ONE-STEP STEAM AND CALCIUM ACTIVATION OF SAWDUST FOR APPLE JUICE PURIFICATION

By

TIMOTHY S. ENGLISH II

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To those who gave me a second chance

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LIST OF ABBREVIATIONS

BET	Brunauer, Emmett, and Teller method for estimating the surface area of porous materials
BJH	Barrett, Joyner, and Halenda method for calculating pore volume for pores with diameters greater than 20 Å
DFT	Density functional theory (non-local) method for determining the micropore and mesopore size distribution of porous materials
GAC	Granular activated carbon. Activated carbon found in a solid, granular form.
HK	Horvath and Kawazoe method for determining the micropore size distribution of porous materials
PAC	Powdered activated carbon. Activated carbon that has been milled and passes a standard 325-mesh screen
ws	With steam. Used for labeling one-step steam activated samples

Abstract of Thesis Presented to the Graduate School
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Timothy S. English II

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Activated carbon was synthesized from a readily available agricultural byproduct, sawdust, using one-step steam activation and calcium impregnation with subsequent one-step steam activation. A carbon dose of 5,000 mg/L was necessary to reach the color removal capacity of 90% for a commercially available activated carbon, CA-50. Carbonized samples of sawdust exhibited minimal pore development, with methylene blue and congo red removals around 16% and 4% respectively. One-step steam samples had apple juice color removals as high as 79% and total pore volumes of up to 0.50 cc/g, as determined by nitrogen gas isotherm analysis. Calcium samples had similar apple juice color removal values (70-87% color removal), but significantly more mesopore volume (80-150% increase) and total pore volume (50% increase) over one-step steam samples. Further analysis of the Horvath-Kawazoe and density functional theory pore size distribution models found that the increase in the calcium samples' mesoporosity occurred due to increased general pore development and not at the expense of micropores. Linear correlations determined that increasing the pore volume of diameters greater than 40 Å led to increased apple juice color removal percentages.

CHAPTER 1
INTRODUCTION

Activated carbon is a highly porous material often employed as an adsorbent for the removal of trace contaminants from aqueous and gaseous systems. The high micro- and mesoporosity of activated carbon allow it to remove contaminants at the molecular level, making it ideal for the “polishing” of solutions in a treatment train design. Activated carbon is typically produced through the gasification or chemical impregnation with subsequent heating of coal and lignin, and is often processed into granular or powdered media.

The goal of this research is to produce a mesoporous and high volume (> 0.75 cc/g) powdered activated carbon (PAC) from sawdust, a readily available agricultural byproduct, for the removal of the natural colors found in apple juice. If a PAC can be produced to effectively remove the color in apple juice, it could then be applied to other industrial and environmental concerns, such as sugar decolorization and natural organic matter removal.

A variety of activation methods were employed during this research, including steam activation and chemical activation with calcium salts. The products of these methods were compared to a high quality commercial PAC using a consistent decolorization protocol and nitrogen gas adsorption analysis. Sawdust was chosen as a precursor because of its low cost and availability.

The proceeding chapters will review the characteristics and production of activated carbon, the experimental procedure and results of this research, and finally a conclusion based on the results and previous research.

CHAPTER 2
LITERARY REVIEW

Introduction to Activated Carbon

Activated carbon has been used as an adsorbent for many centuries, but large scale industrial production of the material did not begin until World War I, when effective adsorbents were needed for protection against chlorine gas attacks (Yehaskel, 1978; Marsh, 2006). Early carbons were primarily created through pyrolysis, where wood or bones were treated under low oxygen conditions and high heat to create charcoals (Bansal, 1988; Bansal, 2005). After the war, manufacturing processes, carbon sources, and expanded uses were significantly researched and developed (Yehaskel, 1978).

Activated carbon is commonly used when chemical constituents need to be removed from gaseous or liquid phases; this includes the treatment of potable water, municipal and industrial wastewater, chemical purification, and solution decolorization (Bansal, 1988; Marsh, 2006; Hameed, 2007). Activated carbon is able to achieve effective constituent removal rates and treatment efficiencies because it has a high adsorptive capacity, caused by its large specific surface area (generally between 400-1,500 m^2/g), high surface reactivity, and extensive pore structures (Hassler, 1974; Bansal, 1988).

Introduction to Apple Juice Decolorization

Decolorizing apple juice for its sugar has been an important goal for the food and juice manufacturing industries for many years. Manufacturers currently use powdered activated carbon, gelatins, ion-exchange media, chemical treatment, and membrane filtration to remove the color. These processes can be expensive and manufacturers are searching for more economical solutions. (Borneman, 1997)

The brown color of apple juice is caused by a combination of phenols, polyphenols, tannic acids, flavonoids, and other organic complexes (Borneman, 1997). Figure 2-1 shows a selection of organic complexes that cause apple juice color. While activated carbon is often used for solution and sugar decolorization, very little published research has specifically targeted activated carbon apple juice decolorization.

Sugar Decolorization

Activated carbon has been used for over a century to decolorize sugar and sugar solutions, such as apple juice (Yehaskel, 1978; Bansal, 1988; Bernardo, 1997; Borneman, 1997; Bansal, 2005; Marsh, 2006). In order to accomplish this, the colored solution must be in direct contact with the activated carbon for a prescribed length of time (dependent on the solution mixture, quantity of activated carbon, and temperature) which is determined using batch reactor or breakthrough analysis (Reynolds, 1982; Bansal, 1988). Past studies have employed fully agitated mixing basins for a given duration that is held constant for the experiment (Bernardo, 1997; Hameed, 2007; Rafatullah, 2010). Since naturally occurring molecules that cause color (e.g. tannic acids, flavonoids, etc.) tend to be relatively large (8,000-15,000 Da), an activated carbon's pore size distribution greatly affects its decolorization capacity (Bansal, 2005).

Color Test Methods (Spectrophotometry)

Since the presence of dyes in waste effluents is an environmental and health concern, studies have been conducted using activated carbon to remove color causing agents before discharge (Hameed, 2007; Rafatullah, 2010). Hameed et al. (2007) investigated using activated carbon to remove methylene blue dye from aqueous solution. This study found base readings from a spectrophotometer for a dyed solution calibrated with deionized water using absorbance values calculated with Beer's Law.

The solution was then put in contact with activated carbon, filtered, and measured with the spectrophotometer. The activated carbon's ability to remove dye from solution was found by comparing readings from a spectrophotometer before and after contact with the carbon. Spectrophotometry is often used for determining color removal because its calibration curves are generally consistent, simple, and reproducible.

Introduction to Activated Carbon Science

As mentioned previously, activated carbon has been well studied since the early twentieth century; this has led to many scientific practices for the measurement and characterization of porous adsorbent materials. Marsh et al. (2007) outlines over 27 different models to "describe the microporous nature of activated carbon". Extensive research has gone into adsorption concepts, surface chemistry interactions, and pore structure manipulation and measurement.

Adsorption

Activated carbon is an effective adsorbent because it has such an extensive pore structure and surface area. Activated carbon is composed of layers of aromatic rings. Pores form in regions between layers that are not directly aligned, and have areas of disorder. It is within these pores that activated carbon achieves its surface area and active adsorption sites (Marsh, 2006).

Adsorption onto an activated carbon's surface can be a physical or chemical process. Physical adsorption occurs when a molecule is attracted to the carbon's surface through hydrogen bonding, dipole-dipole moments, and van der Waals forces (Reynolds, 1982; Marsh, 2006). These physical attractions are much weaker than chemical adsorption, which occurs when molecules attach to the carbon's surface with covalent or aromatic bonds. Chemisorption is generally less frequent than physical

adsorption and is irreversible as the adsorbate becomes incorporated into the activated carbon's surface (Menendez, 1996).

Pore Structure and Adsorbate Diffusion

The pore structure of activated carbon is an important aspect to consider when evaluating its ability to adsorb chemicals. As mentioned previously, pores form when aromatic carbon ring stacks are misaligned (Marsh, 2006). Pores are classified by their diameter (d) as either micropores (d < 20 Å), mesopores (20 Å < d < 500 Å), or macropores (d > 500 Å) (Everett, 1972). Since the micropores contain the bulk of the surface area, most of the adsorption occurs within them (Reynolds, 1982; Faust, 1983; Marsh, 2006). For adsorbate molecules smaller than 20 Å, the mesopores and macropores tend to act as a conduit to the micropores. For molecules larger than the micropore diameter, the mesopore surface area may be the site of adsorption (Bansal, 1988; Yang, 2003).

After an adsorbate makes contact with the activated carbon, it moves to active adsorption sites by means of diffusion. This process is relatively slow compared to the adsorptive attachment stage (Snoeyink, 1980). The adsorbate's molecular size is an important factor in adsorption; if the molecule adsorbs to a site in a pore of comparable size, it is possible for the pore network past the adsorption site to be blocked for other molecules. If the molecule is larger than a given pore size, that pore will not aid in adsorption (Snoeyink, 1980; Yang, 2003).

Gas Adsorption Isotherm Models

The specific surface area (m^2/g) of activated carbon is often determined using the Brunauer, Emmett, and Teller (BET) method (Brunauer, 1938; Faust, 1983). This method uses gas adsorption over a range of relative pressures to determine the volume

of nitrogen gas (V_m) that would be required to cover the surface area of the material with a monolayer of the gas. This is found by plotting the adsorption isotherm of nitrogen gas and comparing it to the BET equation:

$$\frac{P}{V(P_o - P)} = \left(\frac{C-1}{V_m C}\frac{P}{P_o}\right) \quad (2\text{-}1)$$

where P is the equilibrium pressure, P_o is the saturation pressure of nitrogen, V is the volume of nitrogen absorbed, and C is a constant for the gas-solid pair. V_m is determined by calculating the slope of $(C-1)/V_mC$. With the volume of nitrogen gas known, the geometric dimensions of the molecule can be used to calculate the surface area (Brunauer, 1938; Faust, 1983).

The Barrett, Joyner, and Halenda (BJH) method is a classical model for calculating the mesopore size distribution of porous materials. The BJH method incorporates the relationship between a nitrogen gas isotherm desorption curve and the pore volume for a given pore diameter (Barrett, 1951; Yang, 2003). This method assumes that all pores are non-intersecting and cylindrical, there is complete wetting of the carbon's surface, and the Kelvin equation is applicable. The Kelvin equation is known to have problems with pore diameters that approach molecular sizes, as it does not account for the effects of fluid-wall interactions, and methods incorporating it, such as BJH, should not be used for micropore analysis (Yang, 2003).

The Kelvin equation (Equation 2-2) is used to determine the radius at which nitrogen condensation occurs for a given pore size at a particular relative pressure. The BJH equation (Equation 2-3) can then be used to calculate the cumulative pore volume for a range of actual and Kelvin pore sizes. The derivative of this plot can be used to approximate the mesopore size distribution.

$$r_k = \frac{4.15}{log\left(\frac{p_0}{p}\right)} \tag{2-2}$$

$$V_p = \left(\frac{\bar{r}_p}{\bar{r}_k}\right)^2 \left(\pi \bar{r}_k^2 l - \Delta t \Sigma S \times 10^{-4}\right) \tag{2-3}$$

where r_k is the Kelvin pore radius, V_p is the pore volume, r_p is the actual pore radius, l is the pore length, Δt is the nitrogen film thickness, and S is the pore area (Barrett, 1951; Lowell, 2004).

In order to measure micropore volumes and determine a micropore size distribution, the Horvath-Kawazoe (HK) method can be applied to a nitrogen gas isotherm at varying relative pressures. This method corrects problems found in the Young-Laplace and Kelvin equations when measuring micropores, and can measure pores smaller than 10 Å at relative pressures less than 2 x 10^{-5}. The basic form of the HK method relates the two equations below:

$$ln\left(\frac{p}{p_0}\right) = \frac{62.38}{l - 0.64} \times \left[\frac{1.895 \times 10^{-3}}{(l - 0.32)^3} - \frac{2.7087 \times 10^{-7}}{(l - 0.32)^9} - 0.05014\right] \tag{2-4}$$

$$\frac{w}{w_\infty} = f(l - d_a) \tag{2-5}$$

where l is the distance between the nuclei of two layers of carbon (pore), d_a is the diameter of the adsorbate molecule (N_2), w is the known amount of nitrogen adsorbed, w_∞ is the maximum amount of nitrogen adsorbed, and w/w_∞ is a function of the Frenkel-Halsey-Hill theory. Finding the w_∞ value and relative pressure isotherm allows one to compare the above equations to find the volume for varying values of l, resulting in a micropore size distribution (Horvath, 1983; Yang, 2003).

The non-local density functional theory (DFT) method is a computer model that measures the volume of micro- and mesopores using statistical mechanics. The DFT model assumes that the carbon has slit pore geometry, the length of the pore is far greater than the width, and that surface functional groups can be disregarded (Lastoskie, 1993). DFT uses complex mathematical iterative modeling to create density profiles. These profiles are then compared and calibrated against a database of real isotherm data from non-porous materials, as well as real physical data (Ustinov, 2006). Using these calibration curves, computer software determines the best fit, from which pore volumes can be calculated and a pore size distribution can be modeled (Lastoskie, 1993).

Activated Carbon Production Methods

This review will highlight three varieties of steam activation: one-step steam, two-step pyrolysis and steam, and chemical impregnation with one-step steam activation. The two-step process, which consists of carbonization and oxidation stages, has traditionally been used for physical activation, while chemical impregnation has been around since the early 1930s and is often used when a carbon with very high surface area (>1,000 m^2/g) is required (Yehaskel, 1978; Bansal, 1988). One-step activation skips the carbonization step, and activates the carbon directly with heat and steam (Laine, 1991; Warhurst, 1997; Alaya, 2000). The ultimate goal of these techniques is to remove disorganized carbon and develop pore networks within the carbon structure (Bansal, 1988).

