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Color Removal From Pulp Mill Effluent Using Coal Ash Produced From Georgia Power Coal Combustion Plants

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COLOR REMOVAL FROM PULP MILL EFFLUENT USING COAL ASH PRODUCED FROM GEORGIA POWER COAL COMBUSTION PLANTS

by

CHRISTOPHER B. WILLETT

(Under the Direction of George Fu)

ABSTRACT

Two environmental concerns currently face Georgia: coal fly ash (CFA) waste from coal power plants, and the effluent generated by pulp mills. Pulp mill effluent discolors surface waters into which it is discharged, and has been proven to negatively impact the dissolved oxygen and carbon necessary for aquatic life. The proposed solution is a cost-effective adsorption treatment using an inexpensive but abundantly available waste material: CFA. CFA possesses beneficial properties that allow it to effectively remove contaminants, and is available at significantly reduced cost. The primary research objective was to define treatment parameters that would result in the maximum removal of effluent color at the lowest CFA dosage and process cost. Experimentation consisted of batch adsorption studies and several test parameters were varied to determine their effect on removal. Kinetic and isotherm studies were also conducted using the optimal conditions, and the data was fitted to existing adsorption models. In addition, a column study was completed to observe CFA in a continuous flow setting. The research produced a cost-effective adsorption process resulting in 80% color removal, and required no effluent pH adjustment. Color removal by CFA was observed to occur primarily in the first hour, with the adsorption achieving equilibrium at 24 hours. Additionally, the Ho et al. kinetic model and the Langmuir and Freundlich isotherm models best described the observed adsorption phenomena.

Overall, this research found CFA to be a promising low-cost adsorbent for the removal of color from pulp mill effluent.

KEY WORDS: Coal Fly Ash (CFA), Pulp Mill Effluent, Color Removal, Adsorption

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DEDICATION

This work is dedicated to Georgia Southern University. I’ve witnessed the enrichment and empowerment of not only my life, but countless others by the caring and dedication of this establishment’s faculty. My gratitude is everlasting for the time I spent there.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1:

INTRODUCTION

1.1 Problem Statement

Historically, one of the worst polluters in the United States has been the pulp and paper making industry. Pulp and paper mills in the US produce 58 million tons of pulp and 90 million tons of paper annually, and are the largest industrial consumer of fresh water (Energetics Incorporated 2005, Office of Water 1997). Approximately 8,000 gallons of water is required to manufacture each ton of pulp and paper, of which up to 85% is discharged as effluent containing numerous organic/inorganic pollutants and coloring compounds (Office of Water 1997, Jain, Kumar and Izazy 2009). The Clean Water Act of 1977 placed stringent restrictions on effluent concentrations of compounds proven to be either acutely or chronically hazardous, such as dichlorodiphenyltrichloroethane (DDT), but other unregulated compounds still pose an environmental concern. One such compound in post-treatment paper/pulp mill effluent is color, the derivative of dissolved wood fibers. Water-borne color is not considered acutely hazardous, but it can negatively affect surface water aesthetics, dissolved oxygen concentrations, and may be toxic to aquatic life (Jain, Kumar and Izazy 2009, Morrison 2012, Singh, et al. 2003).

Environmental damage from paper/pulp mills discharge is especially pronounced in the Southern US, which is the largest paper-producing region in the world (Wear and Greis 2002). The South hosts 70% of domestic pulp mills due to the proximity of wood sources (Energetics Incorporated 2005) with Alabama, Georgia, and South Carolina having 17, 14, and 10 pulp mills, respectively. In terms of the monetary value of pulp produced, Georgia ranks fourth in the nation (Kramer, et al. 2009). A prominent local example of environmental degradation by pulp mill effluent is that of the Altamaha River, which is considered the state's 2nd dirtiest by the Georgia Water Coalition (Cook and Ingle 2011). As recently as 2011, its waters remained colored brown by the effluent discharged by a pulp mill in Jesup (Morrison 2012). Commercial fishing in the area has witnessed a resulting downturn as “Fishermen catch seemingly healthy fish only to find them reeking of nauseating pulp mill odors when they begin to clean them” (Cook and Ingle 2011). Clearly, a cost-effective solution for color removal must be made available to the local pulp and paper industry to avert similar situations in the future.

A proven and widely used method of color removal from effluent is adsorption via activated carbon. Activated carbon is characterized by high porosity and specific surface area, both of which contribute to its ability to effectively remove a variety of contaminants from water sources (Singh, et al. 2003). The disadvantage of activated carbon is its prohibitive procurement cost, which to date has limited its widespread use in wastewater treatment plants (Jain, Kumar and Izazy 2009). Due to the high cost of activated carbon, there is an emerging body of research characterizing various low-cost adsorbents (LCAs), alternatives to activated carbon that are easily obtainable by wastewater treatment facilities (Singh, et al. 2003). One such material in particular shows promise: Coal Fly Ash (CFA), the combustion byproduct of coal-burning power plants. A collection of studies conducted within the last decade report the successful removal of color and other contaminants from wastewater by CFA (Mishra, Mishra and Khan 2010, Kushwaha, Srivastava and Mall 2010, Ahmaruzzaman 2010, Wang and Wu 2006).

The environmental engineering community is searching for additional constructive uses for CFA, because ash disposal can be extremely costly and represents a serious environmental concern. In 2011, Georgia power plants generated 6.1 million tons of CFA, of which only 40% saw beneficial reuse in agricultural, commercial, or engineering applications (Evans, Becher and Lee 2001, Kosson, et al. 2009). The remainder was likely disposed of in any of the 29 coal ash ponds present in Georgia. Coal ash ponds are disposal sites operated by power plants that hold ash mixed with water for an indeterminate period of time, and represent the greatest environmental challenge of coal combustion (Evans, Becher and Lee 2001). Given the abundance of CFA in Georgia and its favorable adsorption characteristics, this material imay be an excellent choice for treating the large volume of pulp mill effluent also generated in Georgia. The proposed solution is to utilize these two waste products synergistically via adsorption to cost-effectively mitigate the environmental hazards posed by both CFA and pulp mill effluent.

1.2 Objectives

In this research project, batch and column adsorption studies were conducted to determine whether CFA can effectively remove color and organic compounds from pulp mill effluent in a laboratory setting. It was hypothesized that CFA can reduce the concentration of color in the effluent by at least 80%, and that this reduction will correlate with a decrease in other organic compounds. The anticipated outcome of this research was to explore an effluent treatment process using CFA as an adsorbent capable of removing 80% of the color from pulp mill effluent.

The specific objectives of this research were to:

a. Determine the optimal CFA dosage that will result in a minimum of 80% removal of the color in pulp mill effluent.
b. Establish what effective initial effluent pH will result in the highest percent color removal.
c. Identify which nominal particle size of CFA will result in the highest percent color removal.

d. Complete a kinetic study to ascertain a reaction equilibrium time and describe the adsorption process using existing kinetic adsorption models.
e. Perform an isotherm study to quantify the adsorption capacity of CFA for color and describe the adsorption process with isotherm models.
f. Describe an approximate relationship between the removal of color and the removal of COD and TOC in treated pulp mill effluent.
g. Monitor levels of heavy metals: lead (Pb), Zinc (Zn) and Chromium (Cr), leached from CFA in treated pulp mill effluent.
h. Perform a continually-operated column study.
i. Estimate the cost of using CFA in a real-world application.

1.3 Summary of Methods

In the batch adsorption study, the effect of several operating variables such as CFA dosage, initial pH of pulp mill effluent, revolutions per minute (RPM) of a shake table, and contact time was investigated. The experiments entailed combining measured amounts of CFA and effluent in flasks and agitating the mixture for several hours. The mixture was then vacuum separated by membrane filtration, and the filtrate collected for analysis. Duplicate samples were used to verify the precision of the results and average measurements between them were recorded. In order to determine a treatment procedure resulting in the maximum possible color removal, each successive batch of samples utilized the optimum treatment parameters defined up to that point.

Sample analysis included the measurement of pH, temperature, and color, COD, Pb, Zn, and Cr. Existing adsorption models were used to characterize the adsorption process parameters. Kinetic and isotherm and kinetic adsorption models describe the interactions occurring between adsorbate (color in pulp mill effluent) and adsorbent (CFA), subsequently aiding in optimization of adsorbent use. Adsorption data from the models also provides a basis of comparison with other adsorbate/adsorbent pairs (Jain, Kumar and Izazy 2009). Student's *t* test was used to determine whether the linear/non-linear estimations of the kinetic and isotherm equation constants were statistically significant at the 95% confidence level ($p < 0.05$). The null hypothesis (H_0) is that the estimations will be non-zero values.

In the column adsorption study, a finite volume of pulp mill effluent was pumped through a hollow glass column containing a measured quantity of CFA to observe the material's capacity to remove color and other contaminants over time. Samples were collected from the column's outlet periodically and analyzed in the same manner as the batch study.

CHAPTER 2:

LITERATURE REVIEW

2.1 Pulp Mill Effluent

2.1.1 Overview

Fresh water is a dwindling resource on this planet, and the shortage is only being compounded by the monumental problem of global water pollution (Jayabalakrishnan, Mahimairaja and Udayasoorian 2009).As of 2004, pulp and paper manufacturing was the fifth largest industry sector in the US economy, and was considered to be the third largest domestic source of surface water pollution. Vast quantities of effluent are produced by pulp and paper mills due to high specific process water consumption. Approximately 4,000 and 12,000 gallons of fresh water per ton of product is consumed, of which 85% is discharged as effluent (Energetics Incorporated 2005, Pokhrel and Viraraghavan 2004). The effluent, which varies depending on themill, is characterized by discoloration caused by organic/inorganic contaminants (Jain, Kumar and Izazy 2009). Increased public concern in the late ‘90s regarding pulp and paper mill effluent led to EPA regulations that limit the concentration of specific pollutant in mill discharge (Federal Register 1998). These measures forced the paper industry to route their effluent through wastewater treatment plants in order to achieve compliant pollutant levels (Pokhrel and Viraraghavan 2004). Pulp mill effluent, specifically, contains far more pollutants than paper mill effluent, and thus are the primary focus of environmental remediation efforts (el khames Saad, et al. 2012). There are two main pulp manufacturing methods: mechanical and chemical pulping. As of 1998, mechanical pulping processes accounted for 10% of US pulp production and results in short, unstable, and impure pulp fibers. Chemical pulp comprised 84% of US production, and pulp manufactured this way is laden with long and strong fibers. The remaining 6% was generated by a combination of mechanical/chemical processes (Office of Compliance 2002).

Due to its prevalence and environmental impact, chemical pulping processes and the resulting effluents were the sole focus of this research. Chemically-derived pulp is composed of cellulose fibers, which have been extracted from input wood by removing a binding agent known as "lignin". Lignin is a natural adhesive present in wood, and is removed by a combination of chemicals, heat, and pressure, collectively referred to as "digestion" (Paper Task Force 1995). The most popular method of chemical pulping in the industry is the Kraft Process, which makes up 83% of annual US pulp production (Office of Compliance 2002). A flowchart of the simplified Kraft Process is shown in **Figure 2-1**.

In the Kraft process, lignin is stripped from wood by digesting it in sodium hydroxide and sodium sulphide (Garg, et al. 2004) in a pressure vessel. Following digestion, the pulp is extracted from the solution. The solution, now referred to as "black liquor", contains lignin and chemical remnants, and is reprocessed to recover most of the chemical mixture (Office of Compliance 2002). Pulp is then treated with a range of acidic bleaching chemicals to remove any remaining lignin. The chemicals include: chlorine dioxide, hypochlorite, oxygen, ozone, hydrogen peroxide, sulfur dioxide, and sulfuric acid. In the "Totally Chlorine Free" variant of the bleaching stage, chlorine dioxide and hypochlorite are omitted (Office of Compliance 2002). The pulp is washed after the application of each chemical. Alkaline lignin extraction and a final wash occur last. The bleaching stage of the Kraft process results in both acidic and alkaline effluent streams (Garg, et al. 2004). After bleaching, the finished pulp is ready to be made into paper. The digestion and bleaching stages of the Kraft process are responsible for the bulk of pollutants in the effluent stream (Office of Compliance 2002).

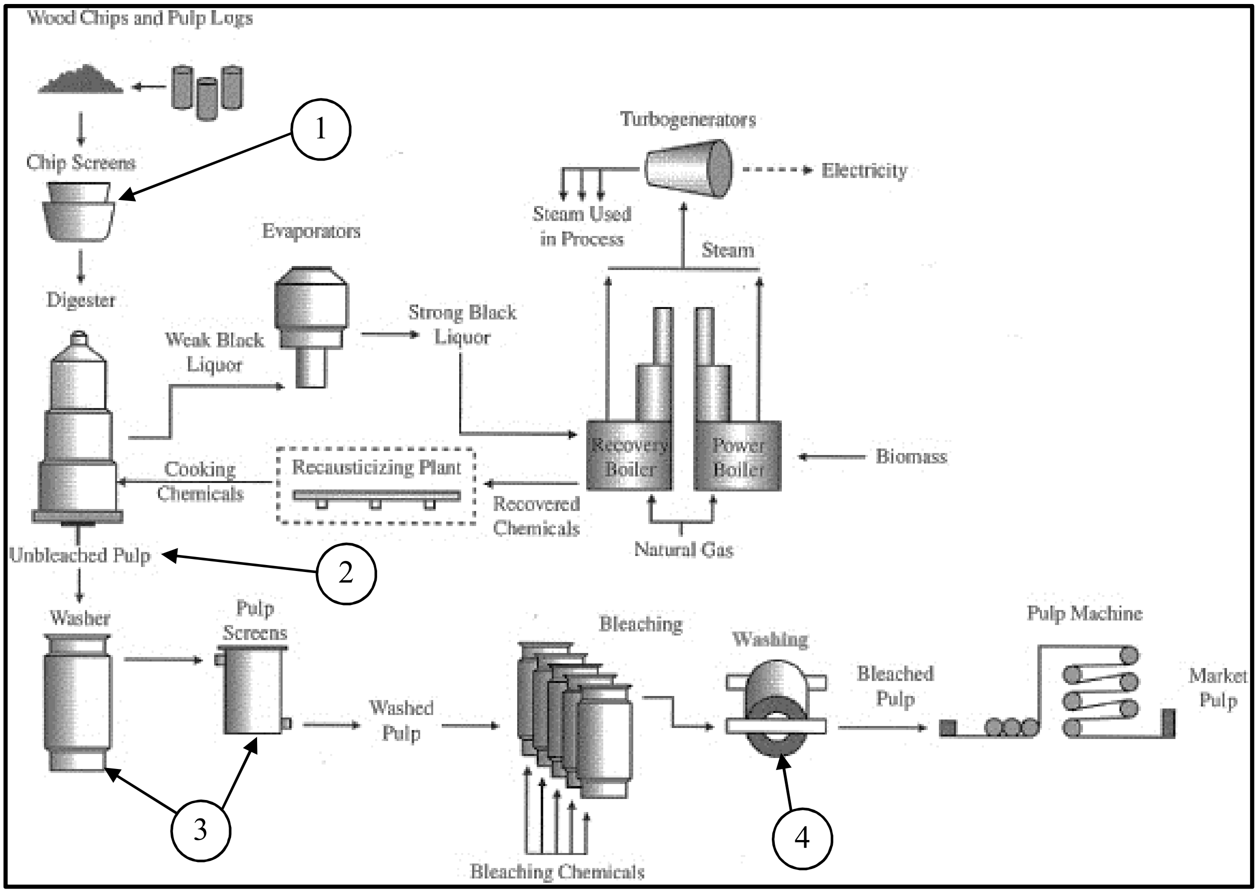

Figure 2-1: Simplified Kraft process diagram. The numbers correspond to the four steps of the process shown in Figure 2-2 (Mercer International Inc. 2012).

By the 1960’s, researchers were becoming aware that untreated pulp and paper effluent was toxic to aquatic species (Dence, Wang and Durkin 1980). Untreated effluent from the Kraft process, specifically, is high in BOD, suspended solids, color, COD, and Adsorbable Organic Halogens (AOX) (Office of Compliance 2002).

These four pollutants (BOD, color, COD, and AOX) are referred to as effluent “summary parameters” because they each measure the aggregate aqueous concentrations of different categories of compounds. BOD is a measure of the dissolved oxygen consumed by microorganisms as they break down biodegradable organic compounds in the effluent. Aquatic biota will suffer from high levels of BOD due to the lack of oxygen (Paper Task Force 1995). Another indicator of organic compounds in effluent is COD, which measures the oxygen demand of chemical contaminants similarly to BOD. However, COD encompasses both the biodegradable and non-biodegradable portion of the effluent (Rice, et al. 2012). The residual chlorine content of organic compounds in effluent is estimated by the parameter AOX. AOX indicates the quantity of adsorbable chlorinated material, but not the toxicity (Paper Task Force 1995). Effluent color indicates the presence and quantity of organic matter from wood, and can obstruct the photosynthetic activity of life in effluent-contaminated waters (Paper Task Force 1995, Jayabalakrishnan, Mahimairaja and Udayasoorian 2009). The effluent pollutants generated by each discreet stage of the Kraft Process are shown in **Figure 2-2**. In this context, VOCs are Volatile Organic Compounds.

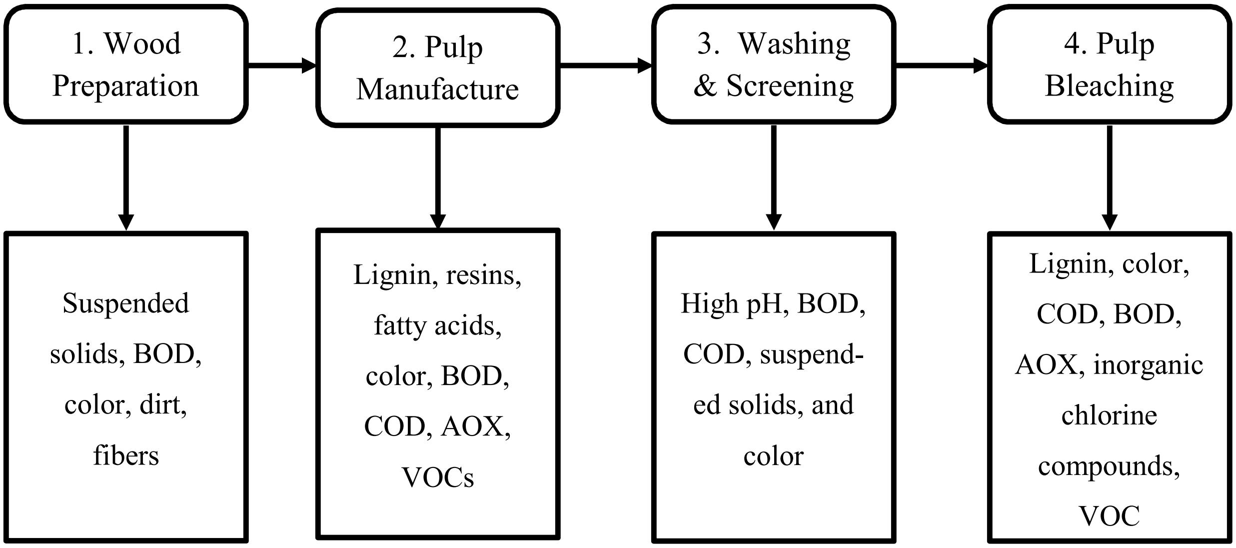

Figure 2-2: Pulp mill effluent pollutants generated at each stage of the Kraft process. (Pokhrel and Viraraghavan 2004)

To decrease pollutant concentrations to EPA-compliant levels, pulp mills treat the effluent in two stages, or more rarely, three stages (Pokhrel and Viraraghavan 2004). The primary stage consists of physiochemical treatment, which removes suspended solids, followed by biological treatment in the secondary stage. Biological treatment involves reacting the effluent with oxygen and microorganisms to remove high concentrations of BOD (Environment Canada 2003). Primary and secondary effluent treatments are generally ineffective at reducing concentrations of color and COD (Pokhrel and Viraraghavan 2004). Not all pulp mill effluent contaminants are biodegradable, so the biological treatment stages have a very limited effect on toxicity and color (Catalkaya and Kargi 2007). Tertiary treatment, which employs processes like adsorption and coagulation to remove color and COD, is rarer in pulp mill wastewater treatment (Environment Canada 2003).

The absence of tertiary treatment processes in most mills is no mystery. Because color is considered an aesthetic property of effluent by the US EPA and other regulatory bodies, no legislation currently exists to limit color (Office of Compliance 1999). Wastewater treatment technology and facilities are expensive (though not as expensive as noncompliance penalties), and the chief concern of managers at most pulp mills is the financial bottom line. In an effort to address ongoing environmental concerns about pulp mill effluent color, significant research into color reduction strategies has been conducted in the last decade (el khames Saad, et al. 2012). Due to the high cost associated with effluent treatment, the majority of current literature focuses on cost-effective methods for removing color. The results of this research will contribute to the emerging body of knowledge related to the removal of color from pulp mill effluent.

