 80 to 85% of the natural color from the particular brand of apple juice used (using 330 nm wavelength absorbance as a measurement). However, chemical activation has yet to prove its worth concerning sawdust.

As for rice husks, steam activation can perform just as well as with the sawdust, with results thus far reaching a maximum removal of 82%. For rice husks, however, the emphasis was on chemical activation with potassium hydroxide, and rice husks truly outshined its sawdust counterpart in this regard. By the end of the experiment, powdered activated carbon samples created using KOH and rice husks were consistently removing 85 to 90% of the natural apple juice color, nearly outperforming the commercially-available powdered activated carbon, CA-50.

The failure of the activated carbon created in our laboratory to outperform the commercially-available carbon, CA-50, casts somewhat of a shadow on this research. It would be convenient to assume that surface chemistry or some other unaccounted for property of the CA-50 gave it an advantage. However, the fundamental reason why CA-50 outperforms the activated carbon created by our laboratory is that the carbon possesses a particularly large average pore size, and our methods were unable to recreate these mesoporous pore structures in

either the sawdust or rice husk char. Had our laboratory been able to create an activated carbon sample with an average pore size of at least 30 Å, I have no doubt that our samples would have outperformed the competition.

It is unknown at this time if the failure lies with the research or the original source materials; it could be that it is simply too difficult to create a highly mesoporous activated carbon from either sawdust or rice husks. However, with so many samples performing so well, it is hoped that eventually the threshold for these materials could be broken, and the activated carbon created could be truly optimized for natural color removal.

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