Physical Activation

Physical activation is the process of exposing a carbonaceous material to high temperatures (ca. 400-1100°C) and an oxidant (H_2O, CO_2, etc.). The exposure has to

be timed and temperatures well controlled for successful, consistent results. Many activated carbons are made using physical activation techniques (Bansal, 1988; Wigmans, 1989; Marsh, 2006).

Two-Step

Step 1 - Pyrolysis. The first step of the two-step activation process is to expose a carbonaceous material (e.g. wood, coal, peat, etc.) to temperatures between ca. 400-850°C in an inert environment, such as nitrogen gas or more practically oxygen devoid; this process is known as carbonization or pyrolysis (Bansal, 1988; Rodriguez-Reinoso, 1995). The purpose of pyrolysis is to remove volatile organics, non-carbon chemical species, and reduce tar formation, resulting in a rudimentary pore structure, with very little surface area (5-20 m^2/g) and pore volume (Bansal, 1988; Wigmans, 1989). Parameters that affect pyrolysis and the resulting char include the final temperature, duration of final temperature, and properties of the material (Bansal, 1988). Experimentation and char analysis are necessary to find the proper pyrolysis methods for a given precursor material.

Step 2 - Steam. In the two-step process, the char is activated with gasification after pyrolysis. The purpose of activation is to increase the pore volume, pore size, and surface area established through pyrolysis (Bansal, 1988; Wigmans, 1989). When an oxidant, such as steam, is combined with temperatures between 600-1100°C the carbon atoms on the pore surfaces of the char can be gasified to carbon monoxide, as shown in Equation 2-6; the steam further interacts with gaseous carbon monoxide to produce carbon dioxide and hydrogen as shown in Equation 2-7 (Bansal, 1988; Marsh, 2006).

$$C + H_2O \rightarrow CO + H_2 - 29\ kcal \qquad (2\text{-}6)$$

$$CO + H_2O \rightarrow CO_2 + H_2 + 10\ kcal \quad (2\text{-}7)$$

The removal of carbon atoms through gasification enlarges existing pores, creates new pores, or combines smaller pores to create larger ones with less surface area (Bansal, 1988). Since steam-carbon gasification is an endothermic process, an external heat source with accurate controls is necessary to maintain the reaction (Bansal, 1988; Wigmans, 1989; Marsh, 2006).

During gasification, the oxygen atom from carbon monoxide or free hydrogen atoms may chemisorb to the char, forming surface complexes. These surface complexes retard the gasification rate, as they tend to be more stable than the surrounding carbon (Bansal, 1988; Marsh, 2006). When using steam, hydrogen is a greater factor on the reaction than carbon monoxide because hydrogen surface complexes are generally more stable. While this inhibition increases activation times and temperatures, it may not necessarily have a negative impact, as slower reaction rates allow for better control of gasification and pore development (Marsh, 2006). Also, Lopez et al. (2003) found that oxidizing an activated carbon's surface resulted in increased vinegar decolorization capacities and rates.

One-Step

Laine et al. (1991), Warhurst et al. (1997), and Alaya et al. (2000), all explored the potential of one-step steam activation. This process combines pyrolysis and activation. This can be advantageous because thermal activation is very energy intensive, and by reducing the amount of time the carbon must be in the furnace can reduce costs. The one-step process has also been shown to increase the yield of the final product (Alaya, 2000).

Alaya et al. (2000) was able to produce activated carbons with BET surface areas of 877 m^2/g and 18% yields from palm branches, 1007 m^2/g and 21% from palm leaves, and 775 m^2/g and 19% from date pits. These carbons were produced using a one-step constant steam process at temperatures ranging from 600-700°C for 2 h. The results show that one-step activation produced a viable activated carbon product with adequate yield from plant-based precursor materials. Warhurst et al. (1997) also had similar results activating seed husks at 700°C for 30-60 minutes. The carbons had high phenol removal rates (90% removal in 30 minutes), but slightly lower yields of 12%.

Chemical Activation

Introduction to Calcium

During the reactivation of granular activated carbon (GAC), calcium collected on the carbon's surface modifies the pore structures (Cannon, 1994; Cazorla-Amoros, 1996; Mazyck, 2000; Juarez-Galan, 2009). Cannon et al. (1994) found that calcium oxides act as a catalyst for carbon gasification during thermal treatment through the CaO to $Ca(OH)_2$ reaction, water/metal interactions, and direct reactions between water and the calcium species. Calcium infused GAC reactivated at 650-750°C has greater micropore losses than if activated at 850-950°C, due to the thermodynamic properties of carbon oxide speciation (Cannon, 1994).

Cazorla-Amoros et al. (1996) further explored the use of calcium catalysis for selective porosity development in plant derived biomass. Calcium impregnated chars had burn off rates that were 25-35% quicker than virgin char. The increased burn off rates also translated to increased meso- and macroporosity and a loss of microporosity. The results suggest that the calcium activation process can be used to create wider pores and greater mesopore volumes than typical steam activation.

Juarez-Galan et al. (2009) used calcium specifically for the development of mesoporosity in plant derived biomass. Nitrogen gas adsorption isotherm analysis had shown that the mesopore volumes of calcium impregnated samples increased up to 330% compared to the calcium free samples. The average 68% reduction in BET surface area suggested that mesoporosity was increased at the expense of microporosity.

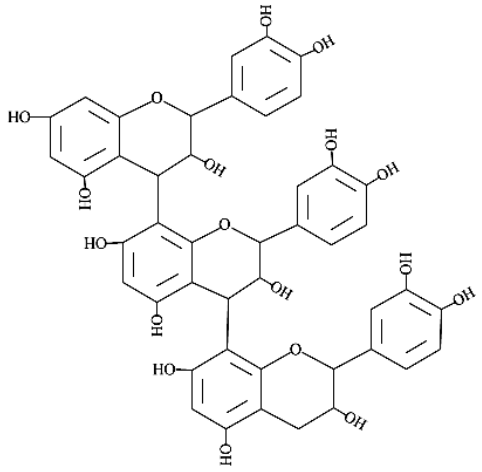
Chemical Impregnation/Activation

In order to activate a carbon precursor with a desired chemical, the material must be impregnated by the chemical. Cazorla-Amoros et al. (1996), Juarez-Galan et al. (2009), and Hu et al. (2001) thoroughly mixed organic precursors in solutions of the desired chemical species (e.g. $CaCl_2$, CaO, KOH, $ZnCl_2$, etc.) for a prescribed length of time; some of the studies used a constant chemical solution protocol, while others varied the ratio of material-to-chemicals.

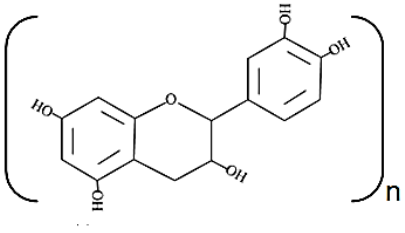
Juarez-Galan et al. (2009) used a constant concentration of $CaCl_2$ (7% by weight) and mass of precursor for 7 h at 85°C. On the other hand, Hu et al. (2001) varied the amount of $ZnCl_2$ added to a constant volume of water in order to achieve $ZnCl_2$-to-precursor ratios varying from 0.25 to 3 by weight. Cazorla-Amoros et al. (1996) used a method similar to Juarez-Galan et al. (2009), but the precursor was activated for 2 h at 850°C under carbon dioxide and then mixed with calcium acetate. Following impregnation, the samples were then subjected to steam and carbon dioxide thermal reactivation.

For these studies, activation was achieved using carbon dioxide and steam as oxidants. Hu et al. (2001) introduced zinc chloride impregnated samples to 800°C conditions for 2 and 3 h. Following activation, the samples were rinsed successively

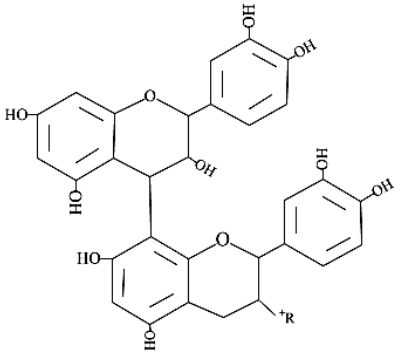
with deionized water and a 0.1 mol/L solution of hydrochloric acid to remove excess zinc and chloride compounds. Juarez-Galan et al. (2009) activated calcium chloride impregnated samples with carbon dioxide at a rate of 100 mL/min for a variety of temperatures and times (750-824°C and 4, 6, and 12 h). The activated samples were then washed with a 5% hydrochloric acid solution to remove any excess calcium. Cazorla-Amoras (1996) used a nitrogen gas/steam mixture to activate calcium acetate impregnated carbon dioxide activated char. Mixtures of 30%, 40%, and 50% steam at 100 mL/min were used at 850°C.



Procyanidin C1



Procyanidin (n=0-13)



Procyanidin B2

Figure 2-1. A selection of color causing apple juice polyphenols (Borneman, 2001)

CHAPTER 3
EXPERIMENTAL METHODS

Pine wood sawdust, a sawmill byproduct, was used to create activated carbon using one-step steam activation, two-step steam activation with pyrolysis, and calcium impregnation with one-step steam activation methods. The carbons were then powdered and tested for apple juice decolorization capacity using batch reactor mixing, filtering, and spectrophotometry analysis. A selection of these carbons were run through nitrogen gas adsorption analysis, creating relative pressure isotherms, from which the BET surface area, total pore volume, average pore size, and pore size distributions (HK, BJH, and DFT) were determined.

Material Preparation

The sawdust was first passed through a 16-mesh sieve and hand sorted to remove any large pieces of wood or bark. The sieved sawdust was then dried in a 110°C oven for at least 24 h before further treatment. This basic sawdust preparation was performed for all samples, regardless of the treatment process.

Two-Step Steam Activation

Two-step steam activation consists of two distinct stages: a pyrolysis stage and an activation stage. All activation and pyrolysis steps were performed in a vertical, upright furnace capable of accurately and consistently holding temperatures from 250-1200°C. A 1½ inch stainless steel pipe ran through the center of the furnace. The bottom opening of this pipe was attached to tubing connected to variable area flow meters (rotameters) capable of precisely delivering nitrogen gas or water to the furnace pipe. When steam was needed, heating tape wrapped around the gas-delivery tubing was

heated to approximately 250°C to flash boil the water. Figure 3-1 illustrates the tubing and furnace pipe set up.

In order to accurately measure the temperature within the furnace pipe, a 24 inch thermocouple was lowered into it. After the furnace had heated to within 50°C of the desired temperature, the gas or steam was turned on at a constant flow rate (1,000 mL/min for nitrogen gas and 1.1 mL/min for water/steam). The temperature controls on a digital temperature control unit were then adjusted until the desired temperature was held constant for at least 10 minutes. Samples were lowered 24 inches into the furnace tube using a stainless steel basket and metal wire; it was important that the length of the basket and wire was the same as the thermocouple, as temperatures inside the furnace tube vary greatly with distance. The basket was equipped with 120-mesh frets to allow gas or steam to flow through the sample while minimizing losses.

Pyrolysis

The first step for pyrolysis was to pre-heat the furnace to the desired charring temperature (450°C, 550°C, 650°C, or 750°C) with a 1,000 mL/min nitrogen gas flow. The high gas flow ensures that the environment within the furnace tube will be inert and oxidant free. For each sample, 6 g of the dried sawdust was massed and lightly packed into the furnace basket. Two 120-mesh frets were installed on the top and bottom of the basket to prevent the sawdust from blowing out of the basket while allowing the nitrogen gas to pass through the sample.

After the sawdust was loaded into the basket, it was lowered 24 inches into the pre-heated furnace with a metal wire. The sample was then allowed to carbonize for 1 h. After pyrolysis, the basket was raised to the top of the furnace tube, where temperatures were much cooler (~150°C), and allowed to cool under the nitrogen gas

flow for 15 minutes. The basket was then removed from the furnace tube and cooled at room temperature for 15 minutes. During the room temperature cooling stage, the thermocouple was placed back in the furnace tube and the temperature checked; if the measured temperature was ±10°C of the desired pyrolysis temperature, the sample was saved, otherwise, it was discarded. Saved samples were funneled into labeled test tubes for storage in a vacuum desiccator until needed for testing or activation.

Steam Activation

After pyrolysis, the furnace temperature was raised to the activation temperature (750°C) under 1.1 mL/min of steam. The carbonized wood was massed and loaded into the basket, which was then lowered 24 inches into the pre-heated furnace tube. Two-step activated samples were held under constant steam flow and temperature for 2 h. After this time, the steam was stopped and replaced with a nitrogen gas flow of 1,000 mL/min. The basket was then raised in the furnace tube to the cooler upper-region of the furnace, where it was cooled under nitrogen gas for 15 minutes. The basket was then cooled at room temperature, while the furnace temperature was checked with the 24 inch thermocouple. As with pyrolysis, samples with temperature variations greater than ±10°C were discarded.

After activation, the cooled sample was massed and then milled with a mortar and pestle until it was a fine powder. This powder was separated with a 325-mesh sieve; the sample that passed through was, by definition, a powdered activated carbon (PAC). This PAC was funneled into labeled vials, and stored in a vacuum desiccator until needed for testing.

One-Step Steam Activation

One-step steam activation used a process similar to two-step activation, without the first, pyrolysis step. The furnace was pre-heated to the desired temperature (450°C, 550°C, 650°C, 750°C, or 800°C) with steam at 1.1 mL/min. Approximately 6 g of sieved, dried wood was lightly packed into the basket which was lowered 24 inches into the pre-heated furnace tube. The temperature and steam flow were held constant for a prescribed length of time (1 h or 2 h). After time was reached, the steam was turned off and replaced with 1,000 mL/min of nitrogen gas, and the sample was cooled in the upper-region of the furnace tube for 15 minutes. The basket was then cooled at room temperature, while the furnace temperature was checked; samples with temperature variations greater than ±10°C were discarded.