2.1.2 Color

Color is a physical property of wastewater. In pulp mill effluent, color comes from the organic compounds extracted from wood during the chemical pulping process, predominantly lignin and tannins. Other compounds, although present in lower concentrations in effluent, can also influence effluent color. These compounds include wood extractives, resins, synthetic dyes, metallic ions and humic matter (Jayabalakrishnan, Mahimairaja and Udayasoorian 2009, Paper Task Force 1995). Lignin extraction from wood occurs throughout the Kraft pulping process, meaning each stage can contribute color to the effluent. However, the majority of color (94%) is generated during digestion and is caused by losses of the black liquor. Oxygen delignification and bleaching supply the other 6% of coloring materials in pulp mill effluent (Johnson, et al. 2012). During bleaching, degradation of lignin by chlorine compounds results in byproducts that also add color to the effluent stream (Jayabalakrishnan, Mahimairaja and Udayasoorian 2009). Also worth noting is the variation in effluent color concentrations due to the type of wood fed into the pulping process. Generally, mills processing softwood lumber will generate more darkly colored effluent than those processing hardwoods, because hardwoods contain less lignin (Johnson, et al. 2012).

Aqueous organic compounds commonly impart a yellow hue to pulp mill effluent, which can range from a very light yellow, to golden-yellow, to dark brown-yellow. Effluent color concentration is quantified using the Platinum-Cobalt scale, a standardized color range based on dilutions of a platinum-cobalt standard solution. A Pt-Co solution concentration of 500 ppm is equivalent to 500 Pt-Co Color Units. The aqueous concentration of color in an effluent sample, in mg/L Pt-Co, can be measured by a spectrophotometer operating between the 400 – 700 nm wavelengths (ASTM International 2000). For context, two examples of primary and secondary pulp mill effluent color concentrations are noted in **Table 2-1**.

Table 2-1: Examples of observed pulp mill effluent color values

	Effluent Source	
Color Values	Elemental chlorine free (ECF) Kraft pulp effluent, Brazil[a]	Bleached Kraft pulp and paper mill effluent, Thailand[b]
Primary Effluent	1022 ± 151.2 mg/L Pt-Co	1100 ± 100 mg/L Pt-Co
Secondary Effluent	794 ± 225.7 mg/L Pt-Co	300 ± 50 mg/L Pt-Co

***Sources:* Data from [a] Lopes, et al. 2013, [b] Kreetachat, et al. 2007**

Even though the negative environmental impact of pulp mill effluent has decreased significantly since the 1980s, color removal is still a problem for most Kraft mills, and is perpetuated by a lack of EPA regulations (Johnson, et al. 2012). There is evidence that contradicts the EPA's stance, however. In addition to degrading the aesthetics of rivers/streams, color from pulp mill effluent can interfere with light transmittance in aquatic ecosystems (Paper Task Force 1995). This, in turn, can reduce the production of dissolved oxygen via photosynthesis and diminishes the "self-purification capacity" of bodies of water (Jain, Kumar and Izazy 2009). In 2003, a research team in Canada assessed the domestic pulp and paper industry. They concluded that there were three main effluent pollutants with adverse environmental impacts: suspended solids, color, and organic compounds (Environment Canada 2003).

Color also serves as an indicator parameter to levels of other pollutants like COD and chlorinated organic compounds (also referred to as AOX) in pulp mill effluent. In their work, Kusuma, et al. (2012) state that "based on the fact that the presence of organic material can cause color, it has been suggested that color can be used as a surrogate measure of dissolved organic matter" in effluent. Lignin, the main cause of color, doesn't contribute to effluent BOD loading. Due to its high molecular weight, lignin creates high concentrations of both color and COD (Hsu 2008). It is also the primary source of chlorinated organic compounds created during Kraft pulp bleaching. Secondary pulp mill effluent, in particular, may contain traces of chlorophenols, which are chlorinated organic compounds considered acutely toxic to aquatic life (Garg, et al. 2012). Even today, the discharge of chlorophenols is considered an ongoing issue (Chandra, et al. 2009). Ideally, the removal of color from pulp mill effluent during treatment will coincide with the removal of toxic chlorinated organic compounds.

The available literature supports the idea that the removal of color will result in a reduction of hazardous organics. **Table 2-2** shows the quantitative relationship between pulp mill effluent color and previously identified contaminants. In Kraft pulp mills, levels of COD and color in the secondary effluent tend to exhibit a proportional relationship; i.e. increased color concentrations will correspond with higher COD levels (Paper Task Force 1995). This trend holds true for the reduction of color and COD, as noted by Sharma, Kumar, & Sharma in their 2013 evaluation of an experimental electrocoagulation treatment for pulp mill effluent. The researchers observed identical increases in the removal of both color and COD with increasing treatment duration (Sharma, Kumar and Sharma 2013). Concentrations of color and COD in pulp mill effluent are also tied to the presence of chlorinated organic compounds (Office of Compliance 1999). A widespread alternative to AOX for detecting chlorinated organics in effluent is Total Organic Carbon (TOC) analysis. In 2007, Catalkaya & Kargi determined a relationship between color and organic compounds in pulp mill effluent. The research examined the efficacy of several advanced oxidation methods on the removal of color, TOC, and AOX from Kraft mill effluent. For all oxidation methods studied, color removal and TOC removal were observed to respond nearly identically to varying treatment parameters. Furthermore, removal of AOX exhibited high correlation with color removal. For example, the photo-Fenton oxidation process resulted in the removal of 82% of color, 85% of TOC, and 93% of AOX (Catalkaya and Kargi 2007). In another study, the effect of ozonation on both color and TOC was examined. The results indicate that as ozone exposure time increases, color will decrease proportionately with TOC (Kreetachat, et al. 2007).

Table 2-2: Contaminant concentrations observed in secondary pulp mill effluent

		Source				
Parameter	*Units*	*(El-Fadel, et al. 2012)*	*(Ali, et al. 2013)*	*(Lagos, et al. 2009)*	*(Lopes, et al. 2013)*	*(Sharma, et al. 2013)*
Color	mg Pt-Co/L	2125	1736	110	794	705
COD	mg O_2/L	1074	1810	1196	263	271
BOD	mg O_2/L	518	960	380	45	-
AOX	mg Cl/L	260	32	-	1.5	-

2.1.3 Possible Solutions

Strategies for effluent color reduction focus on either process modification or "end-of-pipe" treatment methods. In process modification, specific components of the Kraft process are altered so that less color is created (Johnson, et al. 2012). An example would be reducing the amount of pulp-borne lignin that enters the bleaching stage by pretreating the pulp with oxygen delignification. Pulp with a reduced lignin content would result in a decrease in color, BOD, and COD compounds discharged from the bleach plant (Paper Task Force 1995). End-of-pipe technologies are synonymous with the tertiary effluent treatment stage discussed earlier. Tertiary treatments are categorized as physical, biological, and chemical; each have advantages and disadvantages. Amongst mills that employ tertiary treatment, membrane filtration, ozonation, coagulation, and adsorption are the predominant methods (Ali, Hashmi and Baig 2013).

2.1.3.1 Physical Treatment

Membrane filtration is the predominant method of physical treatment for removing color. In membrane filtration, pressure forces water through the microscopic pores in the membrane, separating the water from any material larger than the pores (Thompson, et al. 2001). Membrane technologies can be subdivided into the following types (in order of decreasing pore size) : microfiltration, ultrafiltration, nanofiltration, and reverse osmosis (Johnson, et al. 2012). Ultrafiltration, specifically, has implemented at a handful pulp mills effluent color reduction (Thompson, et al. 2001). Ultrafiltration membranes have a pore size of 0.005 - 0.1 μm, and can effectively remove 70% of lignin from effluent (Johnson, et al. 2012). Only low-volume effluent streams are subject to ultrafiltration, as the cost of treatment increases proportionately with volume of fluid treated. One major issue with this technology is that effluent must be pre-treated prior to passing through the membrane in order to avoid fouling it (Johnson, et al. 2012).

2.1.3.2 Biological Treatment

The most effective type of biological treatment for removing color and COD is fungal treatment. In a laboratory environment, fungal treatments have been able to remove 50% of pulp mill effluent color and 60% COD (Pokhrel and Viraraghavan 2004). White rot fungi are the most-used type of fungus used in such treatments. At present, research into fungal treatments for the removal of color is ongoing, but the technology is currently not mature enough for industrial implementation (Johnson, et al. 2012).

2.1.3.3 Chemical Treatment

Chemical treatment methods remove compounds with materials that cause specific chemical reactions. In general, such processes are expensive to implement, and some can result in undesirable byproducts requiring an additional treatment step (El-Fadel, Abi-Esber and Salem

2012). One commonly used tertiary treatment of pulp mill effluent is coagulation and flocculation (Pokhrel and Viraraghavan 2004). In coagulation, metallic salts are used to chemically precipitate lignin and other color-related compounds. Alum, lime, and ferric salts are common coagulants (Jain, Kumar and Izazy 2009). Removal of precipitated compounds is enhanced by agitating the mixture and adding polymers in a process as "flocculation". Polymers aid in the formation of large, easily removed particles called "flocs". Solid materials formed by the coagulation/flocculation process are then removed by dissolved air flotation (Johnson, et al. 2012). In dissolved air flotation, pressurized air is dissolved into the effluent. The pressure is then released in a settling tank, forming small bubbles that carry particles to the surface for removal by skimming. One of the main drawbacks of coagulation/flocculation is the high quantity of sludge generated, which is difficult to dispose of. The process is also expensive (Jain, Kumar and Izazy 2009).

Oxidation by ozone ("ozonation") is another tertiary treatment that can disinfect and de-color pulp mill effluent. Ozone is generated on-site at water treatment facilities by passing dry oxygen or air through a system of high voltage electrodes. This process can effectively remove 85% of color from pulp mill effluent, in addition to significantly reducing COD and toxicity (Ali, Hashmi and Baig 2013). Other sources estimate a 70% reduction in color. However, ozonation treatment requires high energy/chemical input, and is markedly less efficient at high dosages of ozone (Johnson, et al. 2012, Lagos, et al. 2009).

The most attractive treatment option to pulp mills for removing effluent color is adsorption. Adsorption is the process in which matter is extracted from one phase and concentrated at the surface of a second phase. This is a surface phenomenon as opposed to absorption where matter changes solution phase. Activated carbon is the most common material for wastewater treatment by adsorption (Y.-S. Ho 2004). Its effectiveness in the removal of organic and coloring material from secondary effluent, attributable to its high specific surface area, is well established in the literature. Approximately 30-50% of effluent color can be removed by adsorption with powdered activated carbon (PAC). Unfortunately, this material is very expensive to procure, and treated effluent must be filtered to remove any remaining PAC (Johnson, et al. 2012). Other adsorbents have also been studied in a laboratory setting, mainly to develop a low-cost, practical alternative to activated carbon. Such materials include: silica, saw dust, peat, fuller's earth, and fly ash (Jain, Kumar and Izazy 2009).

2.1.3.4 Combined Treatment

Optimum color removal from pulp mill effluent usually occurs with a blend of treatment technologies. A combination of ultrafiltration and dissolved air flotation can remove 70% of TOC and color from pulp mill effluent. Another treatment process involving coagulation and ozonation has resulted in a lignin reduction of 75%. (Ali, Hashmi and Baig 2013). Color and COD can also be removed effectively with a combination of ozonation, adsorption and coagulation (Thompson, et al. 2001).

2.2 Adsorption

2.2.1 Overview

Adsorption, as it pertains to effluent treatment, is a surface phenomenon wherein matter in the liquid phase (the "adsorbate") is extracted from solution and concentrated on the surface of the solid (the "adsorbent"). Extraction occurs at both the exterior and interior pore surfaces of the adsorbent, and is driven by the ionic nature of the adsorbate. Adsorption processes are categorized as either physical or chemical. In physical adsorption, which is common at low temperatures, the adsorbate is retained by van der Waals forces. In chemical adsorption, the adsorbate interacts chemically with the adsorbent's surface, forming stronger bonds. Such bonds are usually formed at higher temperatures. Because both types of adsorption can occur in a system simultaneously, it is difficult to distinguish between them. Both the solubility of adsorbate and solution concentration/pH/temperature affect adsorption efficiency. Adsorption is also influenced by the pore characteristics and available surface area of the adsorbent. The overall rate of adsorption is controlled by the diffusion of the adsorbate into the pore structure of the adsorbent. In general, diffusion progresses more slowly than the adsorption of matter onto a solid's surface (Weber 1972).

There are two types of adsorption treatments for removing contaminants from effluent: batch and column systems. In a batch system, a fixed mass of the adsorbent is mixed continuously with a measured volume of the liquid containing the adsorbate in solution. The mixture is agitated until equilibrium is attained, and then the solid is separated from the liquid. Column systems involve pumping effluent through a column packed with a measured quantity of adsorbent (Weber 1972).

Batch adsorption studies are laboratory-scale batch systems conducted to determine the adsorption capacity of an adsorbent for a specific adsorbate. Adsorption capacity (q_e) is defined as the mass of adsorbate adsorbed per unit mass of the adsorbent at equilibrium (in mg/g). This value is the primary performance indicator for a given adsorbate/adsorbent pair (Ahmad and Hameed 2010). A batch study consists of a series of tests in which a particular test parameter is varied and others are held constant to determine the effect of that parameter on adsorbate solution concentration at equilibrium (C_e, in mg/L). Adsorption systems at equilibrium are described by functions that express q_e as a function of C_e at constant temperature called "isotherms" (Weber 1972). Isotherms are generally used in two ways: the information may be used to "determine suitability of adsorption treatment for a given application" (Sarkar and Acharya 2006), as well as aid in a "predictive modeling procedure for analysis and design of adsorption system" (Sarkar and Acharya 2006). The rate of adsorption for a given system is described by the sorption kinetics, which relate contact time, t, to adsorption capacity at time t (q_t). Kinetic models are used to quantitatively describe the rate of adsorption based on adsorption capacity, as well as to designate a reaction order for the adsorption system (Y.-S. Ho 2006). Both kinetic and isotherm adsorption models are employed to optimize full-scale adsorption systems (Foo and Hameed 2010). The specific models used in this research are described in further detail in Sections 3.3.2 and 3.3.3.

In continuous-flow column systems, effluent is usually pumped downward through the column containing the adsorbent. In this context, the adsorbent volume/mass is referred to as the "packed" or "fixed" bed. The depth of the bed is the defining characteristic of the column. Rate of adsorption is primarily influenced by the concentration of the adsorbate in the solution (C), which in the context of this research is the concentration of color in pulp mill effluent. Continuous-flow column systems are seen as superior to batch systems because there is always fresh solution passing through any given layer of adsorbent (in this case, CFA). This means the adsorbate concentration remains at maximum during column operation, and therefore maximum adsorption takes place until the adsorption capacity of the adsorbent is exhausted. An equilibrium condition is not attained during column operation, as contaminant adsorption onto the bed is continuous. Column systems are characterized by the inlet (C_{in}) and outlet (C_{out}) adsorbate concentrations. Initially, the C_{out} will be very low because the adsorption primarily occurs in the upper layers of the bed in a distinct adsorption zone. The lower layers remove any remaining adsorbate. As the adsorbent becomes saturated, the adsorption zone moves downward through the bed, and the C_{out} increases. When the column's outlet/inlet concentration ratio (C_{out}/C_{in}) reaches 1, the column is in equilibrium with the input liquid, and is considered exhausted. The plot of C_{out}/C_{in} as a function of effluent throughput volume is expressed as a breakthrough curve (Weber 1972). The useful life of the bed will be determined by the shape of the breakthrough curve. The shape of the breakthrough curve is affected by transport processes specific to the adsorbent, and is used to determine the operational life of the bed. This information is in turn used to design full scale effluent treatment processes for treatment plants (Ahmad and Hameed 2010). Column studies, compared to batch studies, are more representative of industrial wastewater treatment processes, and thus are relatively more useful to treatment facilities (Chen, et al. 2012).

2.2.2 Adsorbents

The oldest and most prevalent adsorbent is activated carbon, a highly porous substance largely made of carbon atoms latticed in a complex structure. It is derived from such materials as coal, coconut shells, and wood (Gupta and Suhas 2009, Cabot Corporation 2014). Activated carbon also possesses a high surface area to mass ratio (referred to as "specific surface area"), thermal stability, and low reactivity with strong acids/bases (Foo and Hameed 2010). Specific surface area is particularly relevant to adsorption because adsorption is driven by surface phenomena. High specific surface area has a positive correlation with an adsorbent's porosity, and both properties heavily influence adsorption (Wang, Ma and Zhu 2008). As noted in the literature, the specific surface area of commercial activated carbon is estimated to be 500 – 2000 m^2/g (Gupta and Suhas 2009). Activation of input material occurs most often by steam treatment, or by chemical treatment. In steam treatment, the raw material is first carbonized at high temperatures in an oxygen-free setting. Next, the material is subjected to super-heated steam to remove some of the carbon. The voids left behind are what impart activated carbon with its characteristic porosity. In chemical treatment, wood or a similar material is combined with a dehydrating chemical and heated. The resulting activated carbon has high pore volume and more developed structure compared to steam treated activated carbon. Either activation method results in a highly porous adsorbent (Cabot Corporation 2014). Steam treatment involves high temperatures over a long period of time, while chemical treatment requires washing the finished product to remove residual chemicals (Gupta and Suhas 2009). Commercially available activated carbon takes two distinct forms differentiated by particle size. Powdered Activated Carbon (PAC) has a nominal particle diameter of 0.15 – 0.25 mm, while Granular Activated Carbon (GAC) particle sizes range from 2 – 0.5 mm (Cabot Corporation 2014).

Though activated carbon enjoys near complete ubiquity in adsorption wastewater treatment, its high cost has spurred research into alternative materials. Currently, research in this field focuses on investigating renewable, low-cost adsorbents that will increase industry use of adsorption treatment processes (Foo and Hameed 2010). A low-cost adsorbent (LCA), by definition, "requires little processing, is abundant in nature or is a by-product or waste material from another industry" (Crini 2006). There are three broad categories of LCAs: 1) waste materials from agriculture and industry, 2) natural materials, 3) bio sorbents. All are considered economically viable, and each category contains adsorbents suitable for removing color (Crini 2006). These sorbents are listed in **Table 2-3**.

Table 2-3: LCAs for the removal of color

Low-Cost Adsorbents		
Agricultural/Industrial waste material	Natural Materials	Biosorbents
Coal fly ash[a]	Fuller's earth[a]	*P. chrysosporium*[d]
Activated coke[b]		*A. fumigatus*[d]
Sugar cane bagasse ash[c]		

Sources: **[a] (Pokhrel and Viraraghavan 2004), [b] (Ayman, Smith and Sego 2001), [c] (Jain, Kumar and Izazy 2009), [d] (Chopra and Singh 2012)**

2.2.3 Advantages and Disadvantages of Activated Carbon and LCAs

Activated carbon's main strength is its versatility. A vast range of adsorbates, both organic and inorganic, may be effectively adsorbed on to activated carbon (Foo and Hameed 2010). In addition, this material exhibits high adsorption capacity in most adsorption systems (Jain, Kumar and Izazy 2009). During their investigation of pulp mill effluent color adsorption onto PAC, Ayman, Smith and Sego observed an adsorption capacity of 250 mg color (Pt-Co units) per gram of activated carbon (2001). Another advantage is that commercial GAC requires no alteration for use continuous, column-style wastewater treatment processes. Also, GAC does not need to be separated from the liquid after treatment (Gupta and Suhas 2009). The chief weakness of activated carbon is its high procurement cost. In developed countries, most water and wastewater treatment plants see activated carbon as a pricey, but worthwhile investment. Treatment plants in developing countries generally have less capital to work with, and thus forgo activated carbon entirely (Jain, Kumar and Izazy 2009). Another disadvantage of activated carbon is exhaustion, the point at which it can no longer adsorb contaminants. Regeneration of activated carbon is expensive, and the refurbished material has a diminished adsorption capacity (Gupta and Suhas 2009). Another issue with adsorption systems employing PAC is the necessary liquid/solid separation step following treatment. That said, PAC is still common in wastewater treatment because it’s less expensive and fast-acting compared to GAC (Foo and Hameed 2010, Gupta and Suhas 2009).