After activation, the cooled sample was massed and then milled with a mortar and pestle until it was a fine powder. This powder was separated with a 325-mesh sieve. The PAC that passed through the sieve was funneled into labeled vials, and stored in a vacuum desiccator until needed for testing.

Chemical Impregnation with One-Step Steam Activation

The chemical samples had significant pre-treatment prior to activation, including sorting, acid washing, chemical impregnation, and several drying steps. This process was streamlined into sequential batches to minimize variations in the protocol; wood was acid washed in larger quantities, capable of creating 5 individual samples, while these samples were impregnated in sequential batches with enough time between batches to allow for furnace activation. After post-activation treatment, the samples were stored and tested at the same time.

Acid Washing

Before impregnation, the sieved, sorted, and dried sawdust was washed in a 10% by volume sulfuric acid solution. Enough wood was acid washed in each batch to create 5 samples at 5 g each (~28 g per acid wash batch). 50 mL of acid solution was used for each gram of wood; therefore each batch had 1,400 mL of acid solution. The massed wood was added directly to the measured acid solution and quickly mixed on a stir plate for 1 h.

After mixing, the acid washed wood was filtered from the acid solution with a very fine mesh. The wood was then rinsed with several liters of deionized water. Each batch of acid washed and rinsed wood was allowed to fully dry in a 110°C oven for at least 24 h prior to further treatment.

Impregnation

For calcium impregnations, a 7% by weight solution of calcium chloride was created in 500 g batches by mixing 35 g of $CaCl_2$-$2H_2O$ solid with 465 mL of Nanopure® deionized water. Samples were impregnated by mixing this solution with 5 g of acid washed sawdust for 8 h on an 85°C stir plate. The chemical to wood ratio was varied by using different volumes of calcium solution, as shown in Table 3-1. After mixing, the slurry was transferred to a 110°C oven, where it was dried for 24 h before activation; this resulted in 32 h of chemical contact time.

One-Step Steam Activation

After drying, the calcium impregnated sawdust was loaded into the basket and activated using a process similar to the one-step steam activation method previously mentioned. The furnace was pre-heated to 750°C with a steam flow of 1.1 mL/min. The

samples were activated for 2 h and cooled under nitrogen gas. The temperature was checked, and samples with temperature variations greater than ±10°C were discarded.

After activation and cooling, the individual samples were washed for 30 minutes in 200 mL of 5% by volume hydrochloric acid solution to remove the calcium and other ions. The samples were then rinsed with approximately 2 L of deionized water in a membrane vacuum filter until a pH of 6-8 was reached. The sample was then dried in a 110°C oven for 24 h. After drying, the sample was massed and then milled with a mortar and pestle until it was a fine powder. This powder was separated with a 325-mesh sieve, funneled into labeled vials, and stored in a vacuum desiccator until needed for testing.

Decolorization Testing

Spectrophotometry

The apple juice used in these experiments was Hannaford® Apple Juice from concentrate. It was tested in a HACH® DR/4000U Spectrophotometer from wavelengths of 300 nm to 500 nm, as shown in Figure 3-2. Since this apple juice didn't have any discernable peaks, the value of 330 nm was chosen as a reference for color removal. Percent color removal was determined using the following equation:

$$Percent\ Color\ Removal = 1 - \frac{A}{A_0} \tag{4-1}$$

where A_0 is the absorbance of the untreated apple juice measured at 330 nm, and A is the measured absorbance of the treated (decolorized) apple juice at 330 nm.

Batch Mixing

Apple juice was mixed in batches with a dose of PAC to determine the carbon's apple juice color adsorptive capacity. A commercially available phosphoric acid

activated PAC, Carbochem® CA-50, was used as a reference and benchmark for setting the decolorization testing protocol. In order to determine the PAC dose for batch analysis of color removal, varying masses of CA-50 were added to 100 mL samples of apple juice. The samples were then tumbled and mixed for 4 h with a control of untreated juice. After mixing, the PAC was removed using a 0.45 µm cellulous membrane vacuum filter and the apple juice was tested with the spectrophotometer at 330 nm. As shown in Figure 3-3, a dose of 5,000 mg/L was chosen for maximum decolorization capacity batch testing. This PAC dose and testing method was used as the testing protocol for produced samples using 200 mg of PAC in 40 mL of apple juice.

Methylene blue and congo red dye removal tests were also performed on the carbonized samples to give a basic analysis of micro- and mesopore development. Solutions of 10 mg/L dyes were made; 100 mL of the solution was mixed with 30 mg of carbonized wood for 4 h. The mixtures were vacuum filtered with a 0.45 µm membrane and the methylene blue removal was tested in the spectrophotometer at 650 nm, while congo red was tested at 487 nm.

Pore Analysis

A Quantachrome® NOVA 2200e surface area and pore size analyzer was used for characterizing the CA-50 and select samples. For each tested sample, nitrogen gas adsorption isotherms were developed using volumes for 20 adsorption and 10 desorption relative pressure values ranging from 0.013 to 0.99. NovaWin® version 9.0 software was used to calculate the BET surface area, total pore volume, average pore size, and the pore size distributions (HK, BJH, and DFT).

BET surface area was calculated using the multipoint method, where the low relative pressure points ($P/P_0 < 0.15$) are used in the BET equations to find an

estimated total surface area. The total pore volume was found by calculating the total amount of N_2 gas adsorbed at the highest relative pressure point (~0.98). The average pore size, HK, BJH and DFT pore size distributions were calculated through analysis of the N_2 isotherm.

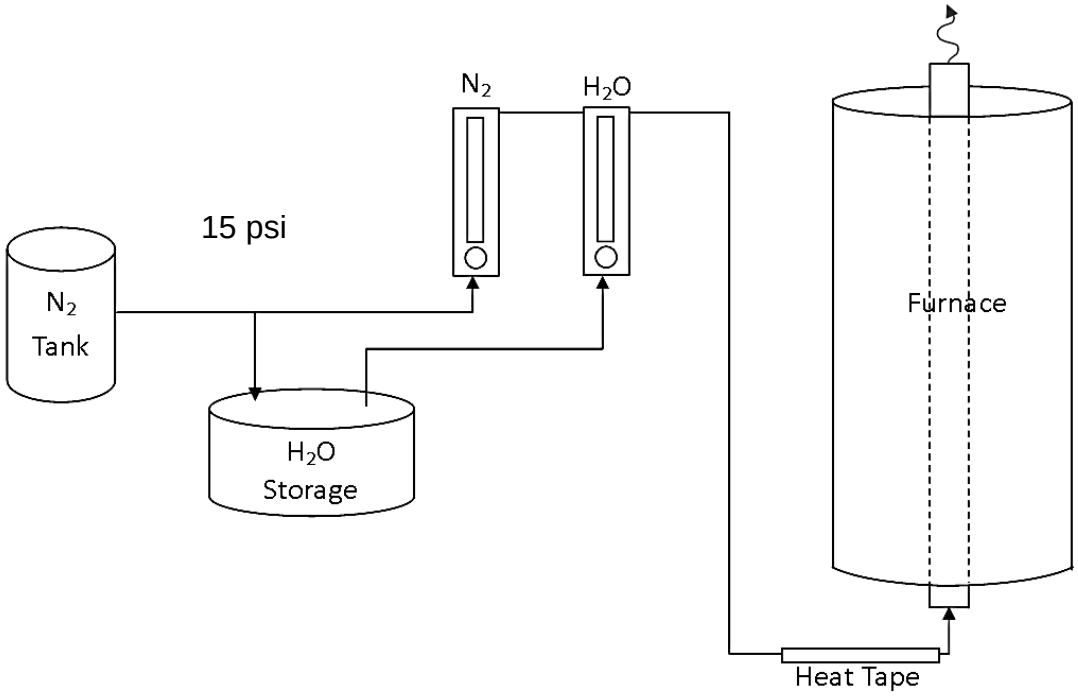


Figure 3-1. Schematic detailing the layout of pipes for N_2 gas and water/steam delivery to the upright furnace

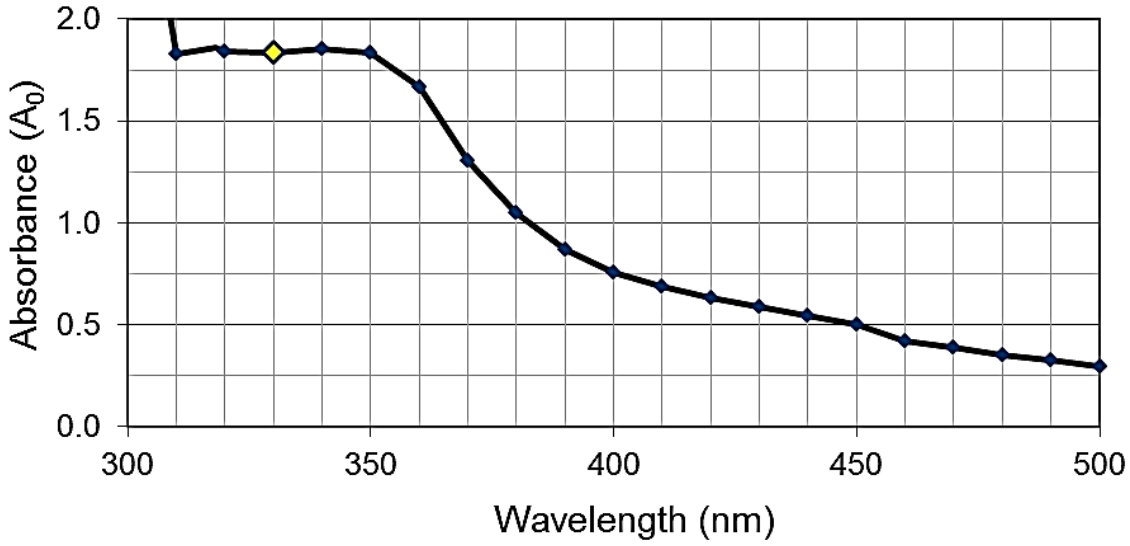


Figure 3-2. Light absorbance curve for Hannaford apple juice from 300 nm to 500 nm wavelengths

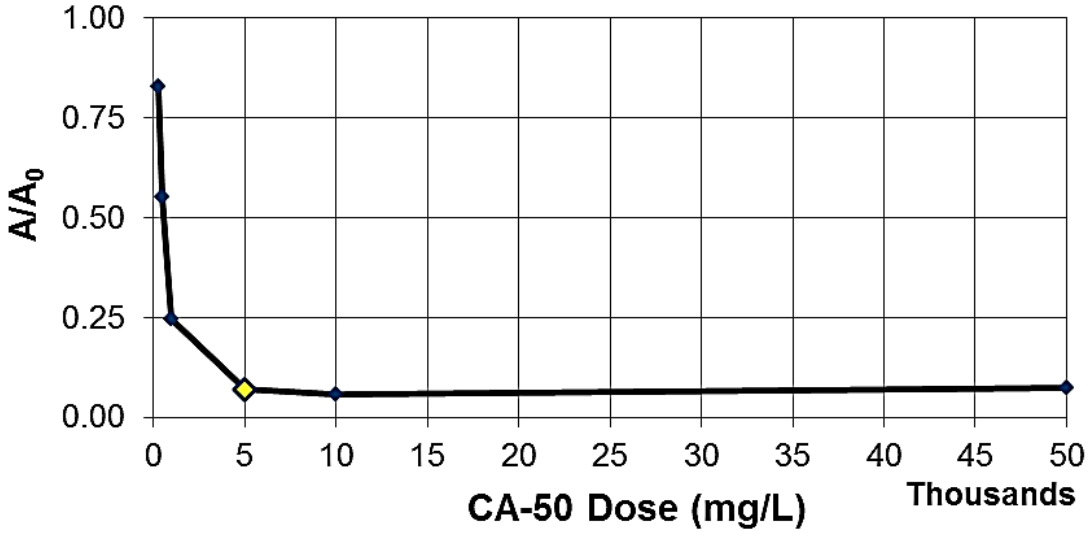


Figure 3-3. Apple juice light absorption ratio for varying CA-50 doses with 4 h of mixing time at 330 nm wavelength light

Table 3-1. Summary of chemical to wood ratios, masses, and solution volumes

$CaCl_2$-$2H_2O$:Wood	Wood mass (g)	$CaCl_2$-$2H_20$ mass (g)	Vol. of 7% solution (mL)
2:1	5	10	143
3:1	5	15	215
4:1	5	20	286

CHAPTER 4
RESULTS AND DISCUSSION

CA-50

The commercially available Carbochem® CA-50 PAC was used as a reference and benchmark for the following set of experiments. As mentioned previously, CA-50 was used to find that the maximum adsorbed color removal was achieved with PAC doses of 5,000 mg/L or greater. Running several apple juice color adsorption tests at 5,000 mg/L PAC for 4 h mixing time found that CA-50 had consistent color removal percentages around 90%, with a mean of 92%, minimum of 88%, and maximum of 94%. While the 5,000 mg/L concentration effectively removes color from apple juice, it is a very high dose, and producing lower cost activated carbons would be very beneficial to industries requiring decolorized apple juice. Also, CA-50 may contain residual phosphorus as a result of its chemical activation methods, which could be leached into the apple juice solution; as a result of this, a more benign activation chemical (e.g. calcium) would be preferable.

A nitrogen gas adsorption isotherm for CA-50 (Figure 4-1) was used to determine the BET surface area, average pore size, and total pore volume, which are shown in Table 4-1. The total pore volume suggests that CA-50 has a well-developed pore structure, the average pore size indicating that there is substantial mesoporosity, and the BET surface area shows that there is also significant microporosity.

Further analysis of the N_2 isotherm using the HK, BJH, and DFT pore size distribution models give more detail into the physical pore structure of CA-50. Figure 4-2 shows that CA-50 has a peak specific pore volume differential at 10 Å with a value of 0.045 cc/Å/g that subsequently tapers off to 0.013 cc/Å/g as it approaches 20 Å. The

micropore volume was found to be 0.50 cc/g or 40% of the total volume. It is within these micropores that the bulk of the carbon's surface area is located. The DFT mesopore size distribution, Figure 4-3, shows that the peak pore volume differentials are much less than in the micropore range, but the overall volume (area under the curve) is much greater. The BJH method found that the mesopore volume is around 60% of the total pore volume (0.74 cc/g). Table 4-1 summarizes the results of the various tests for CA-50.

Pyrolysis

Pyrolysis is used to remove non-carbon chemical species and volatile organics from the sample and create a rudimentary pore structure prior to activation. It is the first step in the traditional two-step activation process. For this experiment, prepared sawdust was carbonized and analyzed for basic pore development. Four samples were made under nitrogen gas flow at 450°C, 550°C, 650°C, and 750°C and tested using methylene blue and congo red adsorption analysis, the results of which are shown in Figure 4-4. Dye adsorption was studied to provide quicker insight into the porosity of the activated carbons, for nitrogen adsorption requires about 30 h per sample.

The methylene blue removal values suggest that there is some microporosity and surface area, but methylene blue removal with the same concentration of CA-50 was 100%. The negligible congo red removals suggest that there is very little mesopore surface area. Table 4-2 further supports these analyses with the isotherm analysis of the 650°C sample; there is some surface area (200 m^2/g) and microporosity (20 Å), but very little pore development (0.09 cc/g).

One-Step Steam Activations

One-step steam activations were performed by placing the prepared sawdust samples directly into the preheated furnace under 1.1 mL/min steam flow at a variety of temperatures and times. Figure 4-5 highlights the apple juice color removal capacities of PACs activated at 450°C, 550°C, 650°C, 750°C, and 800°C for 1 h. At 450°C and 550°C there is no substantial color removal; this is due to a lack of porosity development. Since the conversion of carbon to CO and CO_2 using steam is endothermic, it is apparent that these samples required more activation energy than that available at 450°C and 550°C. On the other hand, samples activated at 650°C and 750°C had significant increases in apple juice color removal values. The 800°C sample shows a very large drop in removal capacity; this is most likely due to pore collapse. When the surface of the micropores is gasified, it expands them until they combine to form larger pores. If enough pores rapidly combine in this manner, the physical matrix of the sawdust can break down, leading to pore collapse.

Since the 750°C 1 h sample had the highest color removal, 750°C was explored at times of 2 and 3 h. These samples all had similar removal values, around 78%. Figure 4-6 compares the different times, as well as a sample made using two-step steam activation, where the pyrolysis step was performed at 450°C for 1 h and activation at 750°C for 2 h. This comparison shows that results of the one-step activation method are comparable to two-step and that greater times in the furnace don’t necessarily result in more color removal.

Several of the one-step steam activated samples were analyzed with nitrogen gas adsorption: 650°C for 1 h (650 ws 1hr), 750°C for 1 h (750 ws 1hr), 750°C for 2 h (750 ws 2hr), and 750°C for 3 h (750 ws 3hr). The N_2 isotherms in Figure 4-7 show that 750

ws 1 hr and 750 ws 2hr have the most pore volume and overall porosity; the steep initial slope ($P/P_0 < 0.15$) for 750 ws 2 hr suggests that it has more microporosity than the other samples. The 650°C 1 h sample (650 ws 1 hr) has the least pore development, as indicated by its lower adsorption volumes.

HK analysis verifies that 750 ws 2hr does have the most microporosity, while 650 ws 1hr had the least. The HK micropore volumes for the samples are summarized in Table 4-3. The micropore volumes do not vary greatly (0.23-0.30 cc/g) and the percentage of microporosity compared to the total pore volume was fairly close as well (47-60%).

The mesoporosity was modeled with the BJH and DFT methods. Figure 4-9 shows that the samples are all fairly close at the peak pore volume differentials. However, 750 ws 1hr has the most overall mesopore volume, while 650 ws 1hr and 750 ws 3hr both have less differential volume between 40-50 Å. As summarized in Table 4-3, 750 ws 1hr had the most mesopore volume, which was 51% of the total volume. The 750°C samples all had more mesopore volume than 650 ws 1hr and better removal values (78-79% for 750°C compared to 67% for 650 ws 1hr).

Calcium Activations

Calcium samples were acid treated and impregnated with calcium chloride prior to one-step steam activation. The ratios of calcium chloride to sawdust used were 2:1, 3:1, and 4:1. Two samples of the 2:1 ratio were created, while seven were created for 3:1. The results of the apple juice decolorization tests are shown in Figure 4-10; for the 2:1 and 3:1 samples, the removal value was calculated from the mean of the samples, while the error bars represent the maximum and minimum removal values. The figure shows that mean color removals are around 80% for 2:1 and 3:1 and 74% for 4:1. The 2:1

samples had a range of 74% and 82%, while the 3:1 samples had a larger range of 70% to 87%. This variability is most likely a result of differences in the initial precursor caused by the small sample size, and slight variations in the acid washing, impregnation, and activation protocols.

Several of the 3:1 samples (labeled as B1-B7) were analyzed with N_2 adsorption. The isotherms for these samples are shown in Figure 4-11. Batch 1 has the most pore volume, while batch 7 has the least. The sharp rise in the isotherms at relative pressures greater than 0.8 suggests that these carbons have some meso- and macropore structures.

The HK micropore size distributions were determined for several of the 3:1 samples and plotted in Figure 4-12. This plot shows that the calcium samples all had similar micropore structures with little variability. The average micropore volume for the samples is 0.28 cc/g, which is about 40% of the total pore volume for samples B1 and B2 and 45% for samples B3, B6, and B7. Table 4-4 shows this information in detail for each sample.

The DFT mesopore size distribution was found for the tested samples and is shown in Figure 4-13. All of the calcium samples had pore volume differential peaks at 35 Å, 45 Å, and 80 Å. The sample B7 had the least mesoporosity and lowest apple juice decolorization value. Using the BJH method, samples B1 and B2 had the most mesoporosity at 0.44 cc/g, or 60% of their total pore volumes; sample B7 had the least mesopore volume at 0.25 cc/g, or 50% of its total pore volume. The mesopore volumes for all of the tested samples are summarized in Table 4-4.

Pore Analysis

The HK, BJH, and DFT pore analyses for CA-50, 650 ws 1hr, 750 ws 1hr, and 3:1 B1 were compared against each other. Figure 4-14 shows that CA-50 has much greater micropore differential volumes than the other samples; this is why CA-50 has such a relatively large BET surface area. Calcium sample 3:1 B1, which has a micropore size distribution that is representative of all the tested calcium samples, has microporosity similar to that of the one-step steam samples, meaning that the increased pore volume of the calcium samples does not come at the expense of microporosity.

The BJH mesopore volume comparisons (Figure 4-15) show that CA-50 has substantial mesopore volume compared to the other samples. The calcium sample had almost twice the cumulative volume than that of the best one-step steam sample. The slope of the curves show that the majority of the mesopore development for all the samples occurs with pore diameters under 120 Å; the decreased slope after that point suggests that there is not significant pore development, in terms of pore volume, beyond this point.

The DFT pore size distributions (Figure 4-16) show that a relatively large portion of the mesopore volume for CA-50 comes from the pores with diameters between 20-75 Å. After 75 Å, the calcium sample's pore distribution begins to match that of CA-50. It was observed in Figure 4-13, that all of the tested calcium activations had this peak at 75 Å. The one-step steam samples do not exhibit this increased mesoporosity at pore diameters greater than 75 Å, suggesting that this region of pore development is related to the calcium catalyzed activation process.

An analysis of the data was conducted to find any relations that might exist between the mesopore volume and apple juice color removal. Figure 4-17 shows a plot

of color removal percentage against total mesopore volume for all of the tested samples. There is a moderate linear correlation (R^2 = 0.69) between increasing mesoporosity and mesopore volume. However, when this analysis is done with just the steam or calcium samples, the correlation is very strong with R^2 values of 0.99 and 0.95 respectively, as shown in Figure 4-18.

The pore size distributions for the calcium sample (Figures 4-12 and 4-13) show that they all have very similar differential volumes under 40 Å, suggesting that differences in color removal due to pore structure are caused by the variations in differential volumes of pores with diameters greater than 40 Å. The bulk of the steam samples' adsorption is most likely in pores with diameters less than 75 Å (Figure 4-16).

Statistical Analysis

The differences between the apple juice color removal and pore structures of one-step steam and calcium samples were verified using a statistical t-test with a 95% confidence interval. The one-step steam, 750°C samples at 1, 2, and 3 h (3 samples) were tested against the 3:1 calcium samples (7 samples for color removal and 5 for pore structure values). For percent color removal, the two-tailed P value is 0.63, meaning that the sample sets are not considered statistically different. The BET surface area was also not statistically different (P = 0.39). For the average pore size, mesopore volume, and total pore volume, P equals 0.005, 0.01, and 0.02 respectively, which are all considered very statistically different. This analysis verifies that the mesopore volume, total pore volume, and average pore size are greater for calcium activated samples, while the BET surface area and color removal values are not statistically different. Thus, the calcium samples had greater mesopore development but this did not come at a loss of microporosity or BET surface area.

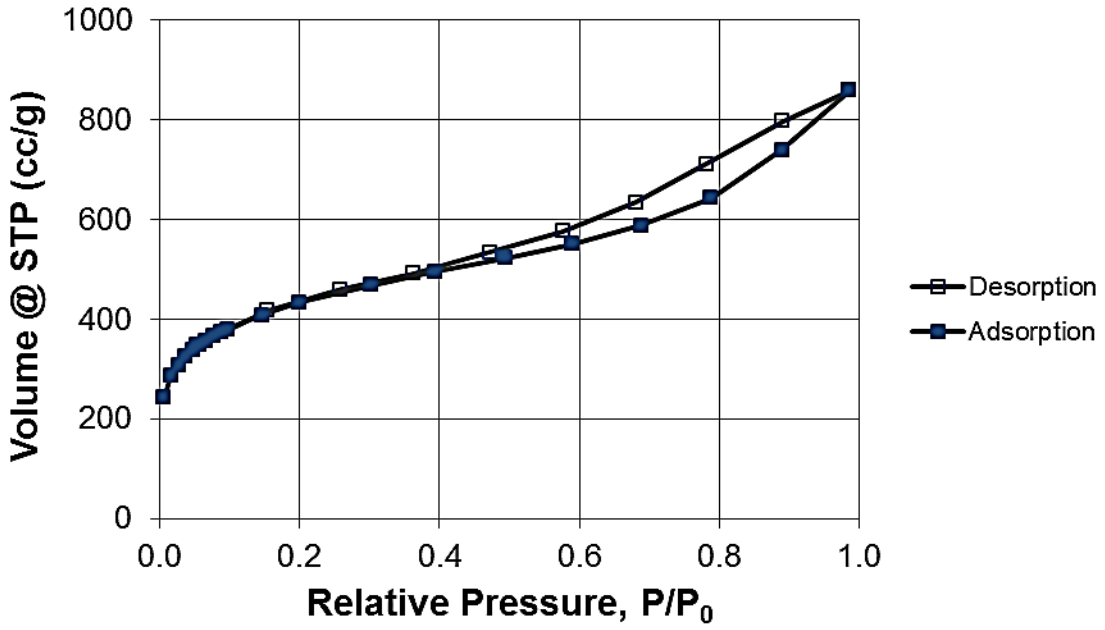


Figure 4-1. Nitrogen gas volume adsorption isotherm for CA-50

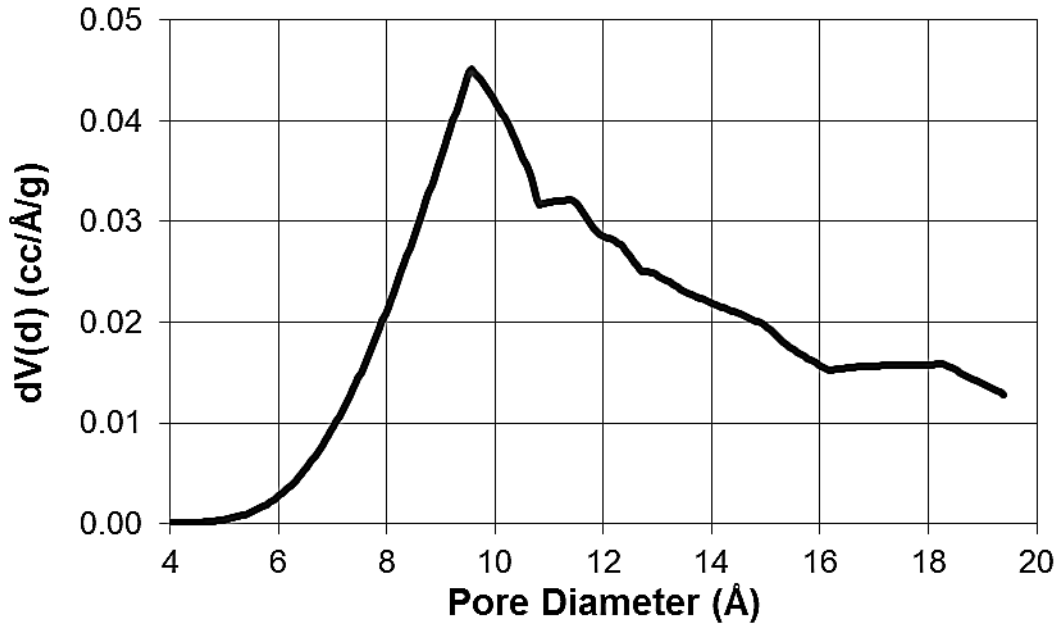


Figure 4-2. Horvath-Kawazoe micropore size distribution for CA-50 derived from a N_2 adsorption isotherm