The primary advantage of LCAs for the removal of color from pulp mill effluent in a treatment plant is their extremely low procurement and operating costs. In their 2009 review of LCAs, Gupta and Suhas reported the estimated cost of ten different LCAs to be $0.10/kg, and commercial activated carbon was $1.50/kg. Other advantages of LCAs are that many: 1) require no chemical alteration to be effective in removing color, 2) have a higher adsorption capacity for target compounds than activated carbon, and 3) exhibit rapid adsorption rates (Crini 2006). Furthermore, the reuse of industrial/agricultural waste materials as adsorbents benefits the sources of those wastes. It is also important to note that as environmental regulations in developing countries become stricter, the appeal of LCAs for wastewater treatment will increase (Gupta and Suhas 2009). On the other hand, LCAs are disadvantaged by their substantial variability. Both the material characteristics and commercial availability of different LCAs can fluctuate, an undesirable trait in industrial-scale applications. Similarly, different experimental conditions can affect the observed adsorption capacity of LCAs, which can impart uncertainty to claims about their effectiveness (Crini 2006). A glaring omission in the available literature on LCAs is obstacle posed by the most LCA’s small particle size. Most LCAs examined thus far have powder to sand consistency, which does not lend itself to use in an adsorption column. Modifying an LCA into a more easily applied granular form adds expense to the material.

2.2.4 Coal Fly Ash

An LCA that has shown potential to remove color from pulp mill effluent is Coal Fly Ash (CFA). At present, only a handful of studies have investigated the adsorption of color by CFA, but they report that CFA is suitable for pulp mill effluent. However, none of those studies originate from the Southeast, and thus the results are not wholly applicable to the pulp produced in this region. In contrast, the adsorption of industrial dyes from wastewater by CFA has been much more extensively explored. CFA was successfully used to remove reactive dyes (Remazol Brilliant Blue, Remazol Red 133, and Rifacion YellowHED), as well as anionic dyes (Acid Black 1, Acid Blue 193) (Dizge, et al. 2008, Sun, et al. 2010). In a review of LCAs for a dye adsorption application, several of the studies discussed report that CFA was suitable for the adsorption of both acid and basic without pretreatment (Gupta and Suhas 2009). In addition, CFA has been found to effectively adsorb various chlorophenols in a laboratory setting (Blissett and Rowson 2012). The simultaneous removal of both color and hazardous organics (such as chlorophenol) from pulp mill effluent by CFA, at little to no cost, would be enormously beneficial to the Southeast's pulp/paper mills.

Coal-burning power plants generate a multitude of combustion byproducts, 75% - 80% of which is CFA. CFA is the fine mineral powder collected by electrostatic precipitators as the ash is carried through the furnace's smoke stack by combustion exhaust gases (Gottlieb, Gilbert and Evans 2010). Of the estimated 70 million tons of CFA generated annually in the US, approximately 39% is reused, usually as cement/concrete filler (Blissett and Rowson 2012, American Coal Ash Association 2012). The remainder is disposed of in landfills or coal ash "ponds". Coal ash ponds are man-made reservoirs of water near the source power plant into which CFA and other byproducts are dumped as a cheaper alternative to landfills. Unfortunately, the long term suspension of ash in water has been proven to lead the leaching of toxic heavy metals into the pond, subsequently contaminating groundwater (Blissett and Rowson 2012, Sierra Club 2009). Due to the issues mentioned, much research is being conducted on beneficial uses of CFA in order to prevent further environmental contamination.

Several physiochemical characteristics of CFA indicate its suitability in an adsorption application, namely: bulk density, particle size, porosity, water holding capacity, and specific surface area (Ahmaruzzaman 2010). As noted earlier, adsorption capacity is strongly tied to both specific surface area and pore volume. Observed physical properties of CFA samples are shown in **Table 2-4**, where S_{BET} is specific surface area, V is pore volume, and D is average pore diameter. For comparison, the relevant physical properties of activated carbon are: $S_{BET} = 627.29$ m^2/g, $V = 3.876 \times 10^{-1}$ cm^3/g, and $D = 22.41$ nm (Noonpui, et al. 2010). The chemical composition of CFA, listed in **Table 2-5**, primarily consists of: silica, alumina, ferrous oxide, calcium oxide, and carbon. CFA carbon content is measured as the mass burned away in a Loss on Ignition (LOI) test (Ahmaruzzaman 2010). As noted in **Table 2-5**, the chemistry of CFA is variable based on the source coal. CFA is classified by the ASTM as either Class F or Class C. Because the chemical composition of CFA affects its suitability as a cement additive, its ASTM classification mostly pertains to that application. Class F CFA has a mass percentage of SiO_2, Al_2O_3, and Fe_2O_3 greater than 70%, whereas Class C contains less than 50% of those compounds. Generally speaking, "Class C CFA is derived from lignite and sub-bituminous coals and Class F CFA is derived from bituminous and anthracite coals" (Blissett and Rowson 2012).

Table 2-4: Physicochemical properties of CFA samples

Fly Ash[a]	S_{BET} (m^2/g)	V (cm^3/g)	D (nm)	LOI (%)
M7LL	13.2	1.31×10^{-2}	3.96	2.20
M7FL	7.0	1.02×10^{-2}	5.86	2.74
WRFL	10.7	1.10×10^{-2}	4.12	12.96
M5LL	21.1	2.04×10^{-2}	3.88	4.84
MPFL	4.0	4.89×10^{-3}	4.08	4.08

Source: **Data from Wang, Ma, and Zhu 2008**

[a] The samples listed here were collected from the same power plant at different times

Table 2-5: Bulk chemical composition of CFA by source coal type

Component (wt. %)	Bituminous	Sub-bituminous	Lignite
SiO_2	20 - 60	40 - 60	15 - 45
Al_2O_3	5 - 35	20 - 30	10 - 25
Fe_2O_3	10 - 40	4 - 10	4 - 15
CaO	1 - 12	5 - 30	15 - 40
MgO	0 - 5	1 - 6	3 - 10
Na_2O	0 - 4	0 - 2	0 - 6
K_2O	0 - 3	0 - 4	0 - 4
SO_3	0 - 4	0 - 2	0 - 10
LOI	0 - 15	0 - 3	0 - 5

***Source:* Data from Ahmaruzzaman, M. 2010**

2.3 Removal of Color by Adsorption onto CFA

Use of CFA in an adsorption application is a relatively recent development in the domain of wastewater treatment. One of the earliest available papers on the subject, published in 1987, detailed batch studies in which CFA successfully removed phenol from an aqueous solution (Kumar, Upadhyay and Upadhya 1987). However, experimentation with color removal by CFA did not begin in earnest until the EPA published several articles profiling the pulp/paper industry in the mid-1990s (Office of Water 1997, Office of Compliance 2002). Studies that investigated CFA for the removal of color from industrial dye wastewater started with the turn of the century, and have continued to the present. Few studies have examined color removal from pulp mill effluent by CFA, however. In addition, most of the available studies utilized simulated effluent (i.e. lab-prepared solutions representative of effluent) as the adsorbate, and are thus somewhat incomplete characterizations of the CFA/effluent adsorption system. Given the focus of this research, only studies in which effluent samples were collected from actual pulp mills are discussed below.

2.3.1 Batch Adsorption Studies

In batch studies, researchers are trying to determine the effect of several different operating variables, or factors, on adsorption removal efficiency. The factors affecting color adsorption by CFA have been well studied and include: mixing speed/time, CFA dosage, initial effluent pH, and adsorbent particle size. The results of three batch studies are discussed below to outline starting points for the various operating variables in the current research.

One study of interest, *Color removal from paper mill effluent through adsorption technology*, investigated bagasse fly ash to assess the material's suitability for effluent treatment. Bagasse fly ash (a solid waste material from the sugar industry) was obtained locally in India, and was used in batch studies to remove color from secondary pulp mill effluent, also sourced locally. The chemical composition of bagasse fly ash closely matches that of CFA. Contact time, effective adsorbent dosage, and adsorbent particle size were varied in the experiments (Jain, Kumar and Izazy 2009).

Another relevant study that examined color removal from pulp mill effluent was by Tantemsapya, et al. 2004. Effluent samples were collected from the pulp mill's activated sludge wastewater treatment plant. Black wood ash from a dust-fired boiler was used as the adsorbent. The primary compound found in black wood ash, silicon dioxide (SiO_2), also forms the bulk of CFA's chemical makeup. Therefore, the color removal efficiency of black wood ash should indicate how CFA will perform. Experimentation by the authors consisted of batch studies to determine the optimum mixing speed/time, pH, and wood ash dosage for the adsorption system (Tantemsapya, Wirojanagud and Sakolchai 2004).

In a similar vein, adsorption treatment of pulp mill effluent by CFA was recently investigated by Andersson, et al. in 2012. Their aim was to address the shortcomings of conventional biological treatment of effluent by using CFA to remove residual lignin compounds, in addition to TOC and COD. A Norwegian thermomechanical pulp mill supplied the effluent samples; CFA samples came from the mill's coal-fired steam boilers.

Additionally, it is important to note the general procedure in batch adsorption studies. Each "batch" consists of several flasks containing measured quantities of adsorbent and adsorbate. The two materials are then mixed continually in the flask by an orbital shake table for a predetermined period of time. After this, the liquid and solid components of the mixture are separated by vacuum filtration through fiberglass filters. The resulting filtrate is then be analyzed by a spectrophotometer for adsorbate concentration (Andersson, Eriksson and Norgren 2012).

2.3.1.1 Mixing Speed / Time

The rotational speed (in revolutions per minute, RPM) at which an orbital shake agitates a CFA/effluent mixture during a batch study determines the frequency with which molecular color compounds come into contact with suitable adsorption sites. Initially, such sites are highly available, leading to rapid color removal at high mixing speeds. Experimental results bear this out, as mixing speed was found to have a significant effect on percent color removal from effluent by the black wood ash. A two-step mixing process utilizing high and low speeds sequentially was determined to be optimal for color removal. Batches of ash and effluent were mixed at 150 RPM for 2 minutes, then 30 RPM for 30 minutes (Tantemsapya, Wirojanagud and Sakolchai 2004). In contrast, researchers utilizing CFA found that the optimum mixing speed/time for color removal was 200 RPM for 6 hours. They also note that 6 hours was the observed equilibrium time for the system (Andersson, Eriksson and Norgren 2012). Due to the differences between the wood ash and CFA in mixing speed/time required for maximum adsorption, the optimum parameters for CFA will be used as a starting point.

2.3.1.2 Effective pH

The effect of initial pH on color removal was studied by Tantemsapya, Wirojanagud and Sakolchai by adjusting pulp mill effluent pH to 2, 4, 6, 8, and 10 prior to adding black wood ash. The results show that the maximum removal efficiencies of color, COD, and lignin were achieved at a lower pH. At a pH of 2, the following removal occurred: 42.2% (color), 31.1% (lignin), and 29.7% (COD) (Tantemsapya, et al. 2004). Given that the chemical profile of CFA most closely matches black wood ash, it is likely that color removal will take place at a lower initial pH. Furthermore, the strong correlation between the removal of color, COD, and lignin by black wood ash indicates that CFA should exhibit a similar capacity for the simultaneous removal of these compounds.

2.3.1.3 Adsorbent Dosage

Adsorbent dosage is the single most important factor affecting removal efficiencies, as it defines to total number of adsorption sites available. Unfortunately, the observed effective ash dosage can vary markedly between different studies. In their equilibrium experiment bagasse fly ash, researchers observed increased color removal (from 28% to 86%) as the adsorbent dosage was incrementally increased from 0.5 to 2.0 g/L. Beyond the effective dosage of 2.0g/L, no significant color removal occurred (Jain, Kumar and Izazy 2009). The effective wood ash dosage for color removal from pulp mill effluent was determined to be 20 g/L. At this dosage, black wood ash achieved the following maximum removal efficiencies at an initial pH of 2: 42% (color), 31% (lignin), and 30% (COD) (Tantemsapya, Wirojanagud and Sakolchai 2004). Researchers investigating lignin removal from pulp mill effluent found that the percentage removed tended to increase with higher CFA dosages. The observed effective dosage of 300 g/L CFA resulted in 97% lignin removal. In addition, lignin removal by CFA contributed to roughly 53-63% of the overall COD removal from the effluent (Andersson, Eriksson and Norgren 2012). The wide range of dosages found to be effective in the various studies suggest that an equally broad range should be explored during experimentation.

2.3.1.4 Particle Size

An evaluation of the effect of ash particle size on color removal from pulp mill effluent showed that smaller particle sizes resulted in the highest percentage of color removal. Removal tended to decrease with increasing geometric mean of particle size (Jain, Kumar and Izazy 2009). Given wide range of particle sizes that constitute CFA, the effect of this parameter on color removal deserves further study.

2.3.1.5 Kinetic Modeling

One of the few available studies that evaluated kinetic adsorption models for color removal by CFA was completed by Prasad and Srivastava in 2009. In their work, CFA was used as an adsorbent to remove color from spent distillery wash. To describe the kinetic parameters of the adsorption system, they evaluated the fit of both the Lagergren pseudo-first order and Ho et. al. pseudo-second order kinetic models to their kinetic study data. The researchers reported that the Ho et. al. model provided the best fit to data, with an R^2 value of 0.996. The Lagergren model provided a less favorable, though still viable fit, with an R^2 value of 0.900 (Prasad and Srivastava 2009). Therefore, both models were evaluated in the current research.

2.3.1.6 Isotherm Modeling

For bagasse fly ash, equilibrium data obtained during batch studies was modeled using the linear versions of the Langmuir and Freundlich isotherm equations, and fit both well (Jain, Kumar and Izazy 2009). Experimental data from black wood ash adsorption studies was also modeled using the linearized Langmuir and Freundlich isotherms, and both returned acceptable correlation. Correlation coefficients (R) for the Langmuir plot ranged from 0.8 – 0.9, while those for the Freundlich plot ranged from 0.78 – 0.92. Overall, the authors concluded that the observed adsorption mechanism of black wood ash is physical adsorption, with a monolayer coverage characteristic (Tantemsapya, Wirojanagud and Sakolchai 2004). The Temkin, Langmuir, and Freundlich isotherms have been used to describe adsorption phenomena observed during experiments utilizing CFA for lignin removal from pulp mill effluent. The experimental data exhibited the best fit with the Freundlich model, but all three models provided acceptable correlation coefficients (Andersson, Eriksson and Norgren 2012). Isotherm equation constants, as estimated by the above authors, are listed in **Table 2-6**.

Table 2-6: Isotherm Equation Constants and Correlation Coefficients for Fly

Fly Ash Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	Q_0 (mg/g)	b (L/mg)	R^2	K_F (mg/g)(mg/L)	1/n	R^2
Bagasse Fly Ash[a]	88.5	1.71	-	68.09	0.0852	-
Wood Ash[b]	20.53	0.00088	0.814	0.9367	0.0177	0.776
Coal Fly Ash[c]	28	0.0017	0.969	0.5	0.53	0.997

Sources: **[a] (Jain, Kumar and Izazy 2009), [b] (Tantemsapya, Wirojanagud and Sakolchai 2004), [c] (Andersson, Eriksson and Norgren 2012)**

2.3.1.7 Leaching of Heavy Metals

Examination of the available literature reveals cautionary information regarding the use of CFA for wastewater treatment. CFA has the potential to leach heavy metals into water, leading to secondary environmental contamination. In general, researchers have found that “the surface layer of fly ash particles probably only microns in thickness, contains a significant amount of readily leachable material which is deposited during cooling after combustion” (Wang and Wu 2006). The specific metals of concern are: arsenic (As), chromium (Cr), lead (Pb), selenium (Se), and zinc (Zn), all which are considered hazardous pollutants. Studies that have evaluated the leachability of heavy metals from CFA into water found that leachability of these elements is relatively low, and also heavily dependent on leaching conditions, especially pH (Blissett and Rowson 2012). Generally, rapid leaching of heavy metals tends to occur only at low pH values. However, because of these concerns, the authors mentioned above advise conducting a “leaching behaviour test for the investigated water system” (Wang and Wu 2006). These considerations were addressed in the experimental design phase of the research.

2.3.2 Column Studies

In their investigation of pulp mill effluent treatment with CFA, Andersson, et. al. (2012) also completed a column adsorption study. Breakthrough curves for the columns were determined by varying the initial effluent concentration and CFA bed depth. The specific bed depths used were 3, 4, and 7 cm. Test conditions for the column study are as follows: glass column with 1.3 cm inside diameter, flow rate of 2 mL/min, and 5 mL sample collection volume. Collected samples were analyzed for TOC, COD, and lignin concentration, and the measurements plotted to obtain breakthrough curves for the adsorption. It was observed that the breakthrough time increased with increasing bed depth, and the shape of the breakthrough curves were different. Similar results were observed for varied initial pulp mill effluent concentration; higher initial concentration resulted in a faster time to breakthrough. In addition, the breakthrough curves showed that COD and TOC adsorption by CFA closely matched the adsorption of lignin (Andersson, Eriksson and Norgren 2012).

The behavior of the adsorption columns was described by the Bed Depth Service Time (BDST), Thomas and Clark models. For a CFA bed depth of 3 cm, the Clark and Thomas were nearly identical. However, at bed depths of 4 and 7 cm, the fit of both models was thrown off by the behavior of the column after a C_{out}/C_{in} ratio of 0.7 was reached. The authors noted a much better fit if the data after this point is omitted from the breakthrough curve. **Table 2-7** lists the column model constants determined in the study. Andersson, et. al. (2012) report that all three models adequately describe the adsorption of lignin from pulp mill effluent onto CFA, and that the adsorption capacity estimated by the BDST and Thomas models, were 9.6 and 13.0 mg/g, respectively.

Table 2-7: Thomas and Clark Constants and Correlation Coefficients for CFA

Bed Depth (cm)	Thomas Model			Clark Model		
	k_{Th} (dm^3/min·mg)	q_0 (mg/g)	R^2	R	A	R^2
3	0.0002	13.3	0.908	0.26	45	0.908
4	0.00009	12.9	0.946	0.13	21	0.942
7	0.00004	9.8	0.938	0.05	3.2	0.941

Source: **(Andersson, Eriksson and Norgren 2012)**

CHAPTER 3:

MATERIALS AND METHODS

3.1 Materials

The secondary pulp mill effluent samples for this research were collected at Weyerhaeuser's Port Wentworth location. This mill produces southern softwood, bleached Kraft pulp for "absorbent, paper grade and specialty" applications (Weyerhaeuser NR Company 2007). It is also important to note that the effluent sample collected was secondary effluent, meaning it had already undergone biological treatment in the mill's wastewater treatment facility. Four samples (approximately 5 gallons each) were collected in plastic buckets on 7/30/2013, 9/27/2013, 12/30/2013, and 3/11/2014, respectively. The effluent sample was stored covered at room temperature (20 ± 1°C) in the Water and Environmental Research Lab (WERL) in Carruth Building at Georgia Southern University (GSU) until needed for testing.

CFA samples were supplied by Boral Material Technologies, which is the exclusive contractor handling CFA disposal for Georgia Power, in a 5 gallon plastic bucket May 10, 2013. The ash was collected from the Georgia Power Plant Bowen, a coal-burning power plant in the north Georgia area.. A sieve analysis was conducted to determine the particle size distribution of the CFA.

3.2 Test Methods

3.2.1 Sieve Analysis

The sieve analysis was completed using a Ro-Tap RX-29 Sieve Shaker and Fisherbrand ASTM E 11 test sieves. The specific sieve sizes used were: No. 10 (sieve opening: 2.00 mm), No. 18 (1.00 mm), No. 35 (0.50 mm), No. 50 (0.297 mm), No. 100 (0.15 mm), and No. 325 (0.044 mm). After first stacking the sieves in order of increasing fineness, the mass of the total CFA sample was measured to the nearest 0.1 g and added to the top most sieve. Next, the sieve stack was placed in the shaker and run for 5 minutes. At the end of the test, the material collected in each sieve was weighed to the nearest 0.1 mg. Finally, a logarithmic plot of the CFA's particle size distribution was then prepared (Haver Tyler, Inc 2010).

3.2.2 Color

Color, as noted in Section 2.1.2, was measured using the platinum - cobalt (Pt-Co) scale, which has a range of 0 – 500 Pt-Co units. In all of the experiments conducted, a Hach DR 5000 Spectrophotometer was used to measure the true color of the pulp mill effluent samples with Hach Method 8025. Method 8025, titled "*Color, True and Apparent*", measures the sample's absorbance of light at the 455 nm wavelength. True color, in this context, means that the effluent being measured has been filtered, leaving only dissolved color. To take a color reading, 10 mL of filtrate was poured into a clear glass sample cell. The cell was then cleaned with lint-free wipes to eliminate interference and placed in the spectrophotometer. Prior to each measurement, the instrument was zeroed with deionized water (Hach Company 2005). On two occasions, a 10 point calibration curve for the spectrophotometer was prepared to document the accuracy of all color readings. The concentrations of Pt-Co standard solution used in the calibration are listed in **Table A-1** and **Table A-2**.