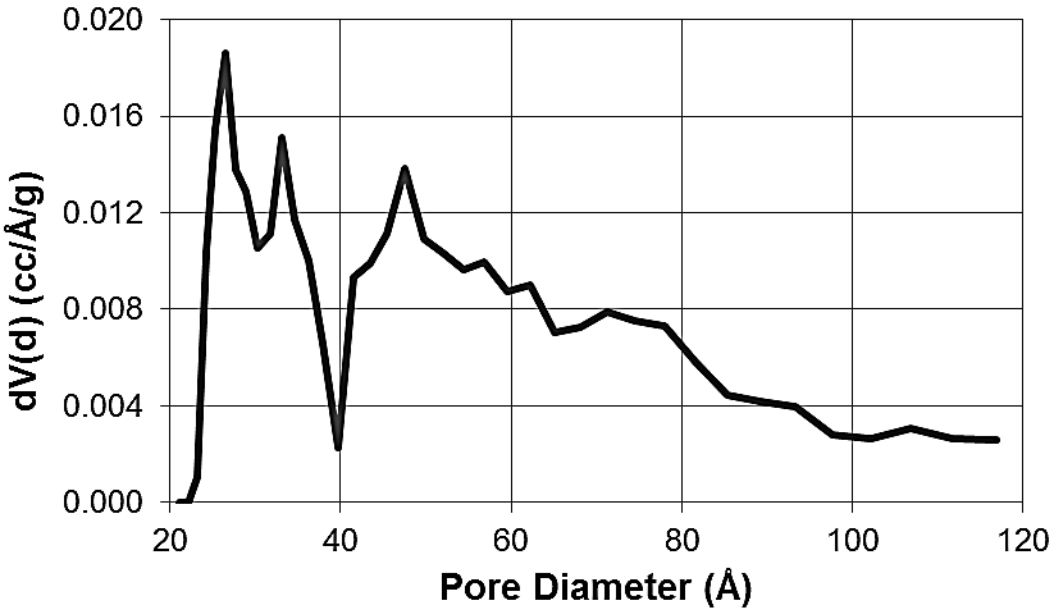


Figure 4-3. Density functional theory mesopore size distribution for CA-50 derived from a N_2 adsorption isotherm

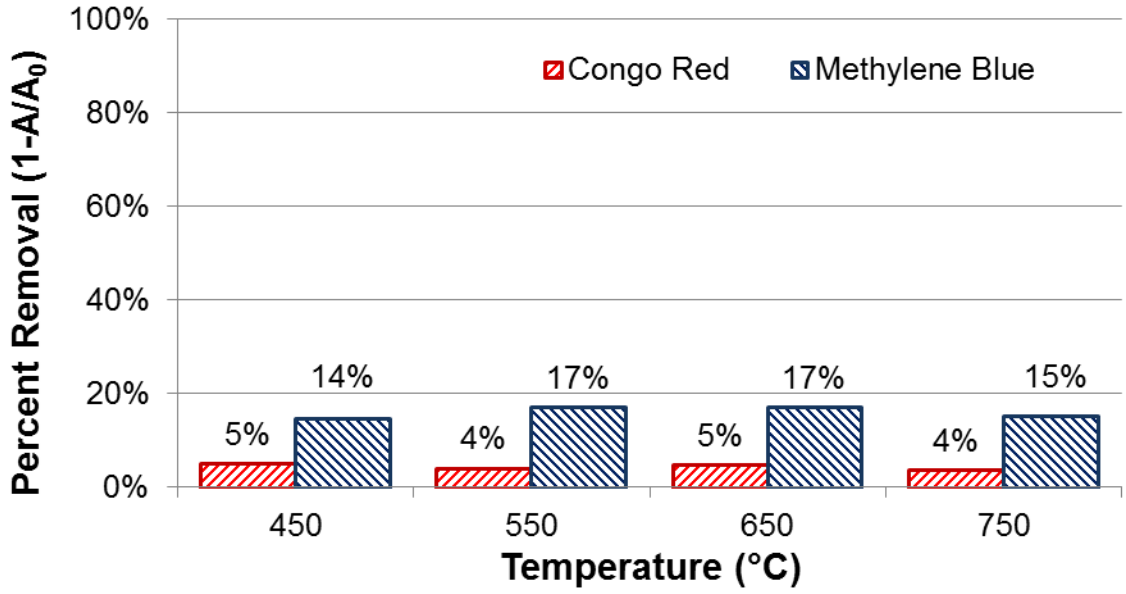


Figure 4-4. Carbonized sawdust congo red and methylene blue removal values at 0.3 mg/L dose for 4 h

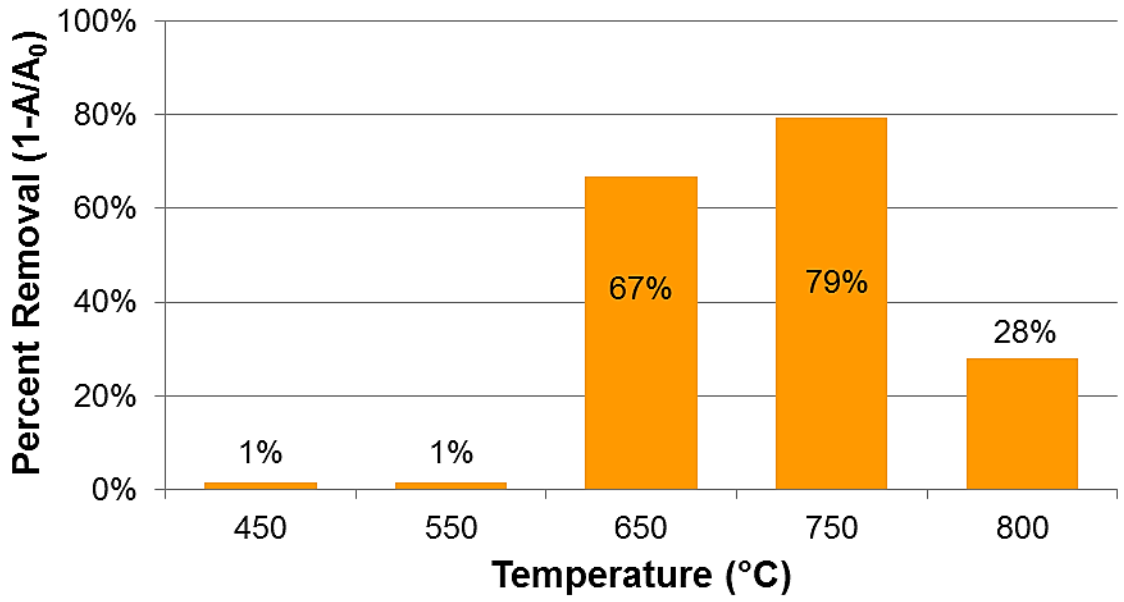


Figure 4-5. Apple juice color removal with 1 h, one-step steam samples at varying temperatures

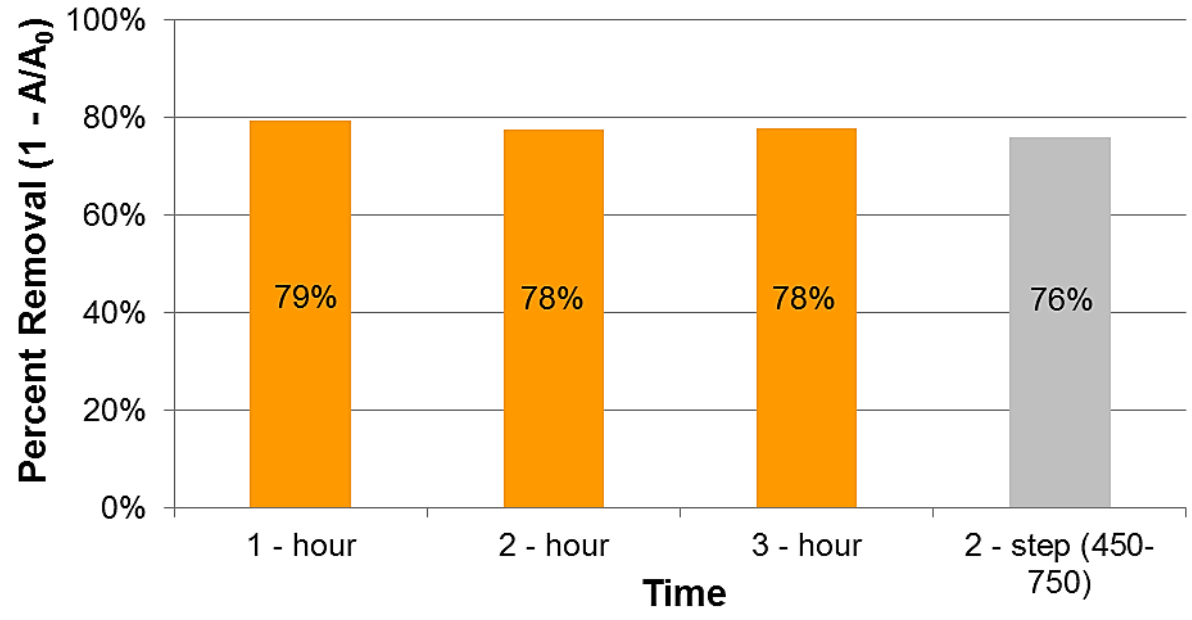


Figure 4-6. Apple juice removal with 750°C one-step steam samples at varying times compared to a two-step activated sample produced using 450°C pyrolysis for 1 h followed by 750°C steam for 2 h

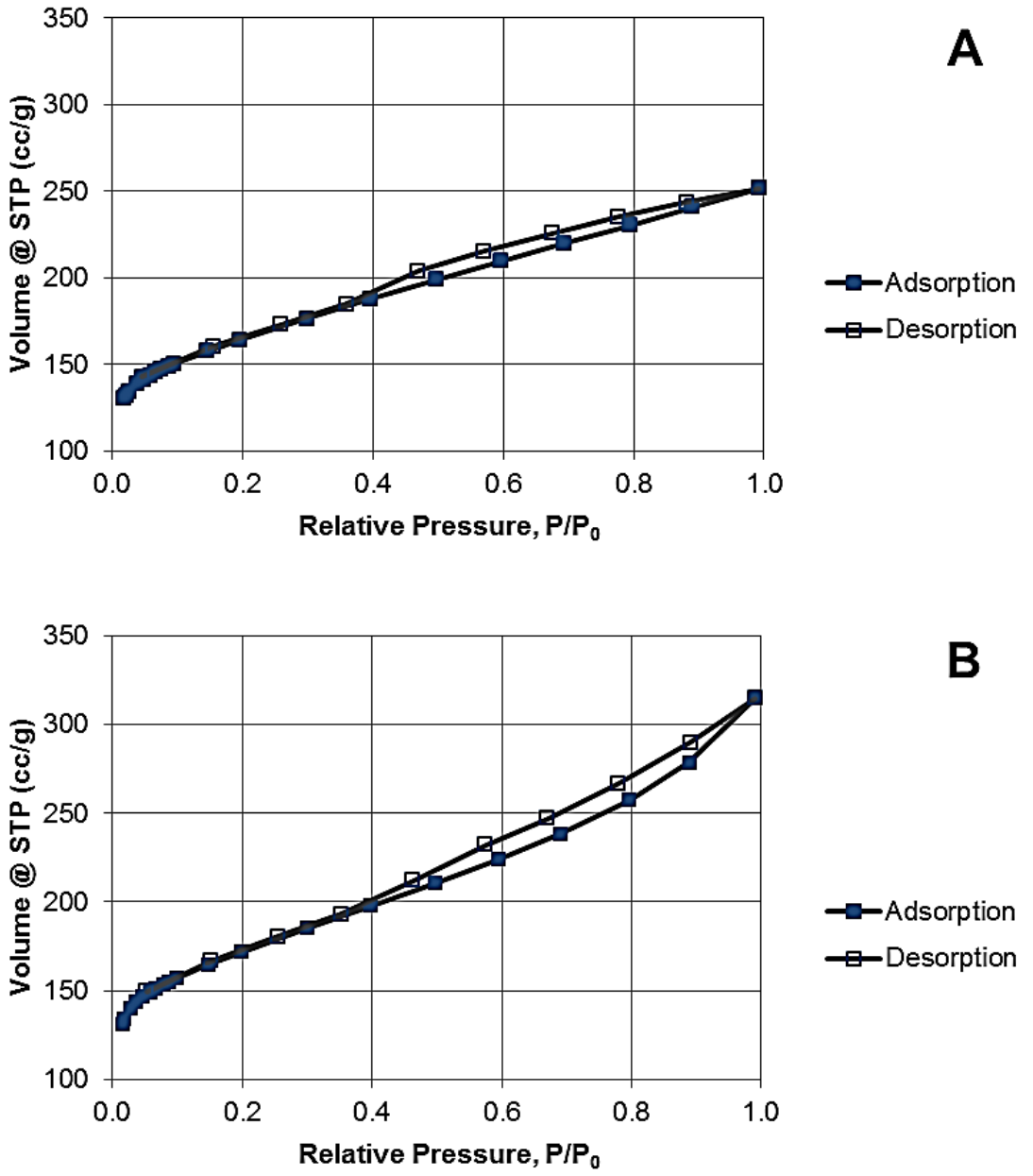
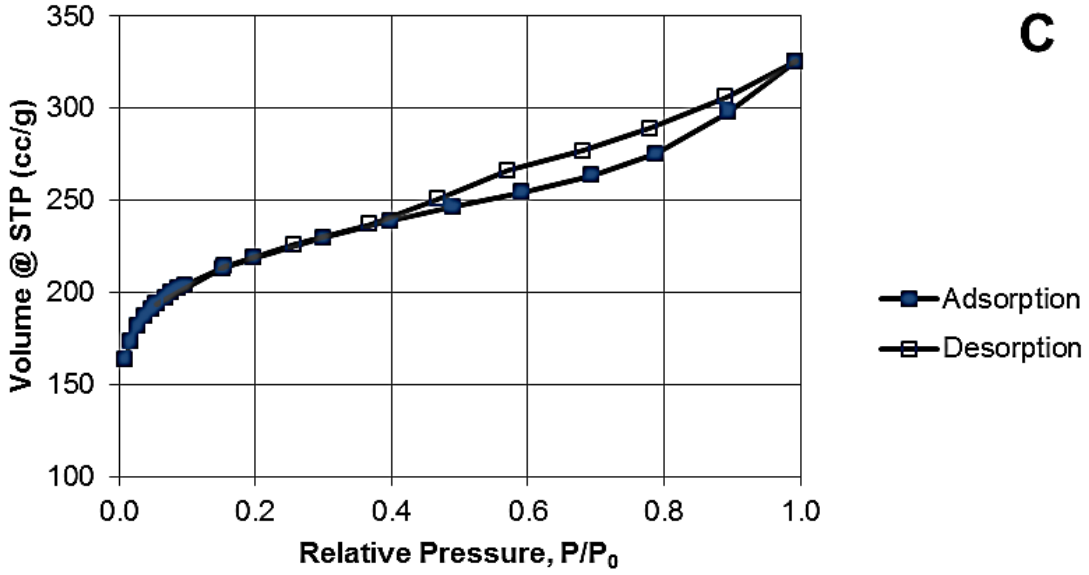


Figure 4-7. Nitrogen gas volume adsorption isotherms. A) One-step steam activation at 650°C for 1 h (650 ws 1hr). B) One-step steam activation at 750°C for 1 h (750 ws 1hr). C) One-step steam activation at 750°C for 2 h (750 ws 2hr). D) One-step steam activation at 750°C for 3 h (750 ws 3hr).



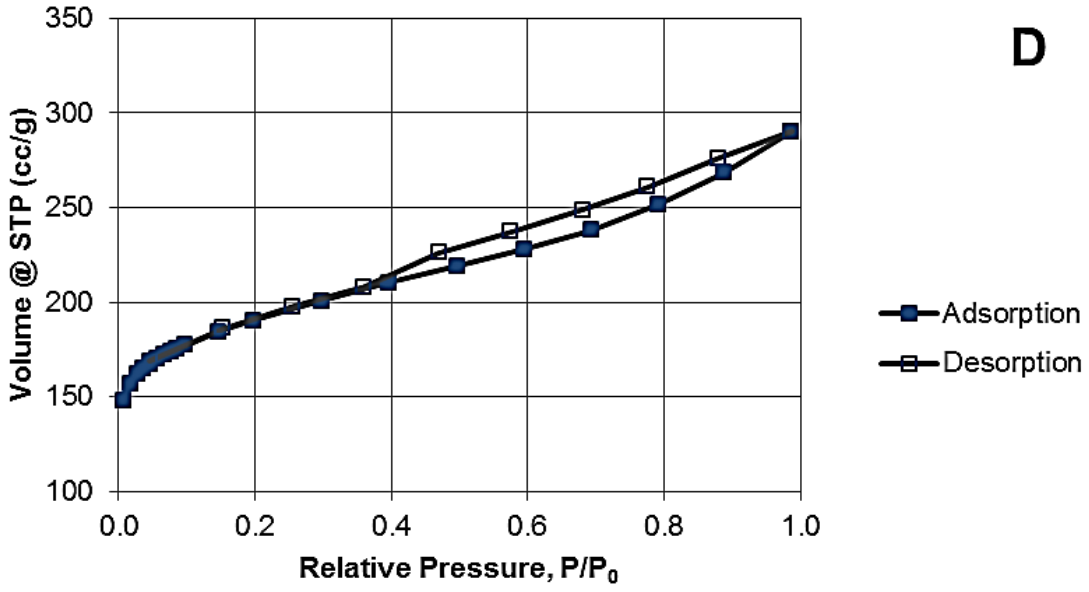


Figure 4-7. Continued

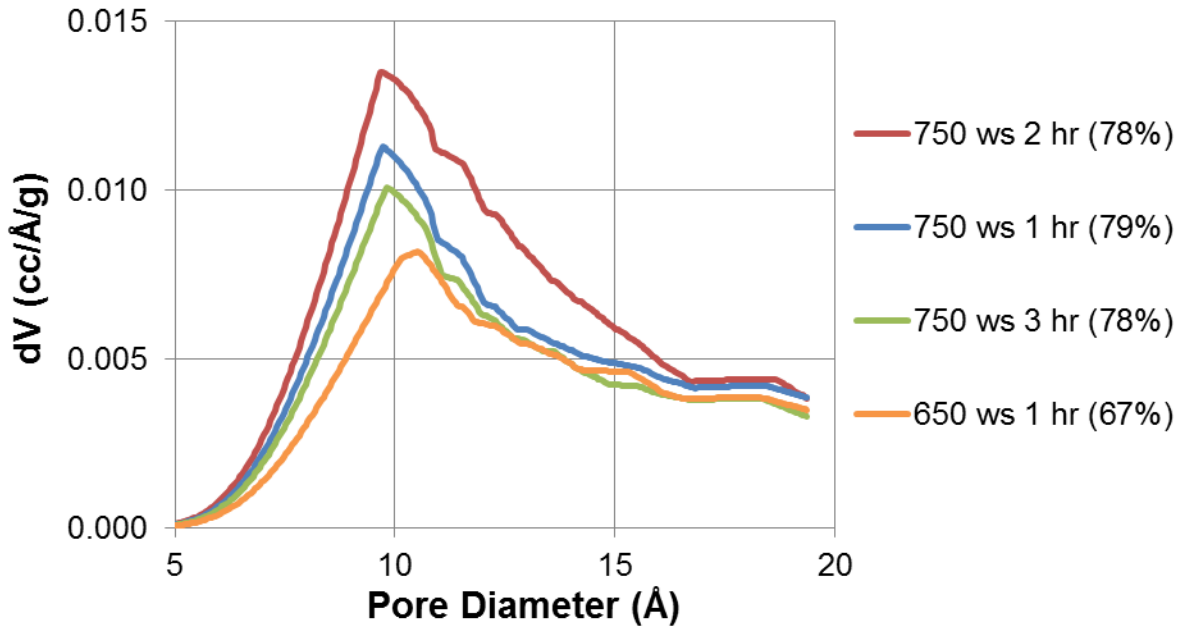


Figure 4-8. Horvath-Kawazoe micropore size distributions for 750°C one-step steam for 1 h and 650°C one-step steam for 1 h samples derived from N_2 adsorption isotherms

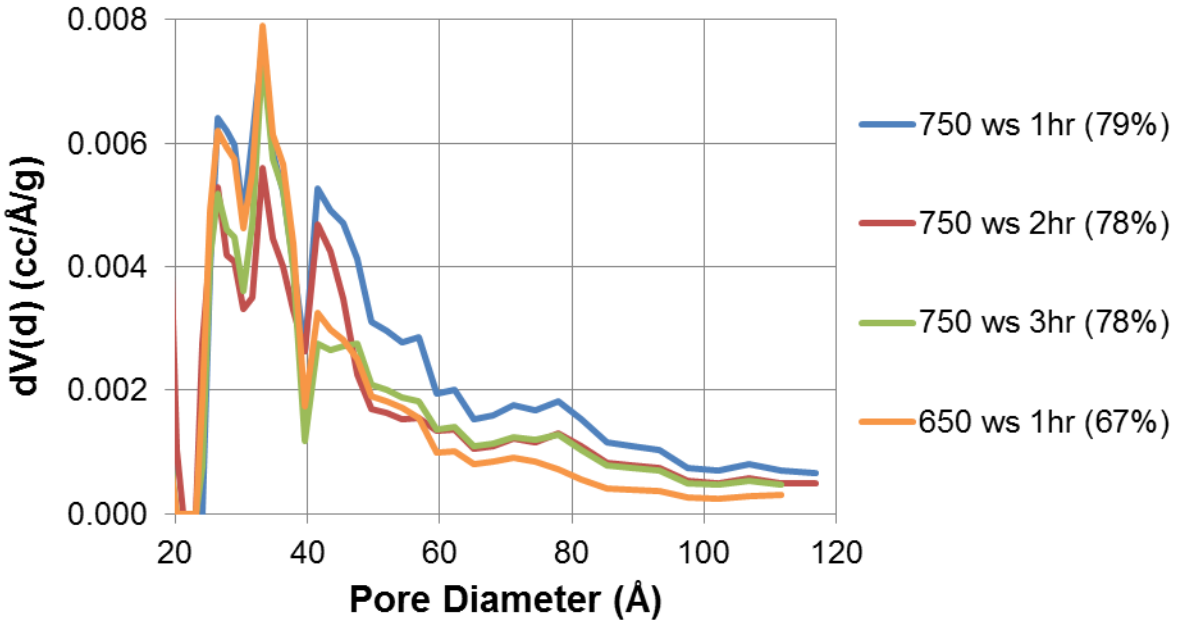


Figure 4-9. Density functional theory mesopore size distribution for CA-50, 750°C one-step steam for 1 h and 650°C one-step steam for 1 h samples derived from N_2 adsorption isotherms

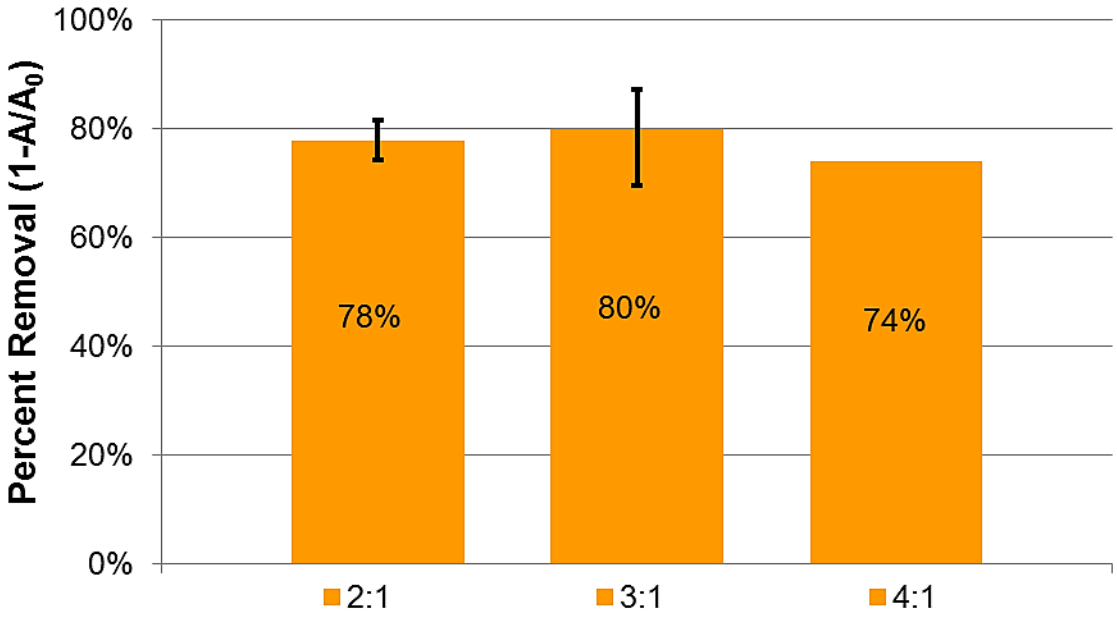


Figure 4-10. Apple juice removal with calcium impregnated samples of varying chemical to wood ratios activated with one-step steam at 750°C for 2 h

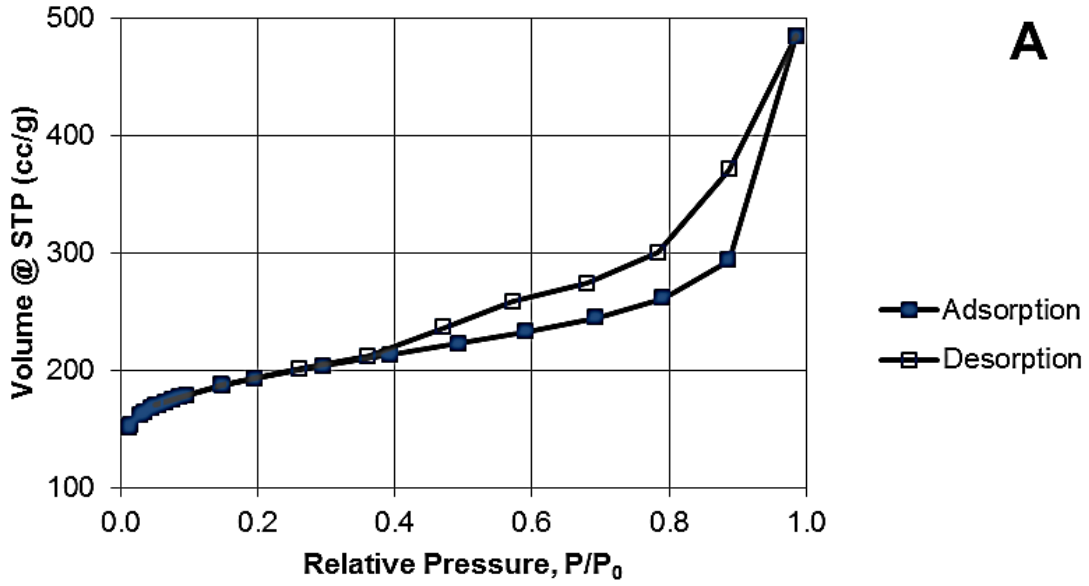
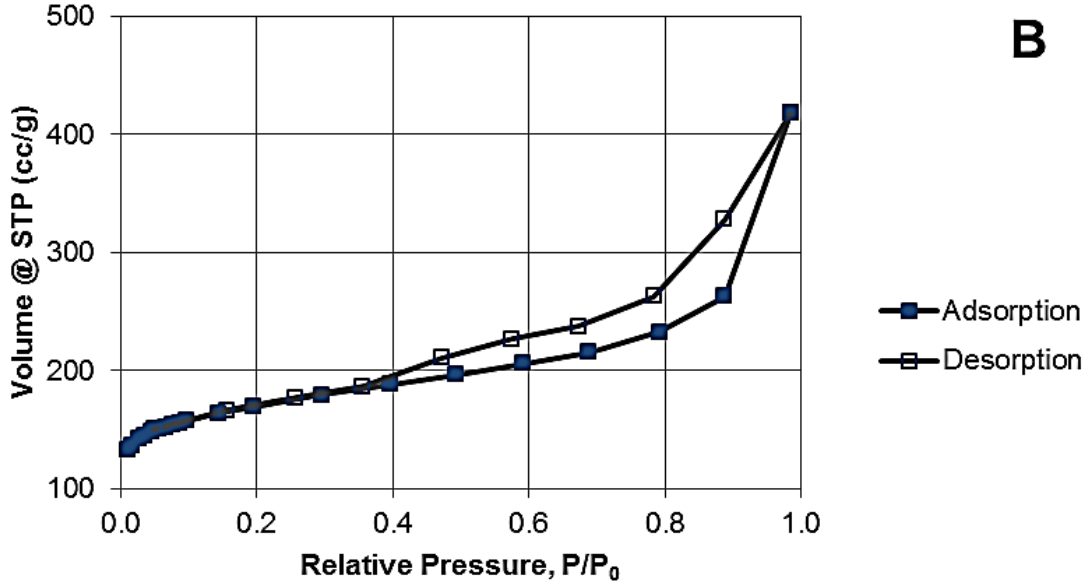


Figure 4-11. Nitrogen gas volume adsorption isotherms for several calcium impregnated samples. A) 3:1 calcium sample, B1. B) 3:1 calcium sample, B3. C) 3:1 calcium sample, B6. D) 3:1 calcium sample, B7.