3.2.3 pH

The pH of untreated and treated pulp mill effluent samples was measured using an Orion 720A pH meter with an Orion 8102BN pH probe. A three point instrument calibration was performed by measuring the pH of 4.0, 7.0, and 10.0 pH standard solutions and adjusting settings as necessary. The pH meter was calibration prior to each batch of sample measurements.

3.2.4 COD

Measurement of COD was completed using the Hach DR5000 Spectrophotometer and Hach Method 8000: USEPA Reactor Digestion Method. The procedure consisted of adding 2.0 mL of the effluent filtrate to a reagent vial and reacting the mixture in a Hach DRB 200 reactor at 150C for 2 hours. The vials were then cleaned and placed in the Hach DR5000 Spectrophotometer for measurement (Hach Company 2005). Only select samples from each batch were measured for COD concentration, due to the secondary importance of the COD parameter.

3.2.5 Heavy Metals

Three heavy metals, lead (Pb), zinc (Zn) and Chromium (Cr), in treated and untreated pulp mill effluent were tested using the Hach DR5000 Spectrophotometer. Only select samples from each batch were analyzed for the presence of heavy metals, due to secondary importance of these heavy metals in regards to the overall research objectives. Pb measurements were completed using Hach Method 10216. The detection range for this method was 0.1 to 2.0 mg/L Pb. Because the effluent filtrate consistently had a pH between 6 and 9, all samples were first using a "Metal's Prep Set", as recommended in the Hach procedure. The Zn concentration of the filtrates was measured via the USEPA Zincon Method (Hach Method 8009). The detection range for this method was 0.01 to 3.00 mg/L Zn. The chromium concentration of the filtrates was measured via the Alkaline Hypobromite Oxidation Method (Hach Method 8024). The spectrophotometer's detection range for this method was 0.01 to 0.70 mg/L Cr.

3.3 Batch Adsorption Studies

In the batch study experiments, 100 mL of secondary pulp mill effluent and a measured quantity of CFA (the actual mass varied by experiment) were combined in a 250 mL Erlenmeyer flask. The flask was then covered with laboratory film to prevent contamination and evaporation. Each batch of flasks was mixed at either 150 or 300 RPM on a Thermo Scientific MaxQ 3000 Orbital Shaker for a predetermined time at a room temperature of (20 ± 1°C). After mixing, the pH and temperature of the mixture was measured. Next, the ash was separated from the effluent by vacuum-filtering the mixture through a Supor-450 47mm 0.45 µm membrane filter. Filtrate from this process was stored in non-reactive sample vials. Immediately after filtration, the color concentration of each sample was measured. Any samples exceeding the spectrophotometer's detection limit of 500 mg/L Pt-Cu were diluted by half with de-ionized and re-measured. A dilution factor for the reading was then recorded.

In all batch study experiments, duplicate flasks with identical CFA and effluent mixtures were used to represent each sample. Color and pH measurements were taken from each flask, and the average reading between the two identical samples was used for data analysis. In addition, blank samples with no CFA were also run for each batch experiment to determine the impact of color removal by the filtration process.

3.3.1 Preliminary Testing

3.3.1.1 Effective Mixing Speed / Time (Batch Study A)

The effect of different agitation speeds on color removal from pulp mill effluent was studied at 150 and 300 RPM to establish the optimum mixing parameters for future experiments. A CFA dosage of 1 g/L was used for all samples. Four duplicate samples were agitated at each speed, and were removed from the shake table at 30, 60, 120, and 300 minutes to estimate the best contact time for future experiments.

3.3.1.2 Effective Dosage (Batch Study B)

In order to approximate the dosage of CFA necessary to achieve an 80% reduction in color, as outlined in the research objectives, six sample batches were tried. The overall dosage range was from 0.1 to 100 g/L CFA. Each batch used sequentially increasing dosage ranges, albeit with some overlap, to facilitate later comparison among the separate batches.

3.3.1.3 Effective pH (Batch Study C)

The effect of initial effluent pH on color removal by CFA was investigated by varying the pH from 4 to 12 during four separate batch experiments, each with at a different dosage. The test parameters for each batch are listed in **Table 3-1**. For the batches at CFA dosages of 150 and 250 g/L, pH values of 8.3 and 8.7 are the raw effluent's pH. Color removal at the raw effluent's un-altered pH was studied because pH-alteration prior to treatment did not improve color removal efficiencies significantly and would increase the cost of treatment at the industrial level. As noted earlier, blank samples for each pH were included in each batch. Net color removal was determined by subtracting the final color concentration of pH-adjusted blanks from that of samples treated with CFA. The initial un-altered effluent pH that resulted in the maximum color removal was selected for subsequent experimentation.

Table 3-1: Effective pH study experimental conditions.

Sample Batch	CFA Dosage (g/L)	Initial pH	Initial Color (mg/L Pt-Co)	Mixing Speed (RPM)	Mixing Time (hours)
C.1	20	4, 6, 7, 8, 10, 12	572	150	6
C.2	100	4, 6, 7, 8, 10, 12	572	150	6
C.3	150	4, 6, 7, 8, 8.3. 10	928	150	6
C.4	250	4, 6, 7, 8.7, 10, 12	1,152	150	6

3.3.1.4 Effective Particle Size (Batch Study D)

The effect of adsorbent particle size on color removal was studied by first separating bulk CFA with the same sieve shaker used earlier. The three most abundant particle sizes (d_P) by mass percentage, $d_P \leq 0.044$, 0.0.44 – 0.15, 0.15 – 0.297 mm, were used in the batch experiments. Experimental conditions, determined in earlier experiments as optimal for color removal, were: CFA dosage = 250 g/L, Mixing Speed = 150 RPM, Contact Time = 24 hours, Initial Color = 1,152 mg/L Pt-Co.

3.3.2 Kinetic Study (Batch Study E)

Kinetic studies were performed at several CFA dosages to observe the progression of color adsorption in relation to time. An equilibrium time for the adsorption process was also determined from the kinetic studies. The experimental conditions of the three completed batches are listed in **Table 3-2**Error! Reference source not found.. For Batch E.3, the first six values listed for mixing time are in minutes. Batch E.3 was completed because in the preceding two batches, color removal occurred too rapidly for detailed observations to be made. The adsorption capacity of CFA at time *t*, q_t (mg/g), was calculated using the equation:

$$q_t = \frac{(C_i - C_t)V}{M} \tag{1}$$

where C_i is the initial color concentration (mg/L), C_t is the color concentration at time t (mg/L), M is the mass of CFA used (g), and V is the volume of effluent (L) (Hameed, Mahmoud and Ahmad 2008).

Table 3-2: Kinetic study experimental conditions.

Batch	Mixing Time (hours)	Initial Color (mg/L Pt-Co)	Initial pH	Mixing Speed (RPM)	CFA Dosage (g/L)
E.1	0, 0.5, 1, 1.5, 2, 3, 12, 24, 48	570	9.34	150	100
E.2	0, 0.25, 0.5, 1, 1.5, 2, 3, 4, 6, 8, 10, 12, 18, 24, 36, 48	882	9.10	150	250
E.3	0, 5, 10, 15, 20, 30, 1, 2, 5, 8, 12, 18, 24	887	9.10	150	200

Well established kinetic models were used to describe the adsorption rate based on adsorption capacity. During a review of the literature, the Lagergren pseudo-first order and Ho et al. pseudo-second order kinetic models were found to be the most applicable to color removal by CFA. (Ho and McKay 1999, Y.-S. Ho 2006). The Lagergren equation is:

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

The Lagergren rate constant of pseudo-first order adsorption, k_1, is determined by non-linear regression of the plot of q_t vs t. It may also be obtained from the linear plot of $log(q_e - q_t)$ vs t, using the linear form of Lagergren's equation (Hameed, Mahmoud and Ahmad 2008):

$$\log(q_e - q_t) = \frac{\log q_e - k_1 t}{2.303} \tag{3}$$

The Ho et al. pseudo-second-order kinetic equation is:

$$q_t = \frac{{q_e}^2 k_2 t}{1 + q_e k_2 t} \tag{4}$$

The second-order rate constant, k_2 (g/mg h) is determined in the same manner as pseudo-first-order model (Ho and McKay 1999). Likewise, the linear form of Equation 4, described as:

$$\frac{t}{q_t} = \frac{1}{{q_e}^2 k_2} + \frac{1}{q_e} t \tag{5}$$

may also be used to obtain a value for k_2 from the plot of t/q_t vs t (Hameed, Mahmoud and Ahmad 2008, Y.-S. Ho 2006). Both kinetic models were evaluated for the adsorption of color onto CFA to determine their applicability to these materials. Regression analysis of the non-linear equations were completed using Minitab 17, while Microsoft Excel was used for the linear regressions.

3.3.3 Isotherm Study (Batch Study F)

To obtain information about the position of equilibrium between solute and sorbent, equilibrium studies were conducted by varying the CFA dosage above and below the effective 250 g/L. Two batches were run, and the experimental conditions are shown in **Table 3-3**. Data obtained from this experiment was used to calculate the color adsorption capacity of CFA. Adsorption capacity, q_e (mg/g), is calculated by the following equation:

$$q_e = \frac{(C_i - C_e)V}{M} \tag{6}$$

where C_i is the initial color concentration (mg/L), C_e is the final color concentration (mg/L), M is the mass of CFA used (g), and V is the volume of effluent (L) (Hameed, Mahmoud and Ahmad 2008).

Table 3-3: Isotherm study experimental conditions.

Batch	CFA Dosage (g/L)	Initial Color mg/L Pt-Co	Mixing Speed (RPM)	Mixing Time (hours)
F.1	100, 125, 150, 175, 200, 250, 275, 300	928	150	24
F.2	150, 175, 200, 250, 275, 300, 325, 350	1,152	150	24

Well established isotherm models were used to describe the adsorption equilibrium. During a review of the literature, the Langmuir and Freundlich adsorption isotherms were suggested as most applicable to CFA (Y.-S. Ho 2004, Foo and Hameed 2010).

Langmuir's Isotherm model is based on two general assumptions about the adsorption process: 1) adsorbate molecules are adsorbed onto the surface of the adsorbent in a single layer and 2) this phenomena takes place at a finite number of suitable sites that do not interact with each other. The general form of the Langmuir isotherm equation is:

$$q_e = \frac{Q_0 b C_e}{(1 + b C_e)} \tag{7}$$

where C_e is the equilibrium concentration of color (mg/L), q_e is the mass of color adsorbed per gram of CFA at equilibrium (mg/g) (Weber 1972). Q_0 (mg/g) and b (L/mg) are Langmuir constants determined by plotting C_e vs q_e and performing a regression analysis. The former constant is defined as “maximum monolayer coverage capacity” (Dada, et al. 2012), in essence the maximum theoretical adsorption capacity. Constant b is related to the energy or rate of adsorption (Bhattacharya, et al. 2008, Hameed, Mahmoud and Ahmad 2008). For the linear regression analysis of the isotherm, the linear form of Langmuir’s equation was used:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \qquad \textbf{(8)}$$

The linear plot of the Langmuir isotherm was generated by plotting (C_e / q_e) vs C_e. In addition, a non-linear regression analysis was also performed to fit the equilibrium adsorption data to **Equation (7)**, as some authors have noted that linearization of the isotherm equation can possibly induce bias into the analysis (Chan, et al. 2012, Foo and Hameed 2010). The non-linear regressions were completed using Minitab 17.

The Freundlich Isotherm is primarily used to describe non-ideal adsorption processes for powdered adsorbents (Bhattacharya, et al. 2008), often in conjunction with organic/inorganic adsorbates (Hsu 2008). In contrast to the Langmuir model, The Freundlich model assumes multilayer adsorption occurs, rather than monolayer. It also assumes “a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface” (Noonpui, et al. 2010). The Freundlich isotherm equation is:

$$q_e = K_F C_e^{1/n} \tag{9}$$

where K_F (mg/g (L/mg)$^{1/n}$) and n are Freundlich constants (Weber 1972). K_F is defined in the literature as the "adsorption or distribution coefficient" (Sun, et al. 2010) and represents adsorption capacity (Foo and Hameed 2010). Constant n corresponds with adsorption intensity (Sun, et al. 2010). These constants were determined by both linear and non-linear regression. The linear form of the Freundlich equation is:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e \tag{10}$$

The linear plot of the Langmuir isotherm was generated by plotting log(q_e) vs log(C_e). A non-linear regression was also used to fit the experimental data to **Equation (9)**.

3.3.4 Comparison of Powdered Activated Carbon (PAC) and Coal Fly Ash

To better understand and interpret the batch study results for the pulp mill effluent and CFA adsorption reaction, a comparison study using (PAC) was completed. The PAC was prepared by pulverizing Fisher Scientific 0.8 mm granular activated carbon (catalogue number C270C), and then sieving the resultant powder to separate particles sizes. The powders were then mixed in a mass ratio that matched that of the CFA. PAC dosages of 2.5, 5, 7.5, and 10 g/L were added 100 mL of raw pulp mill effluent in conical flasks shaken at 150 RPM for 24 hours. Following this, the mixtures were filtered in the same manner as earlier batch studies, and the filtrates were analyzed for color, COD, pH, and temperature.

3.4 Column Study

In the continuous column study, 12 grams of CFA was packed into a glass column with an inside diameter of 1.27 cm and length of 30 cm. Trial runs of the column study experiment showed that liquid progresses very slowly through CFA when it is packed in a column. Therefore, the CFA was staggered in four separate layers (~ 1.5 cm each), separated by 3 cm of non-reactive sand, as shown in **Figure 3-1**. The CFA was isolated from the sand by sandwiching it between layers of fiberglass to prevent movement of the ash between layers. To eliminate possible interference, the sand was thoroughly washed prior to packing it in the column. Raw pulp mill effluent was pumped into the column at a rate (*Q*) of 0.8 mL/min by a peristaltic pump, as outlined in Figure 3-1. This flow rate was the maximum flow rate achieved in trial runs. Effluent samples were collected at regular intervals: 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 75, and 90 minutes. Samples were immediately analyzed after collection for color concentration. The column was considered to be exhausted when the concentration ratio of effluent to influent (C_{out}/C_{in}) exceeded a value of 0.8.

To better describe the behavior of color removal from pulp mill effluent under column adsorption, the breakthrough data was fitted to the Thomas model. The Thomas model, given in **Equation (11)**, makes three assumptions about the adsorption system being studied: it follows the Langmuir isotherm, it obeys second order reversible reaction kinetics, and that there is no axial dispersion of the adsorbent (Prasad and Srivastava 2009).

$$\frac{C_{out}}{C_{in}} = \frac{1}{1 + e^{\left[\left(\frac{k_{Th}}{Q}\right)(q_0 M - C_{in} Q t)\right]}} \tag{11}$$

In the Thomas model, k_{Th} is the Thomas rate constant (mL/min•mg), q_0 is the maximum color adsorption capacity of CFA (mg/g), M is the mass of CFA (g), and t is time (min) (Fu and Viraraghavan 2003). The linear form of the Thomas equation is:

$$\ln\left(\frac{C_{in}}{C_{out}} - 1\right) = \frac{k_{Th} q_0 M}{Q} - k_{Th} C_{in} t \tag{12}$$

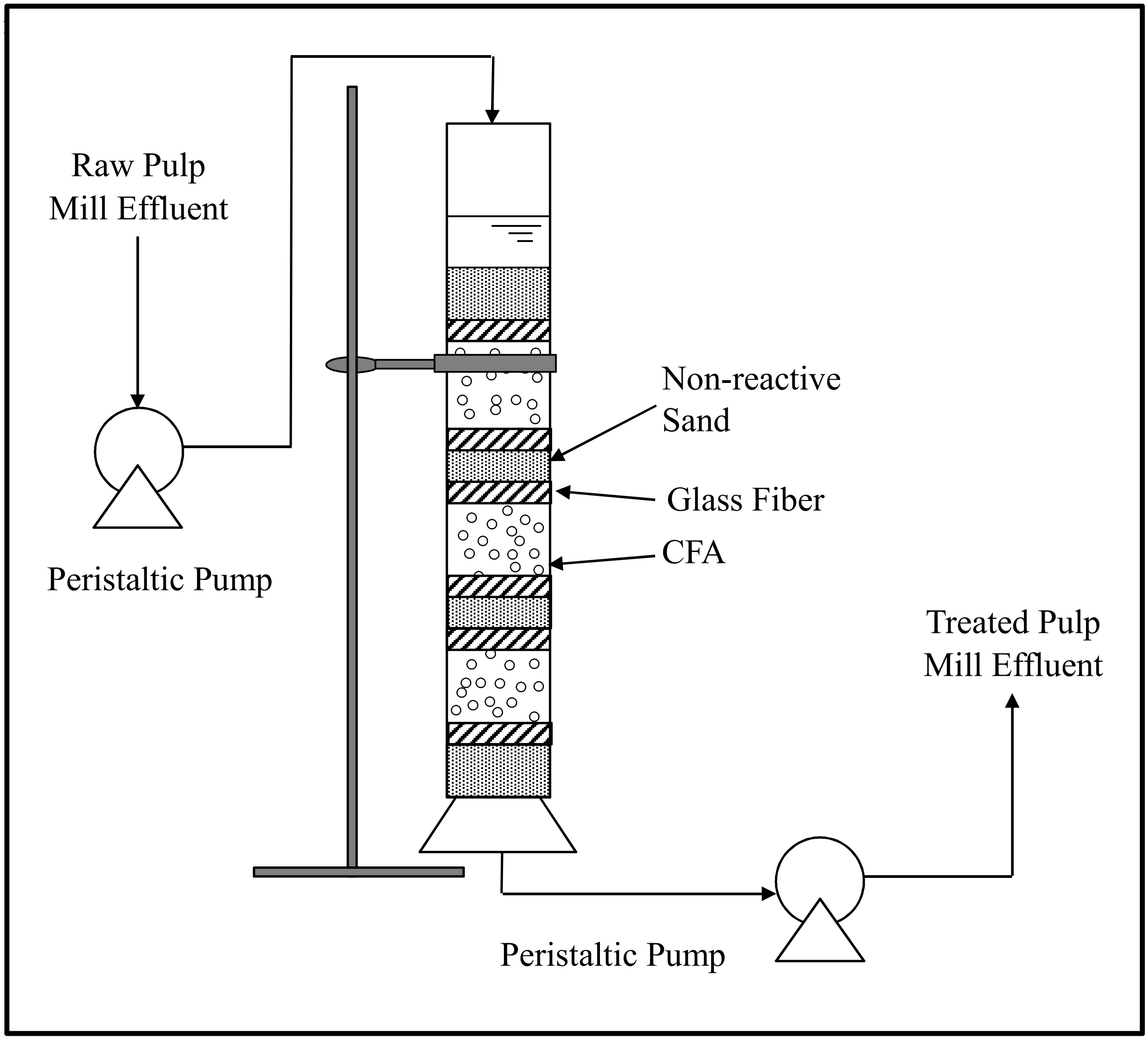

Figure 3-1: Flow diagram for CFA column study.

CHAPTER 4:

RESULTS AND DISCUSSION

4.1 Hach DR5000 Spectrophotometer Calibration for Color Measurement

Calibration curves for Hach Method 8025, along with coefficients of determination, are shown in **Figure 4-1** and **Figure 4-2**. The second calibration was performed prior to analyzing pulp mill effluent samples from the column study to ensure the accuracy of measurements. The high R^2 values indicated that the existing instrument calibration required no adjustment, and that color measurements were accurate throughout experimentation.

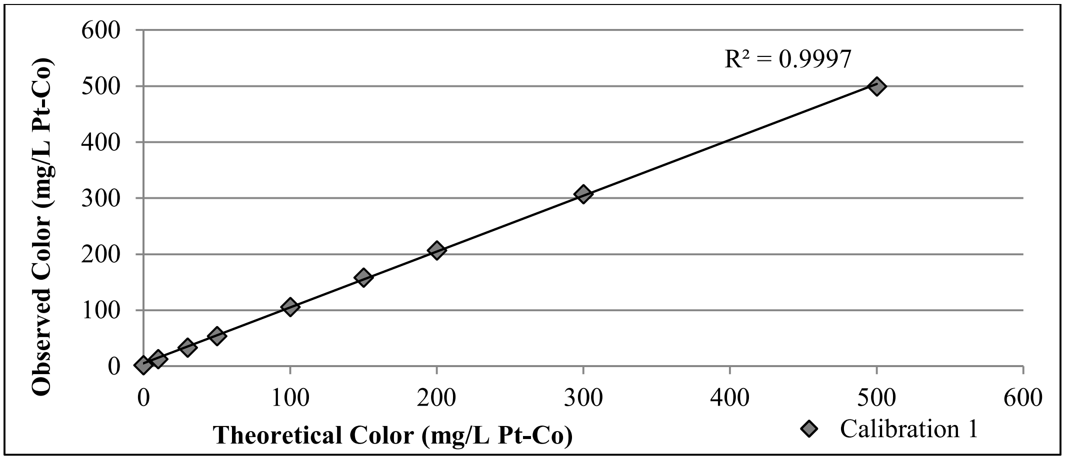

Figure 4-1: Hach DR 5000 Spectrophotometer calibration for color measurement from 8/10/2013.