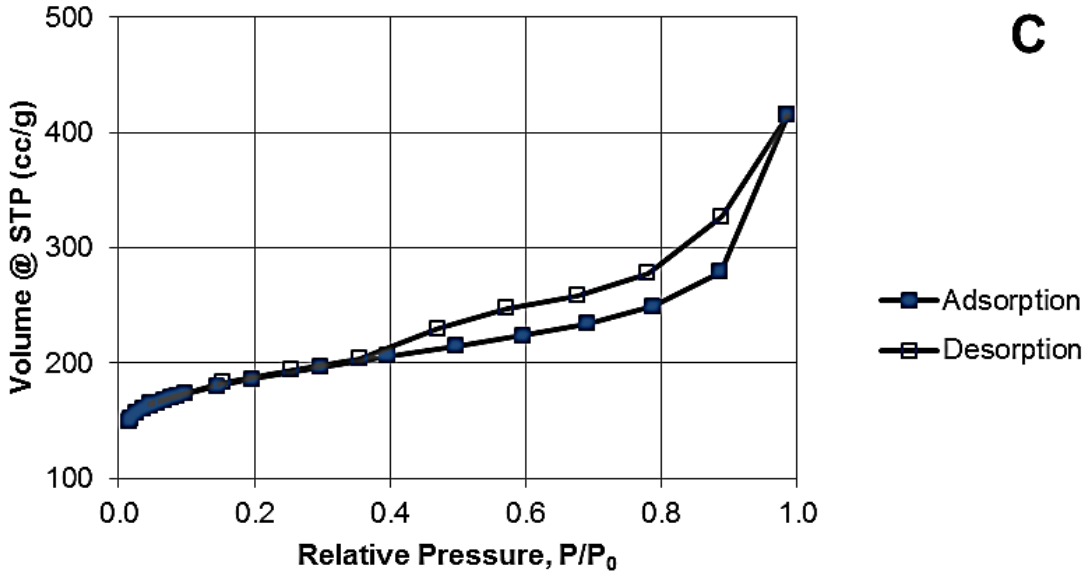


Figure 4-11. Continued

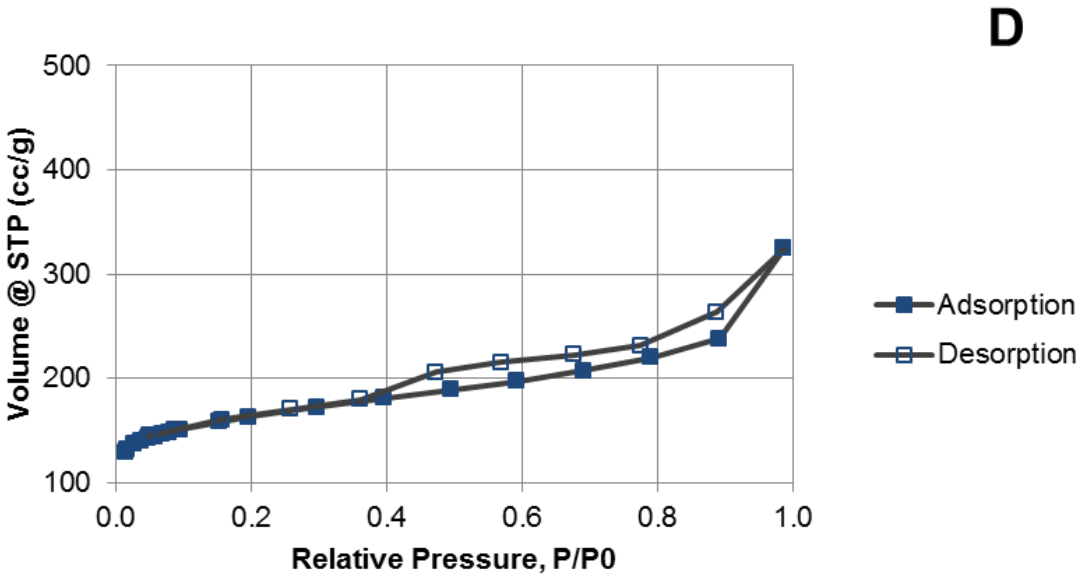


Figure 4-11. Continued

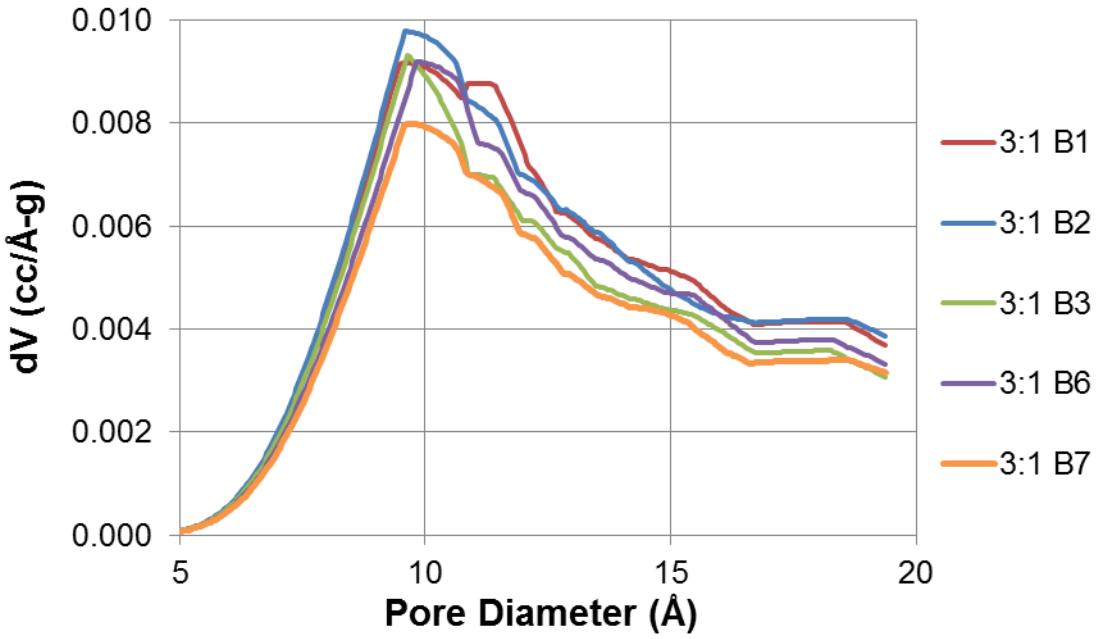


Figure 4-12. Horvath-Kawazoe micropore size distributions for several 3:1 calcium impregnated samples, derived from N_2 adsorption isotherms

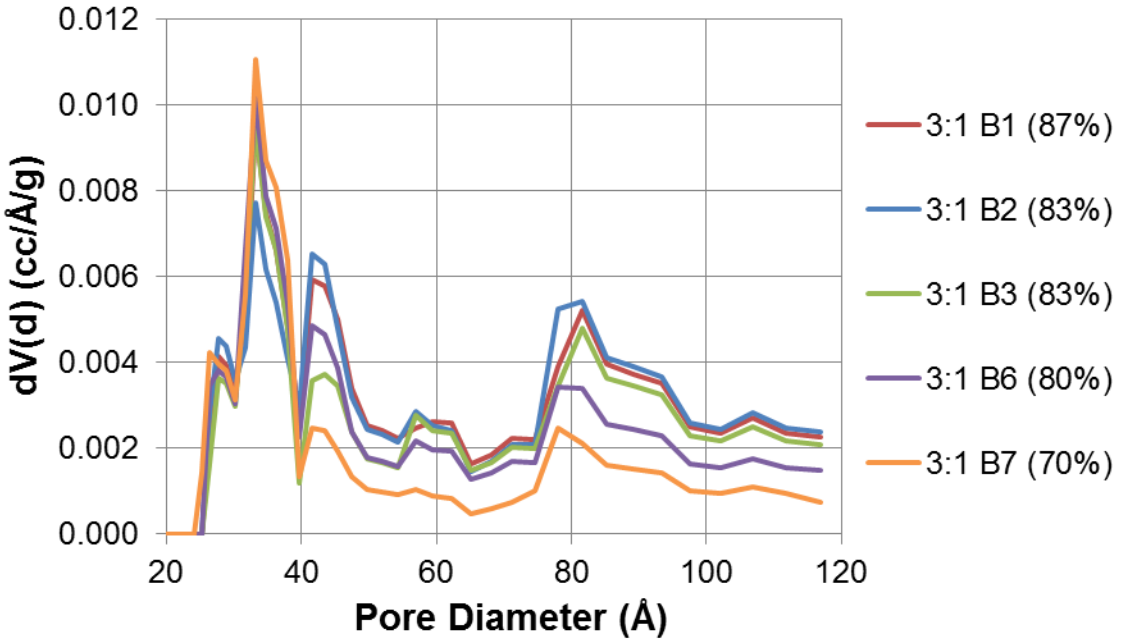


Figure 4-13. Density functional theory mesopore size distribution for several 3:1 calcium samples, derived from N_2 adsorption isotherms

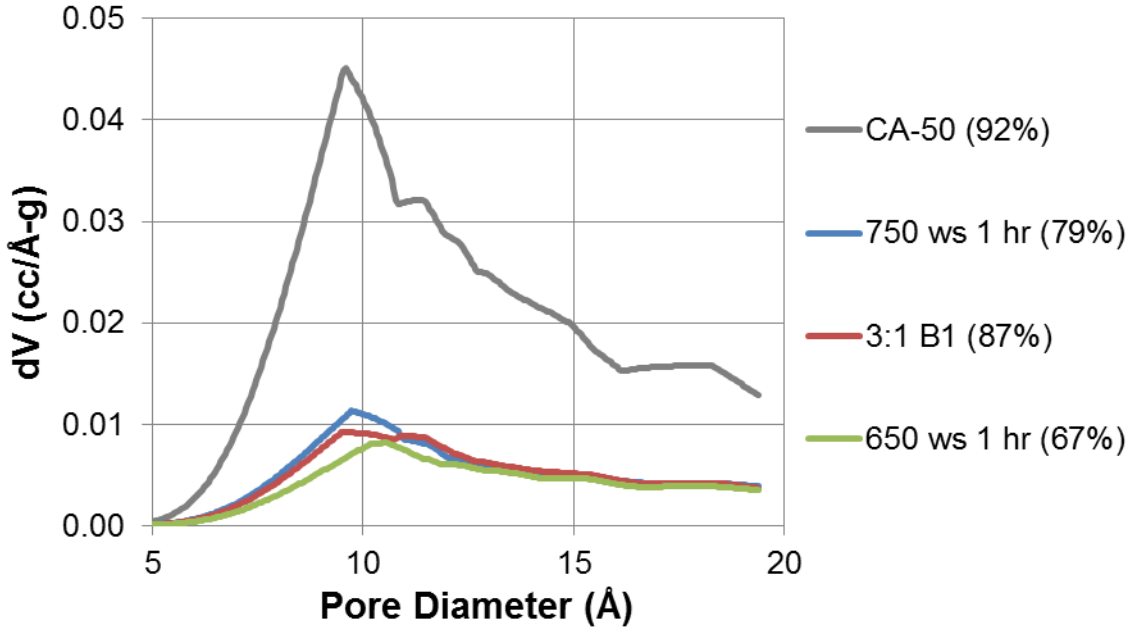


Figure 4-14. Horvath-Kawazoe micropore size distributions for CA-50, 750 ws 1hr, calcium sample 3:1 B1, and 650 ws 1 hr

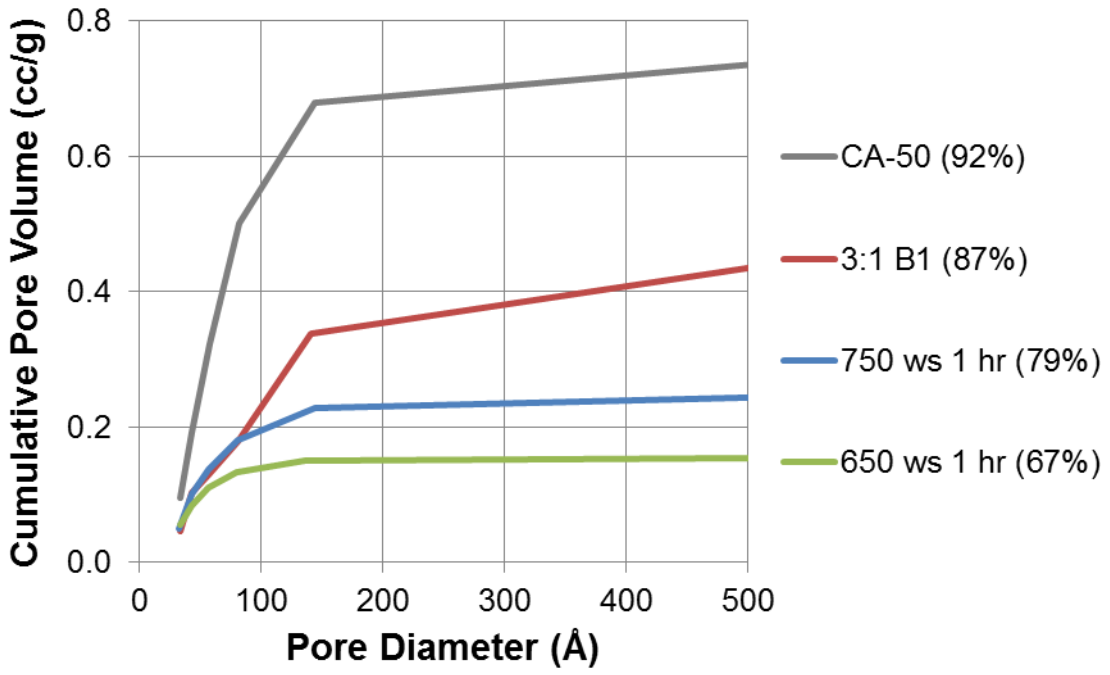


Figure 4-15. Brunauer, Emmett, and Teller mesopore cumulative volume model for CA-50, calcium sample 3:1 B1, 750 ws 1 hr, and 650 ws 1 hr.

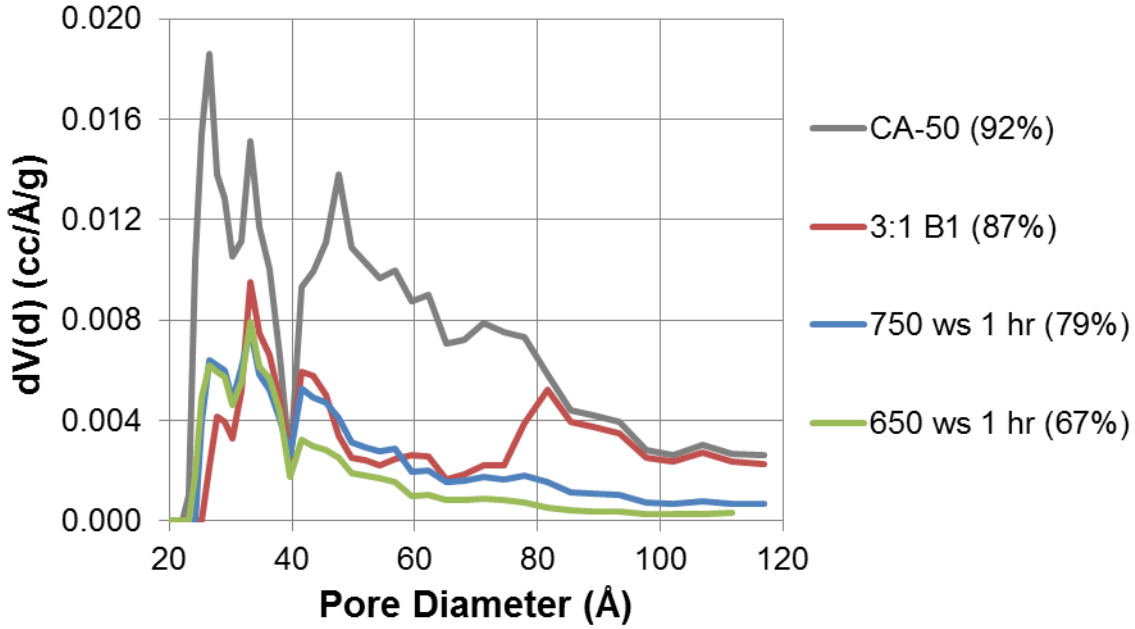


Figure 4-16. Density functional theory mesopore size distribution curves for CA-50, calcium sample 3:1 B1, 750 ws 1 hr, and 650 ws 1hr

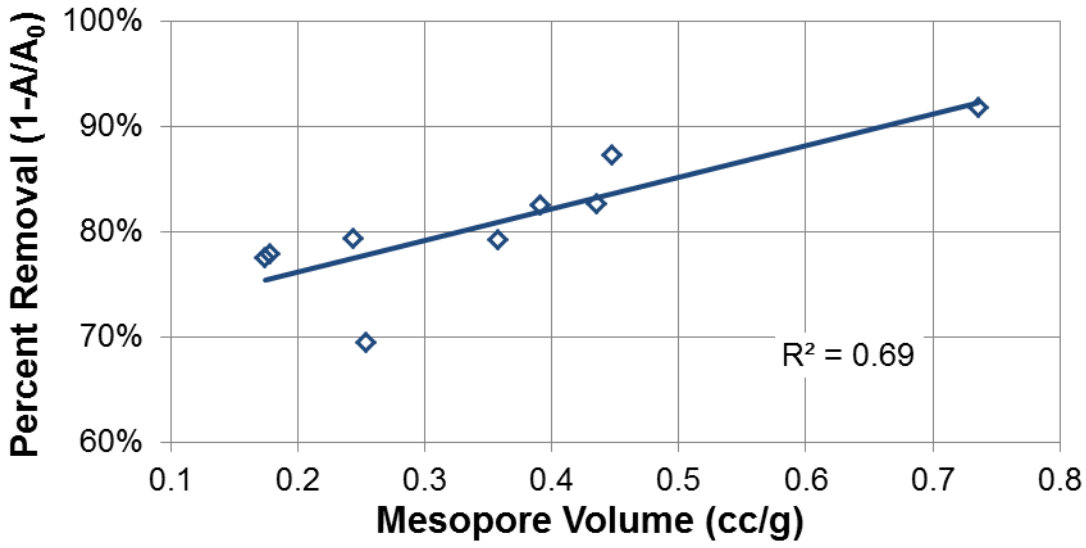


Figure 4-17. Percent apple juice color removal against mesopore volume for all samples with nitrogen gas adsorption isotherms

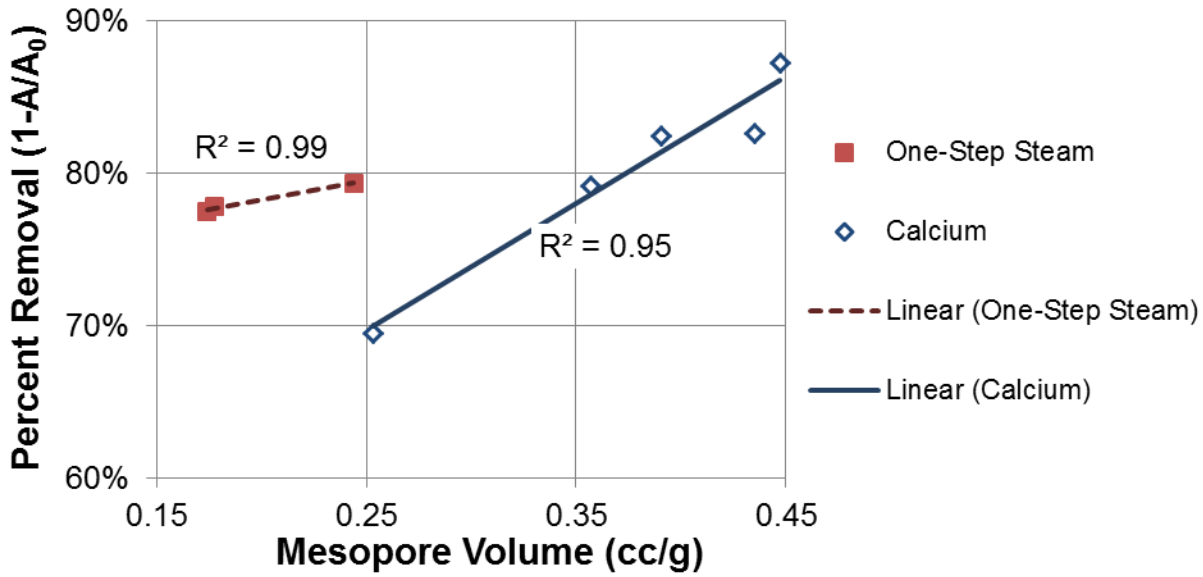


Figure 4-18. Percent apple juice color removal against mesopore volume for tested one-step steam and calcium samples

Table 4-1. Summary of CA-50 decolorization and pore analysis tests

Apple juice decolorization	BET surface area (m^2/g)	Avearge pore size (Å)	Micropore volume (cc/g)	Mesopore volume (cc/g)	Total pore volume (cc/g)
92%	1,500	34	0.5	0.74	1.30

Table 4-2. Summary of pore analysis for 650°C, 1 h carbonized sample

BET surface area (m^2/g)	Average pore size (Å)	Total pore volume (cc/g)
200	20	0.09

Table 4-3. Summary of 650°C one-step steam for 1 h and 750°C one-step steam at 1, 2, and 3 h decolorization and pore analysis tests

Activation temp. (°C)	Activation time (h)	Apple juice decolorization	BET surface area (m^2/g)	Avg. pore size (Å)	Micropore vol. (cc/g)	Mesopore vol. (cc/g)	Total pore vol. (cc/g)
650	1	67%	600	25	0.23	0.15	0.39
750	1	79%	630	30	0.23	0.25	0.49
750	2	78%	820	25	0.30	0.18	0.50
750	3	78%	710	25	0.25	0.19	0.45

Table 4-4. Summary of 3:1 calcium samples B1, B2, B3, B6, and B7 decolorization and pore analysis tests

3:1 Sample	Apple juice decolorization	BET surface area (m^2/g)	Avg. pore size (Å)	Micropore vol. (cc/g)	Mesopore vol. (cc/g)	Total pore vol. (cc/g)
B1	87%	710	42	0.29	0.45	0.75
B2	83%	710	41	0.29	0.44	0.74
B3	83%	630	41	0.26	0.39	0.65
B6	80%	690	37	0.28	0.36	0.64
B7	70%	600	33	0.24	0.25	0.50

CHAPTER 5
CONCLUSION

The goal of this research was to produce a mesoporous and high volume (> 0.75 cc/g) PAC from sawdust for the removal of the color found in apple juice. Apple juice color adsorption tests were performed at the lowest, maximum color removal dose of 5,000 mg/L. This high of a dose can become very costly when used to treat large quantities of apple juice.

Pyrolysis and subsequent methylene blue and congo red dye adsorption and nitrogen gas adsorption tests verified that pyrolysis at varying temperatures under nitrogen gas led to a very rudimentary pore structure with little BET surface area (650°C: 200 mg/g) and pore volume (650°C: 0.09 cc/g).

One-step steam activation at a temperature range of 450°C-800°C for 1 h had apple juice color test results that showed that there was not enough energy at 450°C and 550°C to produce significant porosity. The 650°C and 750°C samples had color removals of 67% and 79% respectively, suggesting significantly more porosity. At 800°C, the removal value drops significantly (28%), most likely due to pore collapse.

Steam samples created at 750°C for 2 and 3 h had color removals near 80%. A two-step, carbonized and steam activated sample tested at similar color removal levels, supporting the claim that one-step steam activation produces activated carbon with comparable color adsorption capacity to that of two-step steam activation. Nitrogen gas adsorption tests found that the micropore volumes do not vary greatly amongst the tested steam samples and that 750°C produced more mesopore volume than the 650°C.

The calcium samples activated under steam at 750°C for 2 h with varying chemical to wood ratios had average color removals similar to that of the 750°C one-step steam samples. The 3:1 chemical to wood samples had a range of 70% to 87%. Compared to CA-50, some of the better performing 3:1 samples had color removal differences of only 5-8%.

Pore analysis found that, on average, the calcium samples had a 40% increase in total pore volume and 80% increase in mesopore volume over 750°C one-step steam activated samples. The calcium samples all had peaks in the DFT mesopore size distribution at 75-90 Å that were unique to those samples, as these pores were created by calcium's catalytic effect on carbon gasification. This peak is where most of the increased mesoporosity comes from. The color removal and BET surface area were not considered statistically different. The statistically substantial increase in mesopore and total pore volumes in the calcium did not come at the expense of microporosity.

For the CA-50, one-step steam, and calcium samples, increasing mesopore volume was linearly correlated to increased apple juice color removal with an $R^2 = 0.69$. Since the calcium and one-step steam samples have very similar pore size distributions before 40 Å, differences in color removal due to pore structure are most likely caused by the variations in the differential volumes of pores with diameters greater than 40 Å.

This research was able to produce a high pore volume PAC with well-developed mesoporosity that also had significant apple juice color removal values (up to 87%) using calcium impregnation combined with one-step steam activation. With further refinement of the chemical activation protocol, a production cost analysis, and an operational cost analysis, it could be possible to produce a consistent calcium activated

PAC that would perform as well as or better than the CA-50 and other similar, more costly activated carbons.

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BIOGRAPHICAL SKETCH

Timothy English II has a Bachelor of Science in Environmental Engineering Sciences from the University of Florida. He received a Master of Engineering in the same program and university. After finishing his degree, he plans on working as a consulting engineer in the fields of water/wastewater treatment and water resources in the state of Florida.