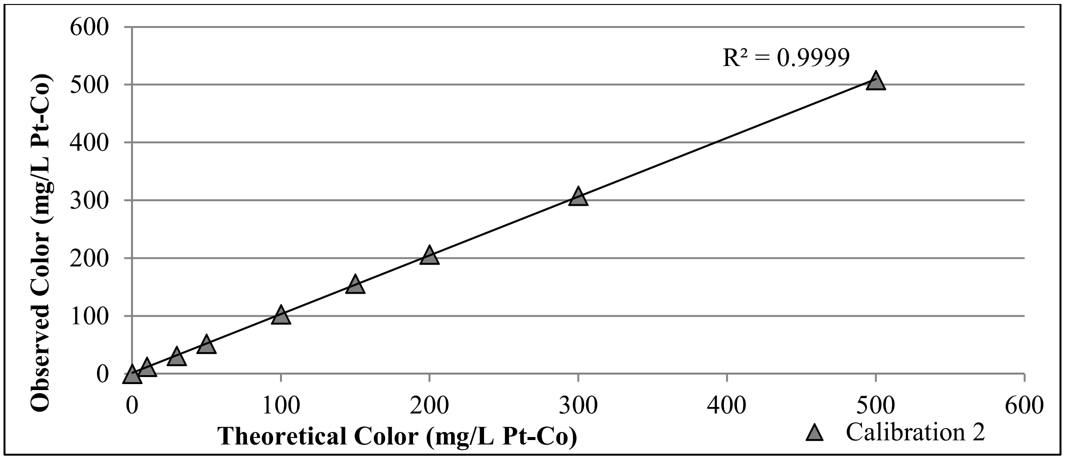

Figure 4-2: Hach DR 5000 Spectrophotometer calibration for color measurement 5/24/2014.

4.2 Raw Material Characterization

4.2.1 Pulp Mill Effluent Characterization

The physic-chemical characteristics of the secondary effluent obtained from the Weyerhaeuser Port Wentworth Kraft pulp mill are presented in **Table 4-1**. The observed raw effluent color concentrations were very similar to those of other Kraft pulp mills (See **Table 2-1** and **Table 2-2**). Effluent pH remained relatively constant across the four samples collected. In addition, there was a distinct correlation between COD and color in the raw effluent; higher levels of color corresponded with higher COD.

Table 4-1: Physico-chemical properties of locally collected secondary pulp mill effluent.

Parameter	Effluent Sample Collection Date			
	7/30/2013	9/27/2013	12/30/2013	3/11/2014
Color (mg/L Pt-Co)	286	571	898	1096
pH	7.96	9.34	9.10	8.70
Temperature (°C)	19.8	15.1	16.6	15.0
COD (mg/L)	-	325	410	630

4.2.2 CFA Characterization

The sieve analysis revealed that most of the Class F CFA obtained from Georgia Power was composed of particles with a d_p less than or equal to 0.044mm. The level of fineness, defined as the mass percentage of CFA that passed through the small sieve (No. 325), was 74.1%. The particle size distribution for CFA is shown in **Figure 4-3**, and the sieve analysis data is presented in **Table A-3**. After completing the sieve analysis, it was determined that the CFA samples provided for this research were neither Class C nor Class F CFA, due to the amount of unburned carbon granules. All of the granules captured by the No. 100 sieve were black, and assumed to be pieces of unburned coal. This development actually benefits the goals of this research, as the CFA samples provided would not be acceptable for use in Portland cement. Thus, the CFA used here would end up in a landfill if no other beneficial reuse could be found.

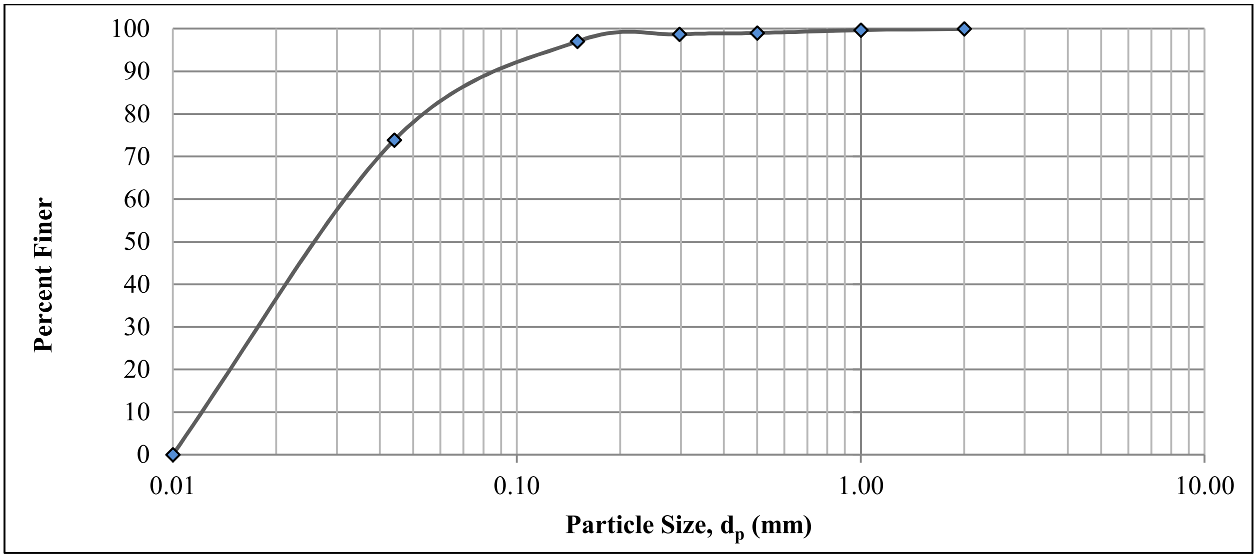

Figure 4-3: Observed particle size distribution of Georgia Power CFA samples.

4.3 Batch Adsorption Studies

4.3.1 Effective Dosage (Batch Study B)

Figure 4-4 and **Figure 4-5** show the results of the experiment over the CFA dosage range studied. The effect of CFA dosage on color removal was the clearest in Batches B.2 and B.4, which are shown in **Figure 4-4**. In the low CFA dosage range (0.1 – 2 g/L), the percent color removal remained nearly constant at 5% as dosage increased. Beginning at 2 g/L, a linear relationship between CFA dosage and color removal develops. The target effluent color removal of 80% was achieved with a CFA dosage of 100 g/L, which then became the standard dosage for future experiments. In **Figure 4-5**, the collective results from all six batches in this study are plotted to emphasize the repeatability with which a specific amount of color can be achieved at a given CFA dosage.

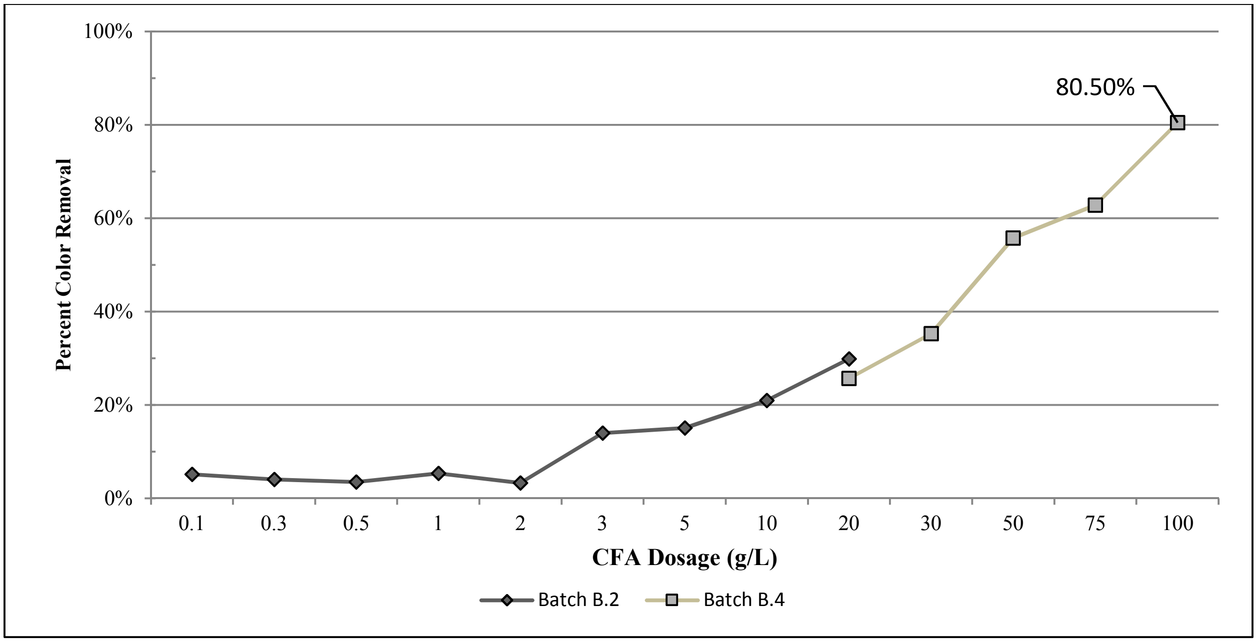

Figure 4-4: CFA Dosage vs. color removal at an initial pulp mill effluent color concentration of 571 mg/L Pt-Co.

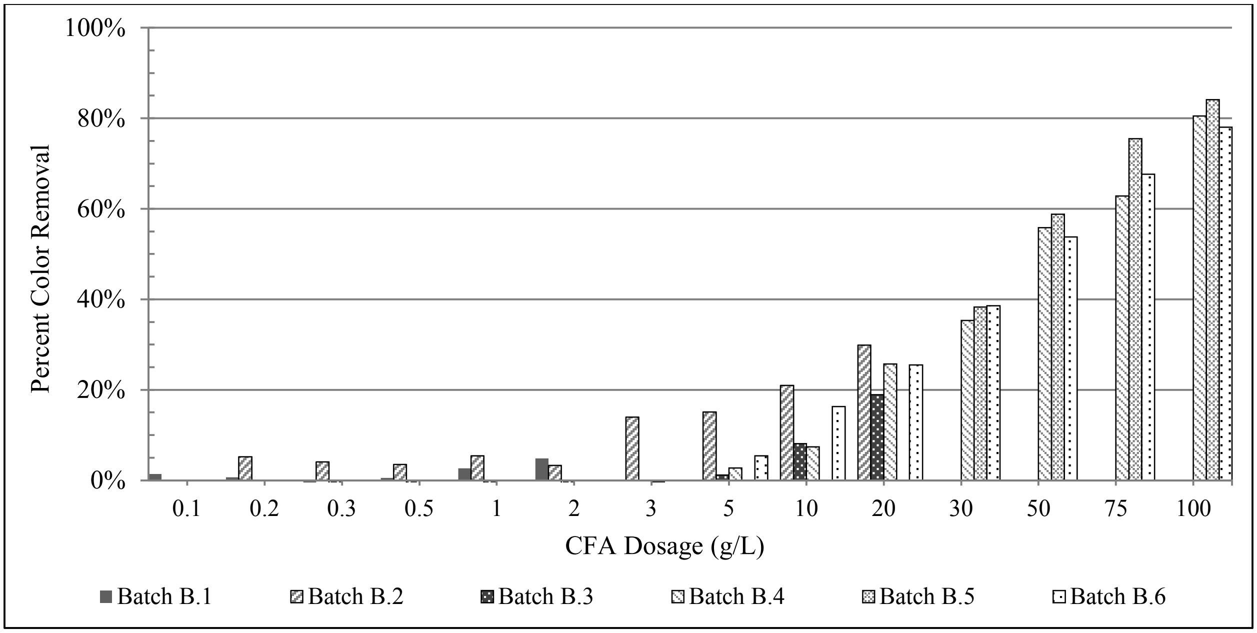

Figure 4-5: CFA Dosage vs. color removal at an initial pulp mill effluent color concentration of 571 mg/L Pt-Co.

After collecting the third sample of pulp mill effluent from the Weyerhaeuser Port Wentworth Kraft pulp mill, color measurements revealed a significantly higher concentration of color from earlier raw effluent (887 vs. 571 mg/L Pt-Co). To maintain a removal efficiency of 80% in future batch studies, a higher CFA dosage was assumed necessary. Therefore, color removal at adsorbent dosage of 150, 200, and 250 g/L CFA were evaluated in a sample batch, and the results of which are shown in **Figure 4-6**. The linear relationship found in earlier studies continues into the high range of dosages, and at 250 g/L CFA, 80% color removal was observed. For the batch studies conducted with raw effluent with color at or above 900 mg/L Pt-Co, a CFA dosage of 250 g/L was used.

Interestingly, there was a broad range of CFA doses reported in the available literature as effective for the removal of color from effluent. Zaharia and Suteu (2013) reported the effective CFA dosage that resulted in 30% color removal from textile mill effluent was 40 g/L. Prasad and Srivastava (2009) noted the effective CFA dosage was 100 g/L CFA, which resulted in 91% color removal. Another relevant study, completed by Andersson et. al. (2012), found an effective CFA dosage for the removal of lignin from pulp mill effluent to be 300 g/L. At that dosage, they observed 97% lignin removal from the effluent.

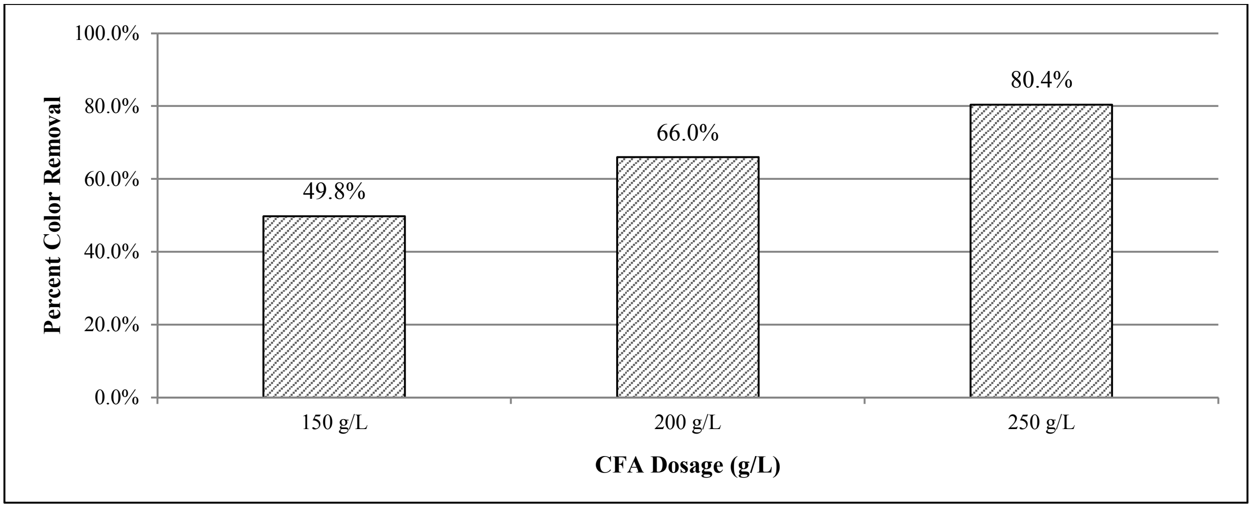

Figure 4-6: CFA dosage vs color removal at an initial effluent color concentration of 887 mg/L Pt-Co.

4.3.2 Effective Mixing Speed (Batch Study A)

The graphical relationship between the rotational speed of the shake table and pulp mill effluent color removal is shown in **Figure 4-7.** It was observed that a higher mixing speed results in higher color removal, although the difference in removal between the two speeds diminishes as contact time increases. The maximum observed color removal at 150 and 300 RPM, with a CFA dosage of 1 g/L, was 9.6% and 6.4%, respectively. Because there was only a 40% difference in maximum color removal values between the two mixing speeds, 150 RPM was selected as the standard speed for future batch experiments. In an industrial setting, the increased energy usage at the higher mixing speed would not be cost effective. Therefore, the results of the batch studies reflect this consideration. For comparison, both Prasad and Srivastava (2009) and Andersson et. al. (2012) found that maximum color removal occurred at a mixing speed of 200 RPM.

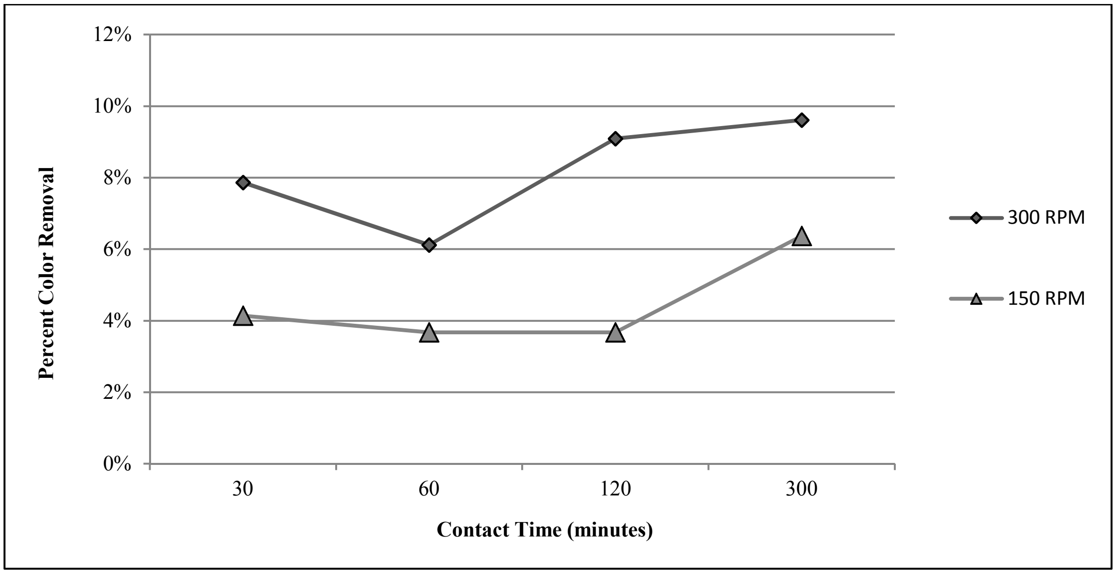

Figure 4-7: Pulp mill effluent color removal vs contact at difference mixing speeds at an initial effluent color concentration of 536 mg/L Pt-Co and CFA dosage of 1 g/L.

4.3.3 Effective pH (Batch Study C)

Figure 4-8 shows the net color removal observed across the pH range for each batch. With a CFA dosage of 20 g/L, the highest net color removal observed was 49% at an initial effluent pH of 4. For all other initial pH values, the average net color removal at this dosage was 14 ± 2%. Because the observed color removal at a CFA dosage of 20 g/L did not meet the research goal of 80%, higher dosages were used in subsequent batches. Maximum color removal for the batches treated with 100 and 150 g/L CFA was observed to be 81% at pH 6 and 57% at pH 7, respectively. These two batches exhibited similar trends across the pH range. Net color removal increased from pH 4 to 6, then decreased from pH 6 to pH 8, and finally increased again as pH became more basic. At a CFA dosage of 100 g/L, a spike in color removal can be observed at pH 12. This may possibly be evidence of researcher error, as no such spike occurs at samples treated with 150 g/L. Disregarding this spike, the average net color removal at 100 g/L was 64± 4%. At 150 g/L, the average color removal was 53 ± 4%. The final batch was treated with 250 g/L CFA, and the maximum net color removal of 77% occurred at pH 6. For an initial sample pH range of 6 to 12, net color removal decreased at pH increased. In general, it was determined that an initial sample pH of 6-7 would result in the maximum amount of color removal at the high CFA dosages necessary to achieve an 80% reduction in color. However, across the pH range, net color removal tended to vary by only ± 5%, indicating the extra effort and cost incurred by pH adjustment does not result in a significant improvement. In support of this finding, Prasad and Srivastava (2009) also found that initial effluent pH had minimal effect on color removal. They reported the most effect pH for color removal to be 7. Therefore, subsequent batch studies occurred at the pulp mill effluent's unaltered pH of 8-9.

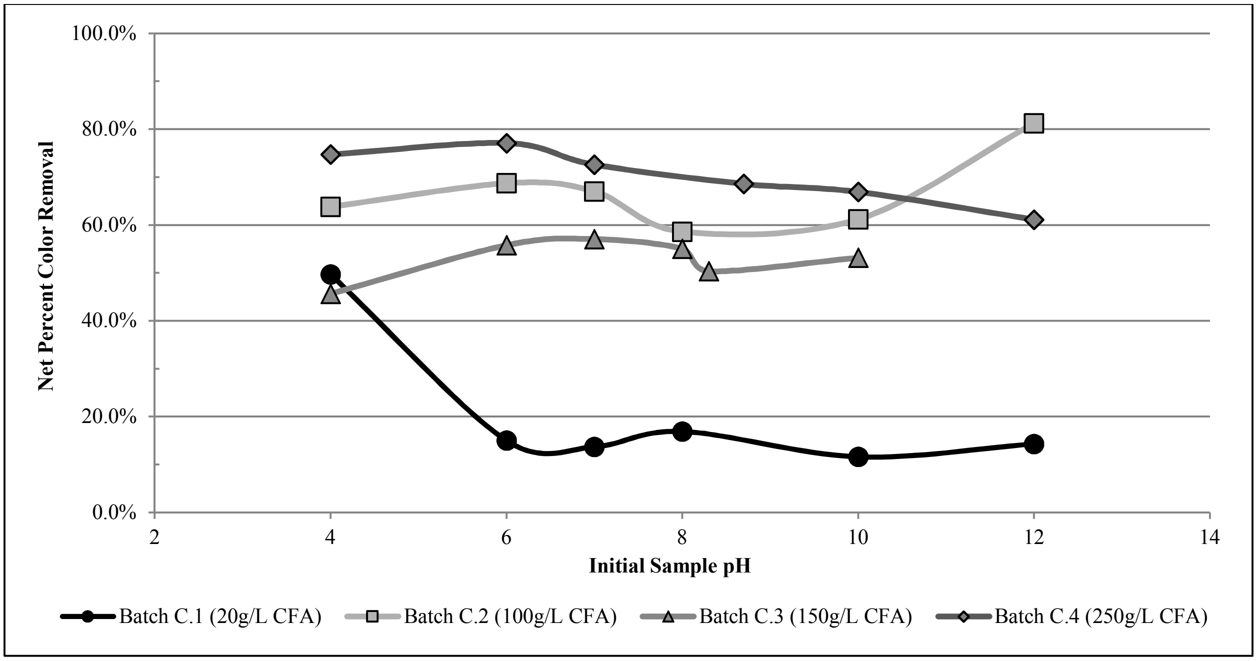

Figure 4-8: Effect of initial effluent pH on net color removal at four different CFA dosages.

4.3.4 Effective Particle Size (Batch Study D)

The particle size of CFA used to remove color from pulp mill effluent was found to have a significant impact on removal efficiency. As shown in **Figure 4-9**, the percent color removal increases linearly as particle size (d_P) increases. The maximum color removal observed (95.2%) occurred with a d_P of 0.15 - 0.297 mm (Sieve #50). Available studies on CFA usage for color removal contradict these findings. Dizge, et al. (2008) found that over a particle size range of 45 – 112.5 μm, the adsorption capacity of CFA for reactive dyes in textile effluent increased as adsorbent particle size decreased. Similarly, Jain et. al. (2009) observed that smaller CFA particle sizes removed more color from pulp mill effluent. The particle size range used in this study was <75, 75–150, 150–200, 200–250, 250–300, 300–425 μm.

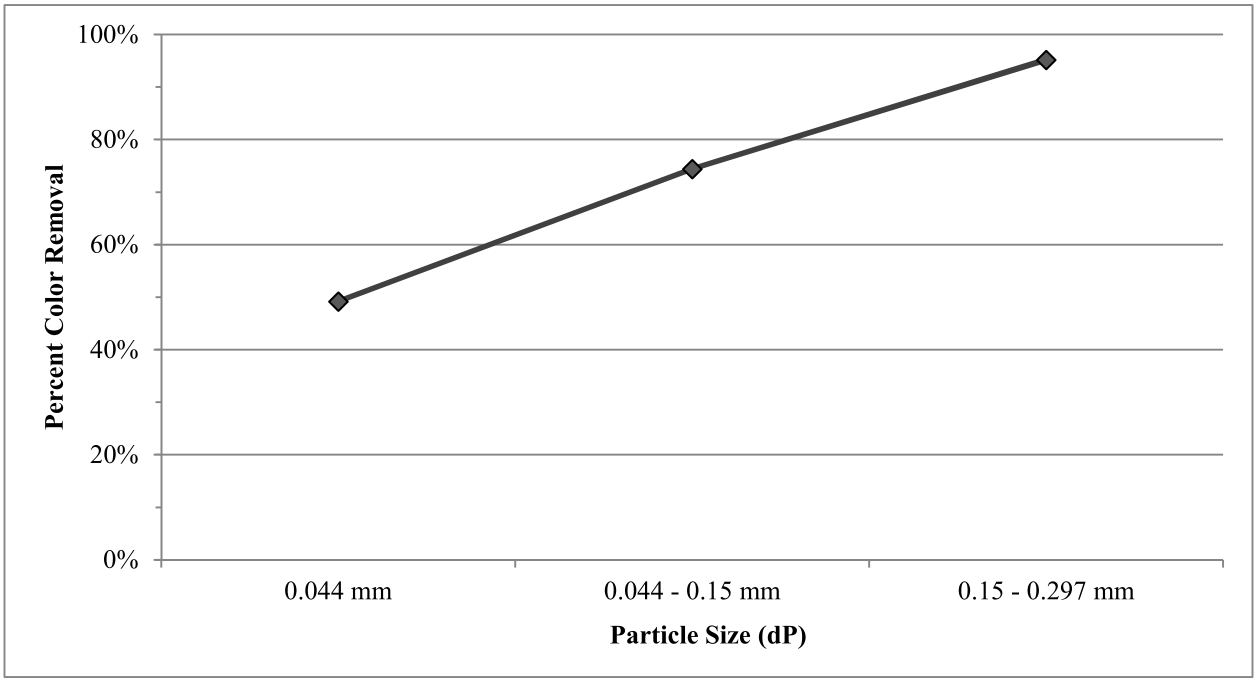

Figure 4-9: Effect of CFA particle size on color removal with the following test conditions: CFA dosage = 250 g/L, Mixing Speed = 150 RPM, Contact Time = 24 hours, Initial Color = 1,152 mg/L Pt-Co Initial Effluent pH = 8.70.

4.3.5 Kinetic Study (Batch Study E)

The kinetic aspects of pulp mill effluent color adsorption onto CFA were examined by varying the contact time for the two materials from 0 to 48 hours for three batches of samples. The resulting color removal has been plotted with respect to time in **Figure 4-10**. The first batch of samples (Batch E.1) were treated with a CFA dosage of 100 g/L, the effective dosage established in earlier experiments. The initial spike of color removal in the data indicates that adsorption of color occured quickly. Within the first hour of contact, the color removal from the effluent rapidly climbed to 35%, and then began to plateau at 12 hours of contact. After 24 hours, no significant additional color removal occurred, therefore, an equilibrium time of 24 hours for the adsorption reaction was established.

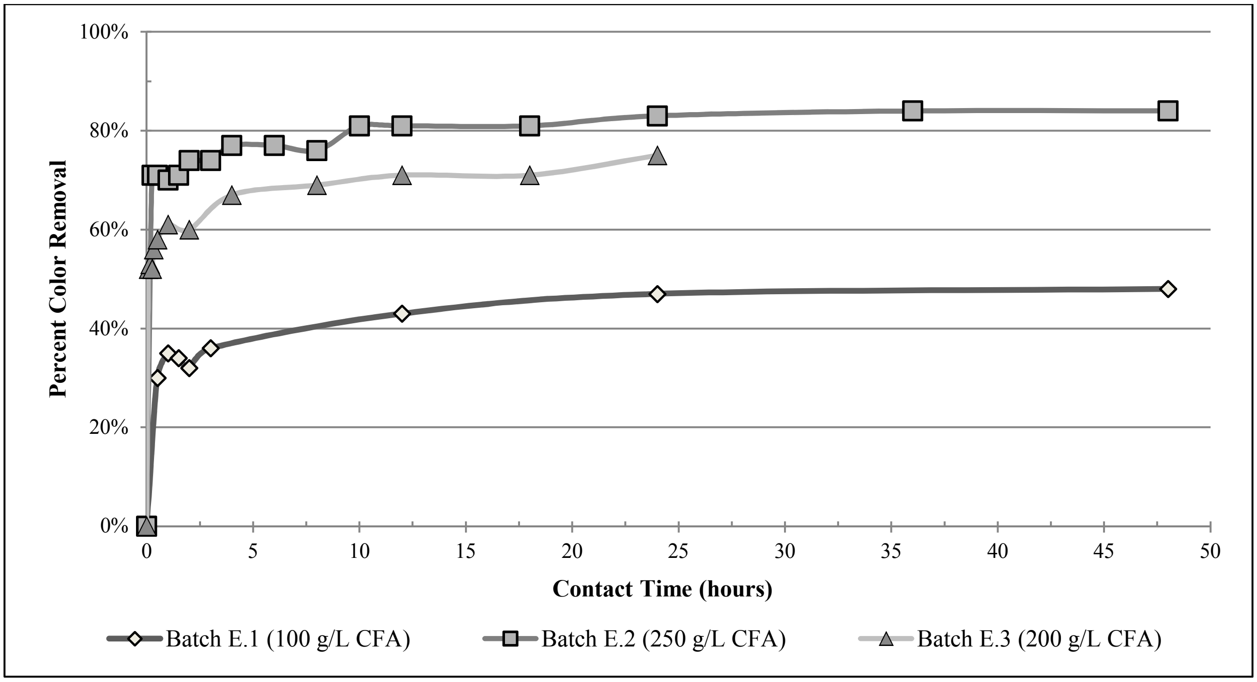

Figure 4-10: Effect of CFA contact time on color removal from pulp mill effluent. Test conditions for the three batches are listed in Table 3-3.

For both the second and third batch of samples, higher CFA dosages of 250 and 200 g/L, respectively, were used. These dosages were previously found to be effective given an effluent color concentration over 900 mg/L Pt-Co. The results from Batch E.2 show that after 15 minutes of contact with the ash, 71% of effluent color had been removed. Beyond this point, color removal began to plateau. By 24 hours, the previously determined equilibrium time, effluent color removal increased to 84%. This extremely rapid rate of adsorption may be attributed to the high initial concentration gradient of the color in pulp mill effluent versus on the surface of CFA particles. In essence, all sites on the adsorbent surface are at first vacant, but as these sites become quickly occupied by the adsorbate, further adsorption of color requires diffusion of effluent into the pores of the adsorbent (Shahmohammadi-Kalalagh, et al. 2011).

Batch E.3 was treated with a slightly lower CFA dosage of 200 g/L to retard the rate of the adsorption reaction. In addition, the contact time intervals during the first hour of the experiment were decreased to observe the initial phase of the reaction in more detail. The experimental data show a trend similar to the previous batch, wherein color is quickly adsorbed during the first hour of contact, and becomes asymptotic after 24 hours. Given their similar results, the equilibrium time for Batches E.2 and E.3 was also determined to be 24 hours.

All three batches tested were characterized by the rapid removal of color by CFA. The effect of contact time versus color removal during the critical first hour of contact is shown in detail in **Figure 4-11**. After only 5 minutes, over 50% of the color was removed from the pulp mill effluent samples in Batch E.3. This trait makes CFA a particularly appealing adsorbent to pulps mills needing to treat effluent swiftly prior to discharge. Similar studies have found that higher color concentrations speed up adsorbate transition from liquid to solid phases (Khalir, Hanafiah and So'ad 2012).

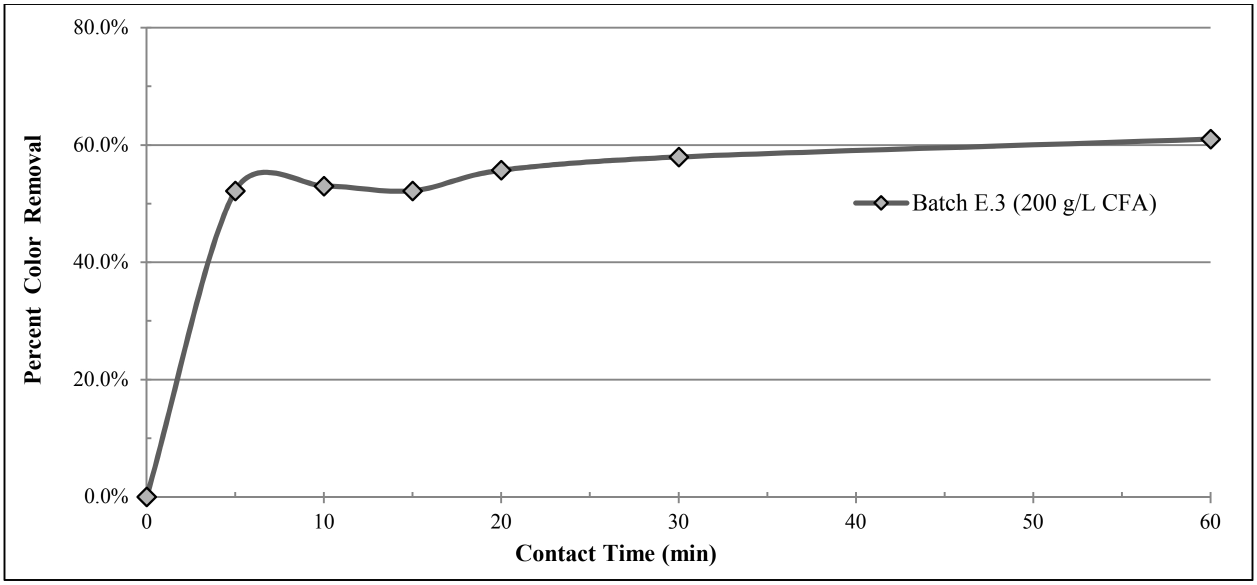

Figure 4-11: Effect of CFA contact time on color removal from pulp mill effluent during the first hour of contact. Test conditions: Mixing Speed = 150 RPM, Initial Effluent Color = 887 mg/L Pt-Co, Initial Effluent pH = 9.10.

4.3.5.1 Kinetic Modeling

Figure 4-12 shows observed values plotted against values predicted the linear form of the Lagergren pseudo-first order kinetic model. Non-linear plots of the Lagergren model are shown in **Figures 4-13**, **4-14**, and **4-15**. In these figures, CI and PI denote the confidence interval and prediction interval, respectively. Equation constants determined from the regressions are listed in **Error! Reference source not found. Table 4-2** and **Table 4-3**. Theoretical adsorption capacity ($q_{e,calc}$) values for CFA estimated by the linear and non-linear regressions ranged from 0.47 – 2.85 mg/g. The R^2 values for the linear estimation of the Lagergren equation constants indicate a satisfactory fit with observed data. However, the *t*-test showed that the linear estimation of the $q_{e,calc}$ value for Batch F.3 was not statistically significant at the 95% confidence level. All other Lagergren equation constants estimated by both linear and non-linear regressions were statistically significant at the 95% confidence level. Accordingly, we cannot accept the null hypothesis for the estimation of the Lagergren Pseudo-First Order equation constants. However, the Lagergren model does provide an acceptable description of the observed adsorption kinetics. In addition, the $q_{e,calc}$ values estimated by the non-linear regression are much closer to observed $q_{e,exp}$ values than those determined linearly. Therefore, the Lagergren pseudo-first order kinetic model adequately describes the adsorption of pulp mill effluent color onto CFA. There is some agreement with this conjecture in the literature, as Prasad and Srivastava (2009) reported the Lagergren model satisfactorily describe the adsorption of color from distillery effluent onto CFA. However, those researchers determined the value Lagergren constants for CFA to be 0.042 1/h (k_1) and 9.37 mg/g (q_e), which are somewhat dissimilar to those obtained in the present research.

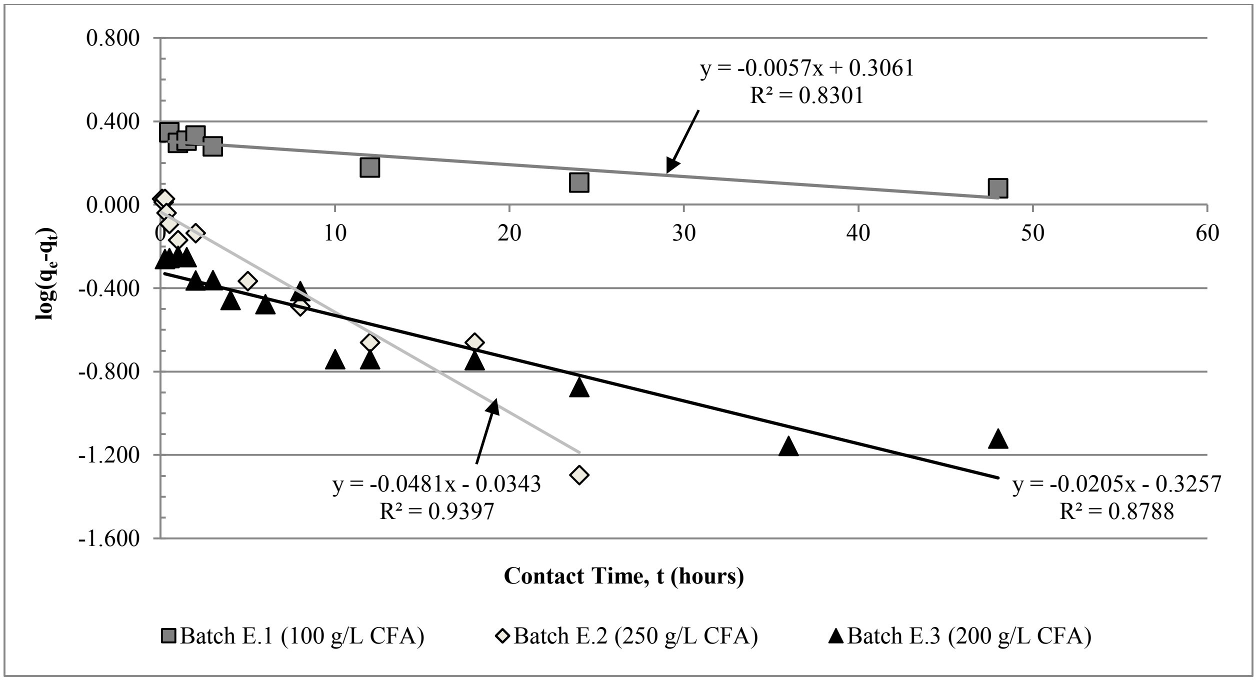

Figure 4-12: Experimental values plotted against values predicted by the linear form of the Lagergren pseudo-first order kinetic model. Test conditions for the three batches are listed in Table 3-3.

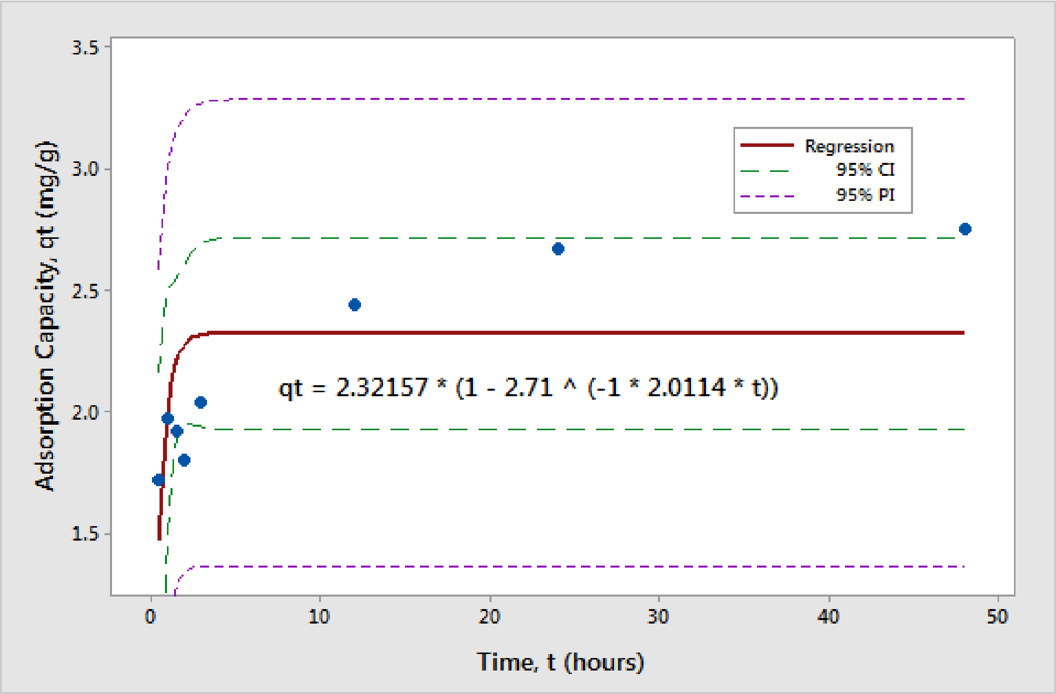

Figure 4-13: Experimental values from Batch E.1 (100 g/L CFA) plotted against values predicted by the non-linear pseudo-first order kinetic model.

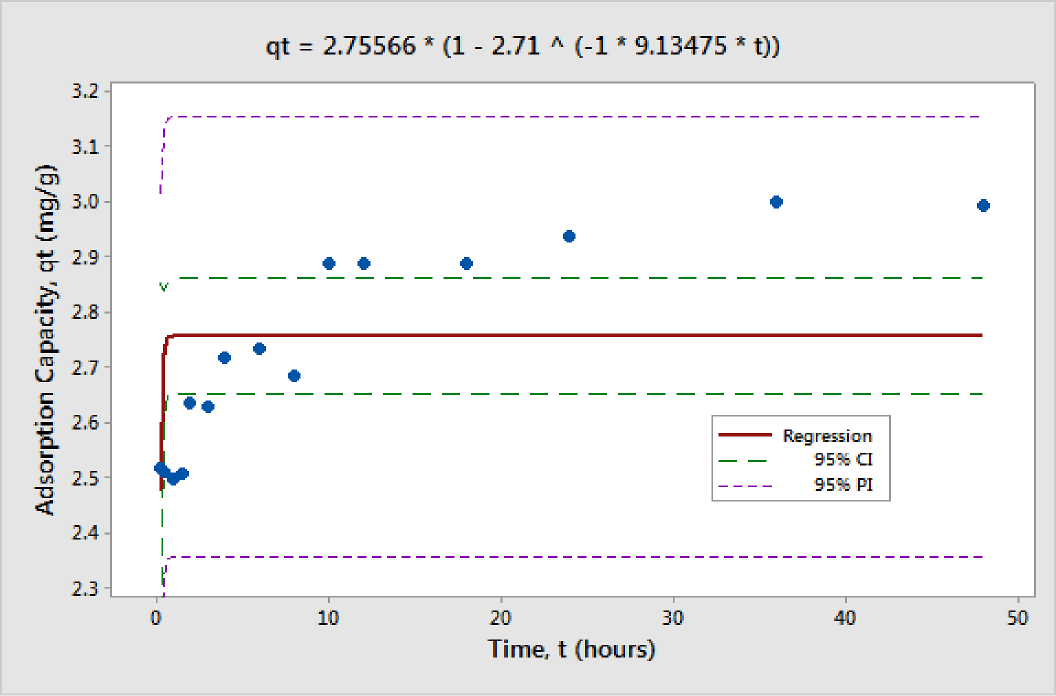

Figure 4-14: Experimental values from Batch E.2 (250 g/L CFA) plotted against values predicted by the non-linear pseudo-first order kinetic model.

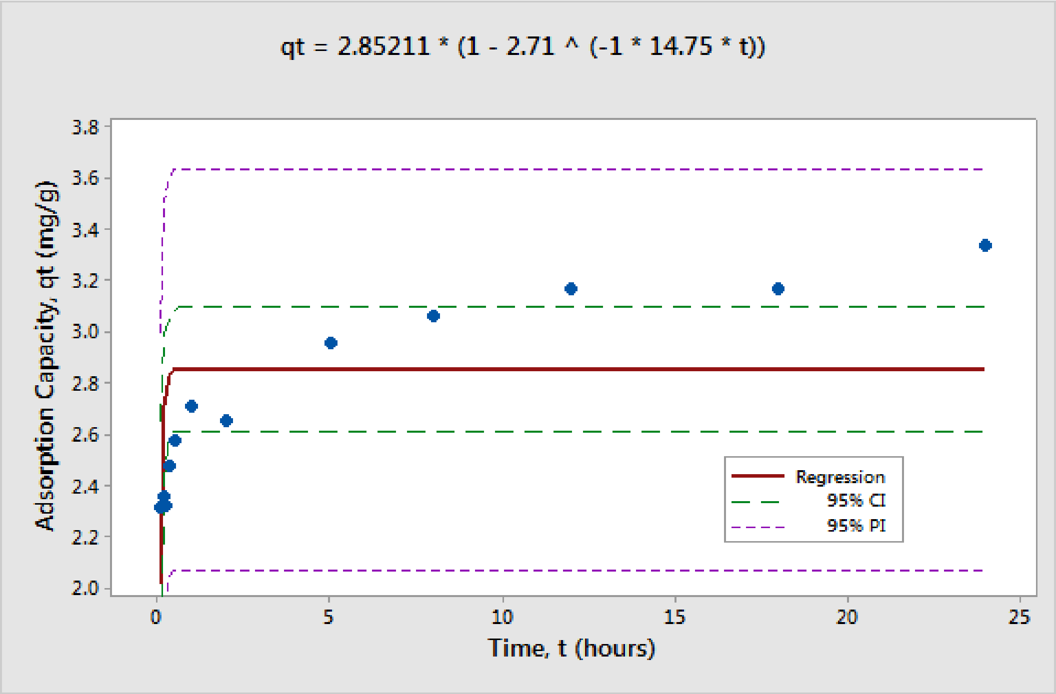

Figure 4-15: Experimental values from Batch E.3 (200 g/L CFA) plotted against values predicted by the non-linear pseudo-first order kinetic model.

Table 4-2: Linear Lagergren pseudo-first order kinetic model constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model			
			$q_{e,calc}$ (mg/g)	$q_{e,exp}$ (mg/g)	k_1 (1/h)	R^2
E.1	571	Estimate	2.02	3.948	0.013	0.83
		P Value	0.000	-	0.002	-
E.2	887	Estimate	0.47	3.066	0.048	0.879
		P Value	0.000	-	0.000	-
E.3	887	Estimate	0.93	3.383	0.114	0.936
		P Value	0.434	-	0.000	-

Table 4-3: Non-linear Lagergren pseudo-first order kinetic model constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model		
			$q_{e,calc}$ (mg/g)	$q_{e,exp}$ (mg/g)	k_1 (1/h)
E.1	571	Estimate	2.32	3.948	2.01
		P Value	0.000	-	0.0383
E.2	887	Estimate	2.76	3.066	9.13
		P Value	0.000	-	0.004
E.3	887	Estimate	2.85	3.383	14.75
		P Value	0.000	-	0.007

The Ho et al. (1999) pseudo-second order kinetic model, in contrast, proved to fit the data very well. Theoretical adsorption capacity ($q_{e,calc}$) values for CFA estimated by the linear and non-linear regressions ranged from 2.54 – 3.29 mg/g. A linear plot of experimental and model-predicted kinetic data is shown in **Figure 4-16**, and pseudo-second model constants are presented in **Table 4-4Error! Reference source not found.** and **Table 4-5**. Non-linear plots of the Ho et al. model are shown in **Figures 4-17**, **4-18**, and **4-19.** In these figures, CI and PI denote the confidence interval and prediction interval, respectively. For all three batches, the linear regression of the data returned R^2 values at or above 0.999. The *t*-test confirmed that both the linear and non-linear estimations of the Ho et al. constants were statistically significant at the 95% confidence level. Therefore, we cannot reject the null hypothesis for the estimation of the Ho et al. Pseudo-Second Order equation constants. In addition, the theoretical q_e values estimated by the regression agreed with observed q_e values. Between the two kinetic models evaluated in the current research, the Ho et al. pseudo-second order kinetic model describes the adsorption kinetics of pulp mill effluent color onto CFA better than the Lagergren pseudo-first order kinetic model. Prasad and Srivastava (2009) stated in their evaluation of kinetic models for color adsorption by CFA that the Ho et al. kinetic model provided the best fit to the observed kinetic study data. However, the pseudo-second order constants obtained in their research, 0.0098 g/mg•h (k_2) and 19.03 mg/g (q_e), are markedly different than those noted in **Table 4-4** and **Table 4-5**.

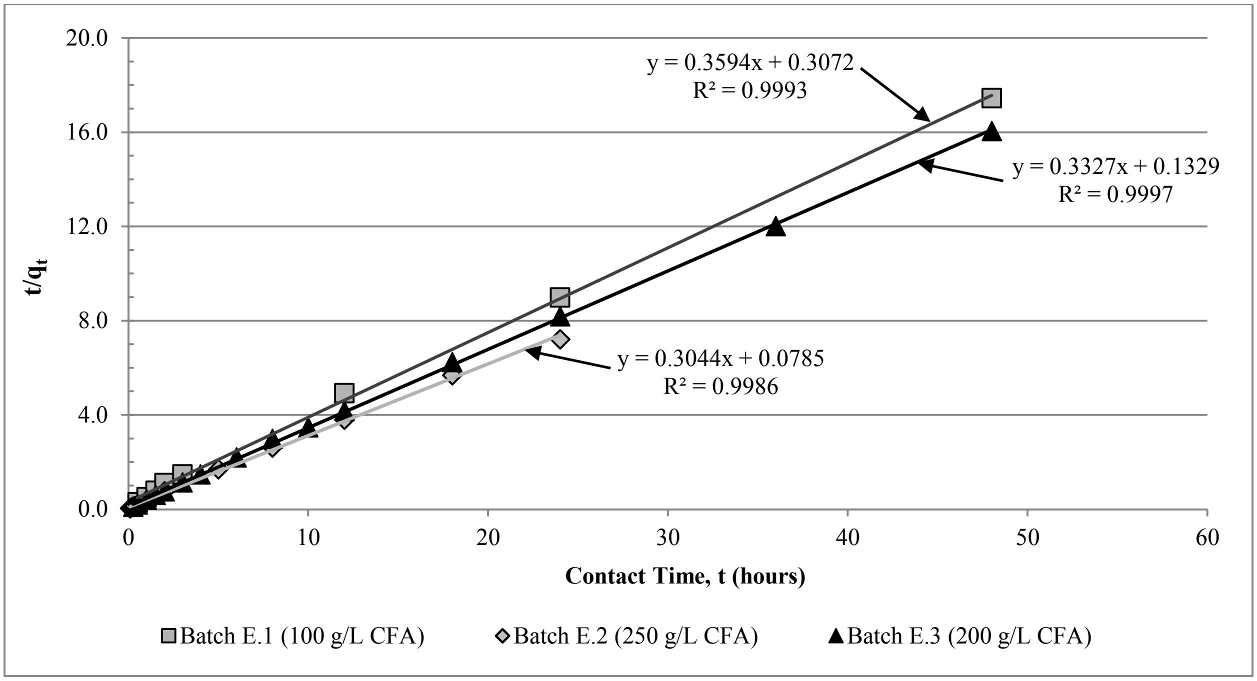

Figure 4-16: Experimental values plotted against values predicted by the linear form of the Ho et al pseudo-second order kinetic model. Test conditions for the three batches are listed in Table 3-3.

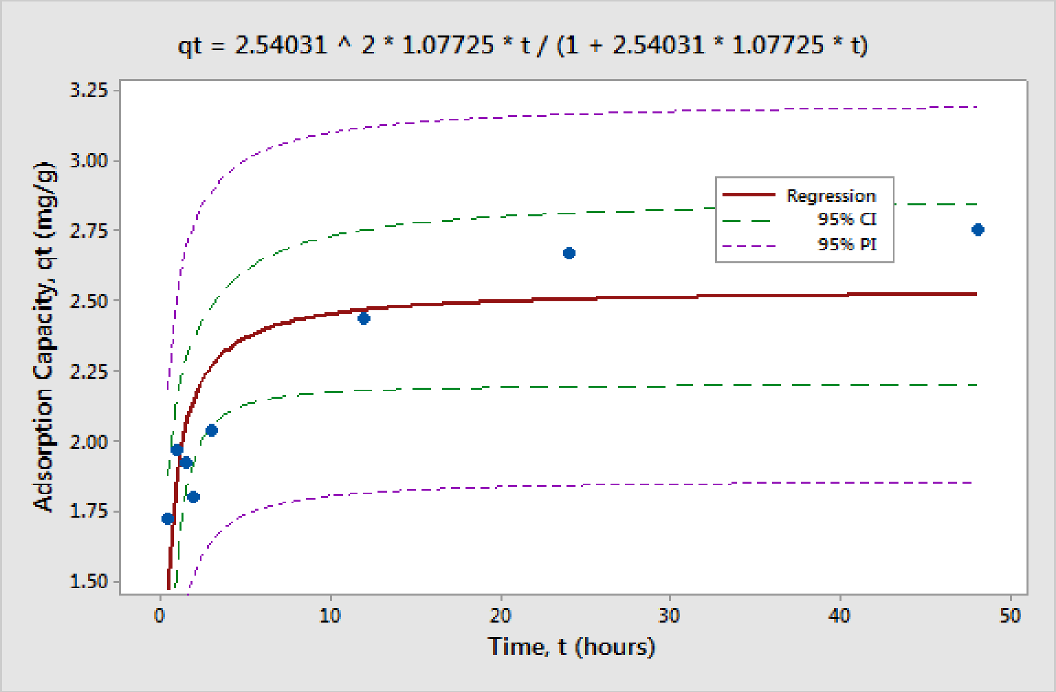

Figure 4-17: Experimental values from Batch E.1 (100 g/L CFA) plotted against values predicted by the non-linear pseudo-second order kinetic model.

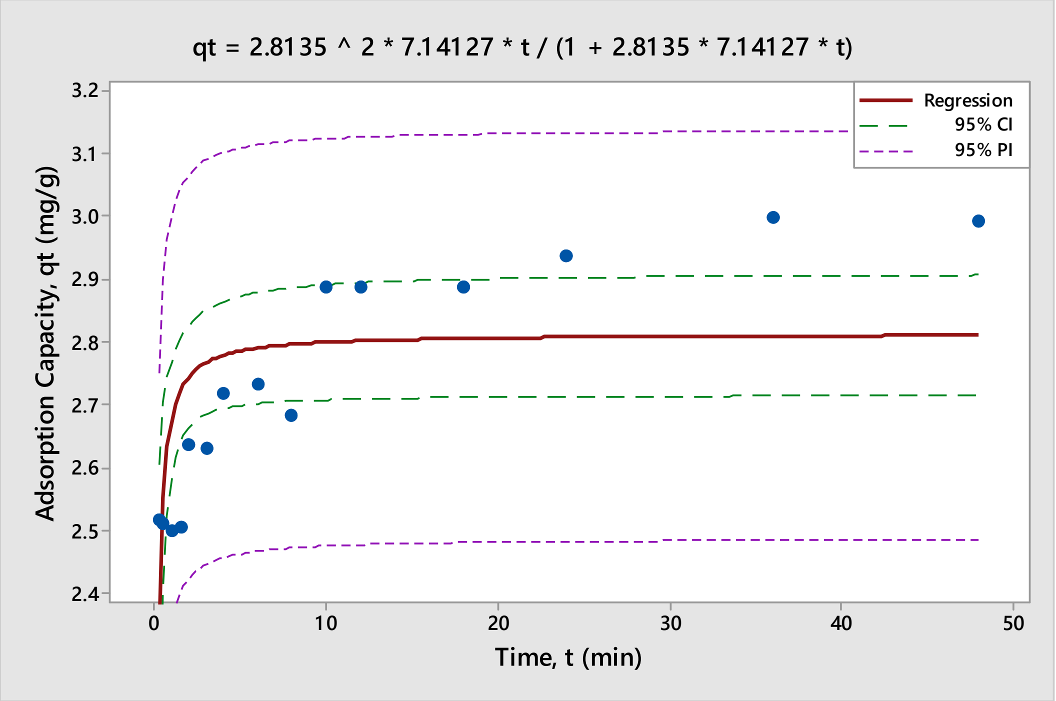

Figure 4-18: Experimental values from Batch E.2 (250 g/L CFA) plotted against values predicted by the non-linear pseudo-second order kinetic model.

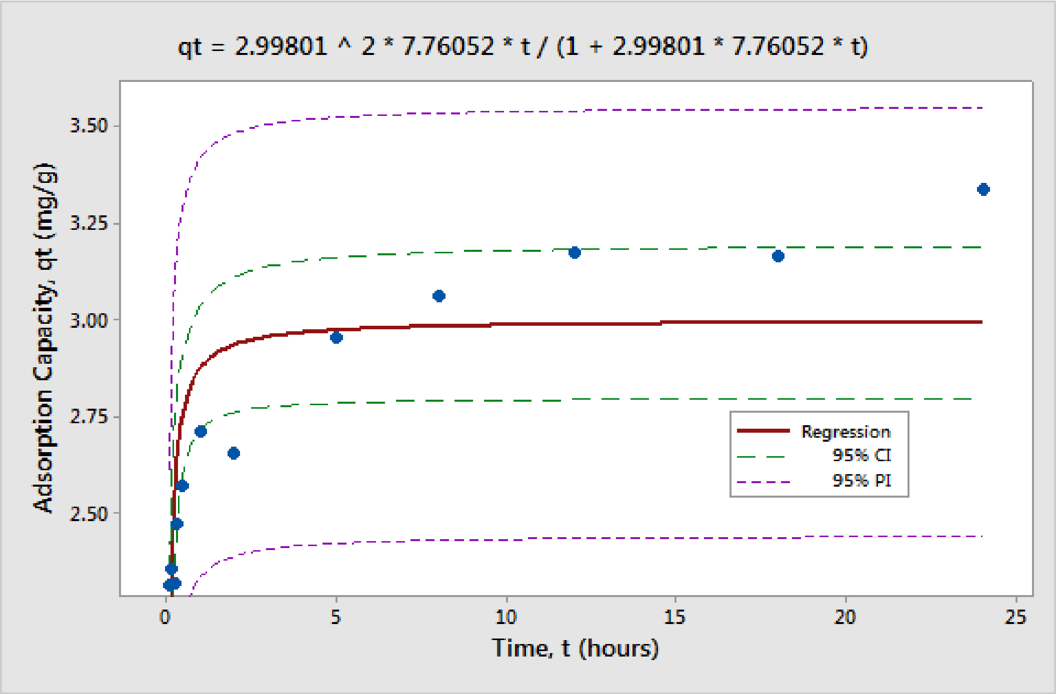

Figure 4-19: Experimental values from Batch E.3 (200 g/L CFA) plotted against values predicted by the non-linear pseudo-second order kinetic model.

Table 4-4: Linear Ho et al. pseudo-second order kinetic model constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model			
			$q_{e,calc}$ (mg/g)	$q_{e,exp}$ (mg/g)	k_2 (g/mg•h)	R^2
E.1	571	Estimate	2.78	3.948	0.42	0.999
		P Value	0.007	-	0.000	-
E.2	887	Estimate	3.01	3.066	0.84	0.9997
		P Value	0.001	-	0.000	-
E.3	887	Estimate	3.29	3.383	1.17	0.999
		P Value	0.05	-	0.000	-

Table 4-5: Non-linear Ho et al. pseudo-second order kinetic model constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model		
			$q_{e,calc}$ (mg/g)	$q_{e,exp}$ (mg/g)	k_2 (g/mg•h)
E.1	571	Estimate	2.54	3.948	1.08
		P Value	0.000	-	0.038
E.2	887	Estimate	2.81	3.066	7.14
		P Value	0.000	-	0.015
E.3	887	Estimate	2.998	3.383	7.76
		P Value	0.000	-	0.008

4.3.6 Isotherm Study (Batch Study F)

Adsorption capacity data was generated by an equilibrium batch study at initial effluent color concentrations of 928 and 1,036 mg/L Pt-Co over a dosage range of 100-350 g/L CFA. The results of the study are shown in **Figure 4-20**. Percent color removed increased linearly with adsorbent dosage up to 250 g/L, which may be attributed to the increase in available adsorbent surface area (Ozturk and Kavak 2005). Past this point, little additional color removal was observed, which indicates CFA's maximum adsorption capacity for a given initial concentration (C_0) of color.

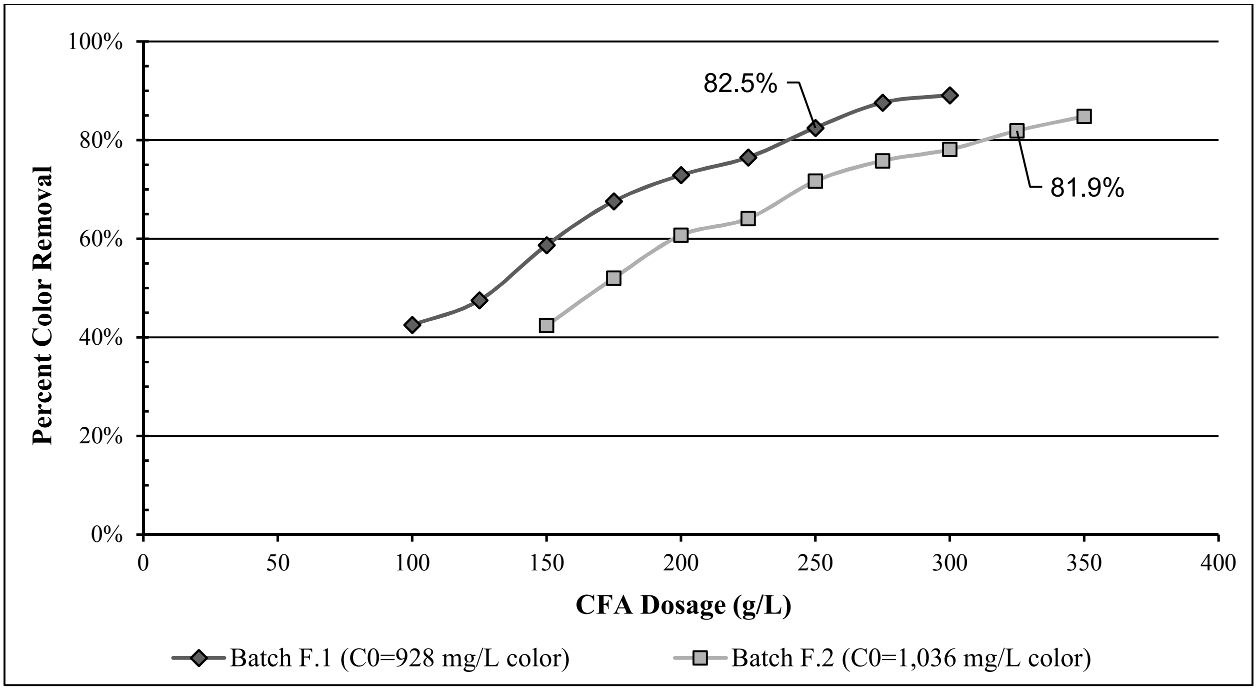

Figure 4-20: Isotherm Studies - Percent color removal from pulp mill effluent vs CFA dosage at equilibrium (24 hours).

The observed and Langmuir model predicted values for C_e and q_e are shown in **Figure 4-21**. The linear and non-linear regressions were determined by the least squares method and Quasi-Newton method, respectively. Values for Q_0 and b estimated by the regressions, along with correlation values, are presented in **Table 4-6** and **Table 4-7**. The linearized Langmuir model was found to fit the experimental data quite well, as indicated by favorable R^2 values. The Langmuir constants estimated by the non-linear regression also exhibited a good fit to the observed data. Furthermore, the *t*-test showed that the both the linear and non-linear estimations of the Langmuir constants were both statistically significant at the 95% confidence level. Therefore, we cannot reject the null hypothesis for the estimation of the Langmuir Isotherm equation constants. A generalized characterization of the Langmuir constants can be made by calculating the constant separation factor, R_L, from this equation:

$$R_L = \frac{1}{1 + bC_e} \tag{13}$$

The value of R_L characterizes the adsorption as either: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$) (Foo and Hameed 2010). All R_L values listed in **Table 4-6** and **Table 4-7**Error! Reference source not found. fall between 0.92 and 0.94, indicating favorable adsorption of color by CFA.

Other studies that investigated the use of CFA for color removal have also reported that the adsorption obeys the Langmuir isotherm model. For the adsorption of color from spent distillery wash onto CFA, Prasad and Srivastava (2009) reported Langmuir constants of 0.00194 L/mg (b) and 85.2 mg/g (Q_0). Similarly Andersson et. al. (2012) determined these values to be 0.0017 L/mg (b) and 28 mg/g (Q_0) for pulp mill effluent color adsorption by black wood ash. The agreement between the b values reported in the literature and those found in the present research (the estimated values for b fall between 0.012 and 0.028 L/m) means that color adsorbs onto CFA with monolayer coverage of the ash particles.

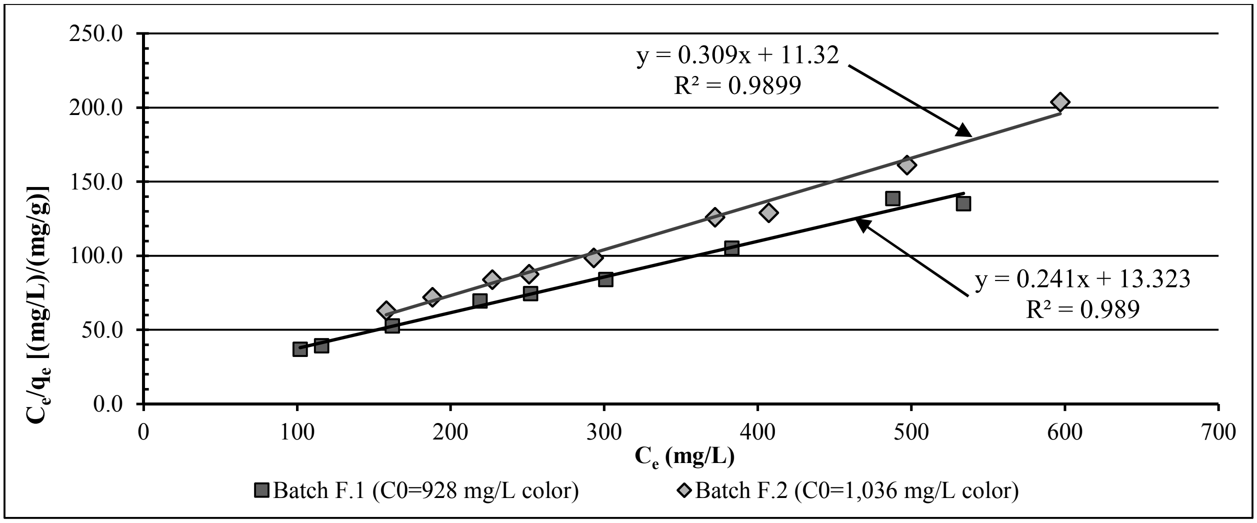

Figure 4-21: Experimental values plotted against values predicted by the linear Langmuir isotherm model.

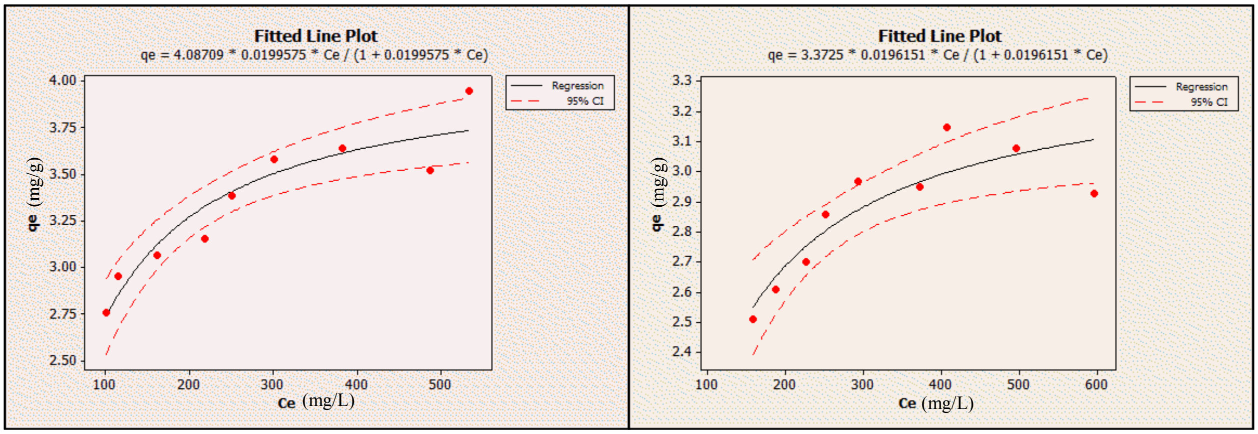

Figure 4-22: Non-linear Langmuir isotherm plots for pulp mill effluent $C_0 = 928$ mg/L (left) and $C_0 = 1,036$ mg/L (right) with regressions fitted. CI and PI here denote the confidence interval and prediction interval, respectively.

Table 4-6: Linear Langmuir constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model			
			Q_0 (mg/g)	b (L/mg)	R_L	R^2
F.1	928	Estimate	4.15	0.018	0.93	0.989
		P Value	0.003	0.000	-	-
F.2	1,036	Estimate	3.23	0.028	0.92	0.99
		P Value	0.034	0.000	-	-

Table 4-7: Non-linear Langmuir constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Non-Linear Model		
			Q_0 (mg/g)	b (L/mg)	R_L
F.1	928	Estimate	4.09	0.020	0.92
		P Value	0.000	0.002	-
F.2	1,036	Estimate	3.37	0.012	0.94
		P Value	0.000	0.0475	-

The plot of $\log(q_e)$ vs $\log(C_e)$, shown in **Figure 4-23**, was used in the linear regression analysis to estimate values of Freundlich constants K_F and n, which are listed in **Table 4-8**, along with correlation values. Non-linear estimation of the Freundlich equation, shown in **Figure 4-24**, was determined by the Quasi-Newton method. The Freundlich constants, as estimated by the Quasi-Newton method, are listed in **Table 4-9**. The slope of the linear Freundlich equation, $1/n$, ranges from 0 to 1, and as its value approaches 0, the adsorbent surface is characterized as being increasingly heterogeneous. Lower $1/n$ values indicate favorable adsorption phenomena (Foo and Hameed 2010). The R^2 values for the linear estimation of the Freundlich equation were lower than those of the Langmuir model, indicating less than favorable fit to the data. In addition, the *t*-test showed that the linear estimations of the Freundlich constant K_F were not statistically significant at the 95% confidence level. In contrast, the *t*-test showed that the non-linear estimations of the Freundlich constants were statistically significant at the 95% confidence level, indicating an acceptable fit of the Freundlich model to the observed data. However, we cannot accept the null hypothesis for the estimation of the Freundlich Isotherm equation constants In general, this means that the Freundlich isotherm adequately describes the adsorption of color from pulp mill effluent onto CFA. Other researchers have also found that the Freundlich isotherm is a fitting descriptor for the adsorption of color by CFA. Both Prasad and Srivastava (2009) and Andersson et. al. (2012) reported that the Freundlich isotherm more accurately described the adsorption system than the Langmuir isotherm. In their research, Prasad and Srivastava (2009) determined the Freundlich constants to be 1.593 mg/g $(\mathrm{L/mg})^{1/n}$ (K_F) and 0.496 ($1/n$). Similarly, Andersson et. al. (2012) calculated values of 0.5 mg/g $(\mathrm{L/mg})^{1/n}$ (K_F) and 0.53 ($1/n$).

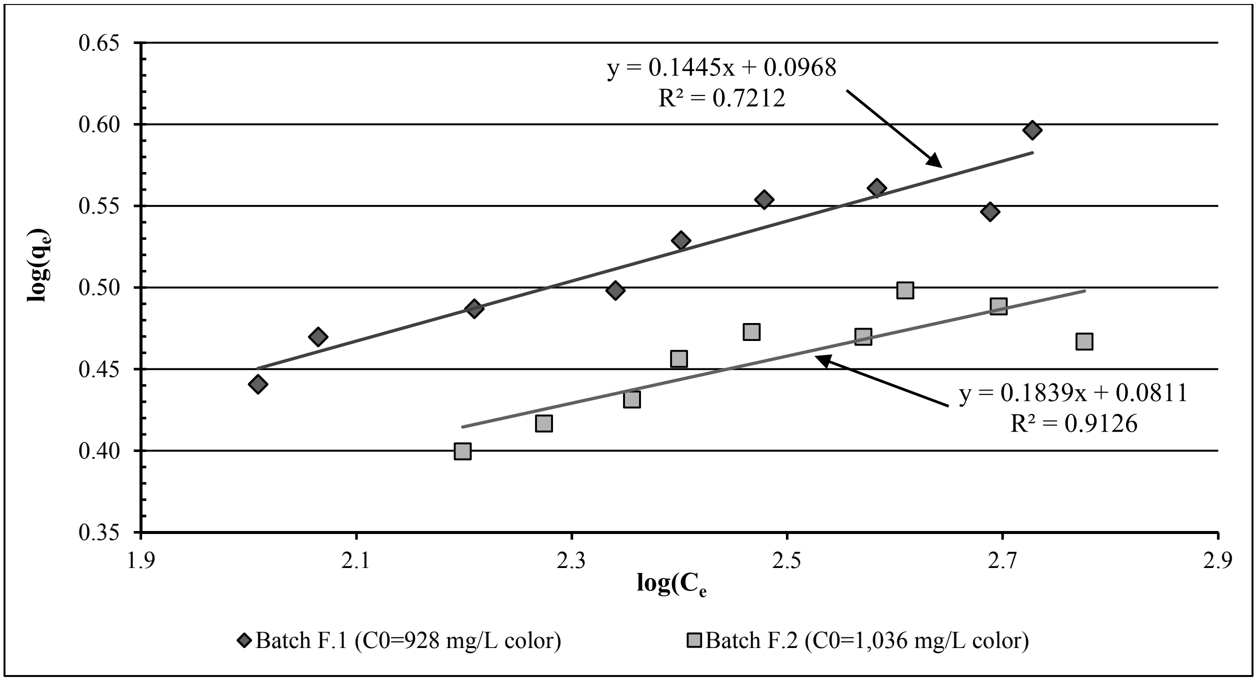

Figure 4-23: Experimental values plotted against values predicted by the linear Freundlich isotherm model.

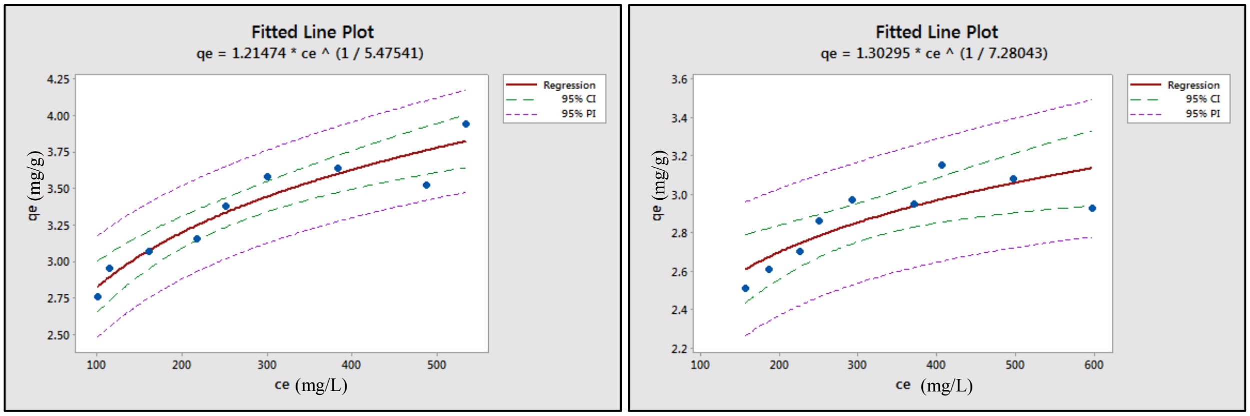

Figure 4-24: Non-linear Freundlich isotherm plots for pulp mill effluent C_0 = 928 mg/L (left) and C_0 = 1,036 mg/L (right) with regressions fitted. CI and PI here denote the confidence interval and prediction interval, respectively.

Table 4-8: Linear Freundlich constants and statistical parameters.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model		
			K_F (mg/g (L/mg)$^{1/n}$)	1/n	R^2
F.1	928	Estimate	1.21	0.18	0.913
		P Value	0.159	0.000	-
F.2	1,036	Estimate	1.25	0.14	0.720
		P Value	0.285	0.004	-

Table 4-9: Non-linear Freundlich constants and statistical parameters for CFA.

Sample Batch	Initial Effluent Color (mg/L Pt-Co)	Statistical Parameter	Linear Model		
			K_F (mg/g (L/mg)$^{1/n}$)	1/n	R^2
F.1	928	Estimate	1.21	0.183	0.913
		P Value	0.000	0.000	-
F.2	1,036	Estimate	1.30	0.137	0.720
		P Value	0.002	0.006	-

4.3.7 Removal of COD

Select isotherm study filtrates were analyzed for COD removal to observe the relationship between this parameter and color removal. **Figure 4-25** shows that higher color concentrations in raw pulp mill effluent coincide with higher amounts of COD. **Table 4-10** illustrates that over the CFA dosage range studied, the data shows a clear decrease in COD as the color concentration decreases in treated effluent. At the previously established effective CFA dosage of 250 g/L, over 80% of color and 40% of COD can be removed from pulp mill effluent. As mentioned in Chapter 2, COD is a widely used water quality indicator parameter, especially with regard to organic compounds present in effluent sources. Therefore, the results of this analysis indicate CFA may be suitable for the removal of organic compounds from pulp mill effluent.

Table 4-10: Effect of CFA dosage on pulp mill effluent color and COD removal.

CFA Dosage (g/L)	**Measured Dosage (±0.001g)**	**Average Filtrate Sample Measurements**				
		pH	Color (mg/L)	Color Removal	COD (mg/L)	COD Removal
0	0.000	9.15	928	-	410	-
100	9.981	9.52	534	42.5%	288	29.8%
150	14.969	9.48	383	58.7%	289	29.5%
200	19.996	9.41	252	72.9%	213	48.0%
250	24.986	9.43	162	82.5%	231	43.7%
300	29.996	9.39	102	89.1%	164	60.0%

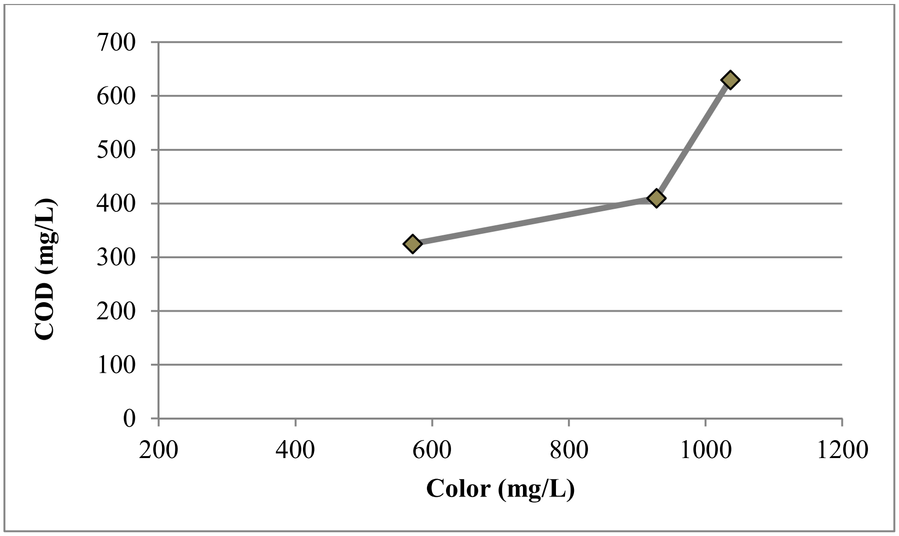

Figure 4-25: Concentration of color vs COD in raw pulp mill effluent.

4.3.8 Monitoring of Heavy Metals Leaching from CFA

When CFA remains mixed with water for an extended period of time, trace amounts of heavy metals on the ash particles can leach into the water. There is, however, some variability in the amount of time necessary for leaching to occur, due to numerous factors like pH and concentration. To err on the side of safety, the heavy metals concentrations in deionized (DI) water and pulp mill effluent were analyzed before and after CFA treatment for changes. **Figure 4-26** and **Figure 4-27** show the lead and zinc concentrations in DI water and pulp mill effluent filtrates treated with different CFA dosages. The filtrates are actually the samples from isotherm study Batch F.1, and the treatment parameters are listed in **Table 3-4**. A full listing of all heavy metal measurements, as well as the percent change in concentration due to CFA treatment, can be found in **Tables A-21 – A-23**.

As shown in **Figure 4-26,** for the DI water filtrates, an increase in lead concentration was observed at CFA dosages of 200 and 300 g/L. The lead concentration of DI water filtrates treated with 0 and 100 g/L CFA were below instrument detection limits. This contrasts with the lead concentrations in pulp mill effluent filtrates, which were all below detection limits, except at 100 g/L CFA. At this dosage, the lead concentration in the effluent was 0.17 mg/L. Because many of the lead readings were below the detection limit of the Hach DR5000, a more detailed analysis should be conducted to determine whether lead from CFA leaches into pulp mill effluent during the adsorption process. A more advanced and accurate instrument, such as an Atomic Adsorption Spectrophotometer, would be better able to detect changes in lead concentration.

There were no significant changes in the zinc concentration of the DI water filtrates treated with CFA. For pulp mill effluent filtrates, zinc concentrations decreased a small amount following CFA treatment. This removal of zinc removal by CFA has also been observed by other researchers investigating CFA Ahmaruzzaman, 2010, Wang and Wu, 2006. In their respective reviews of

CFA utilization, both list several studies where CFA was successfully used as an adsorbent for zinc removal. Removal tends to be highest when the initial zinc concentration is low.

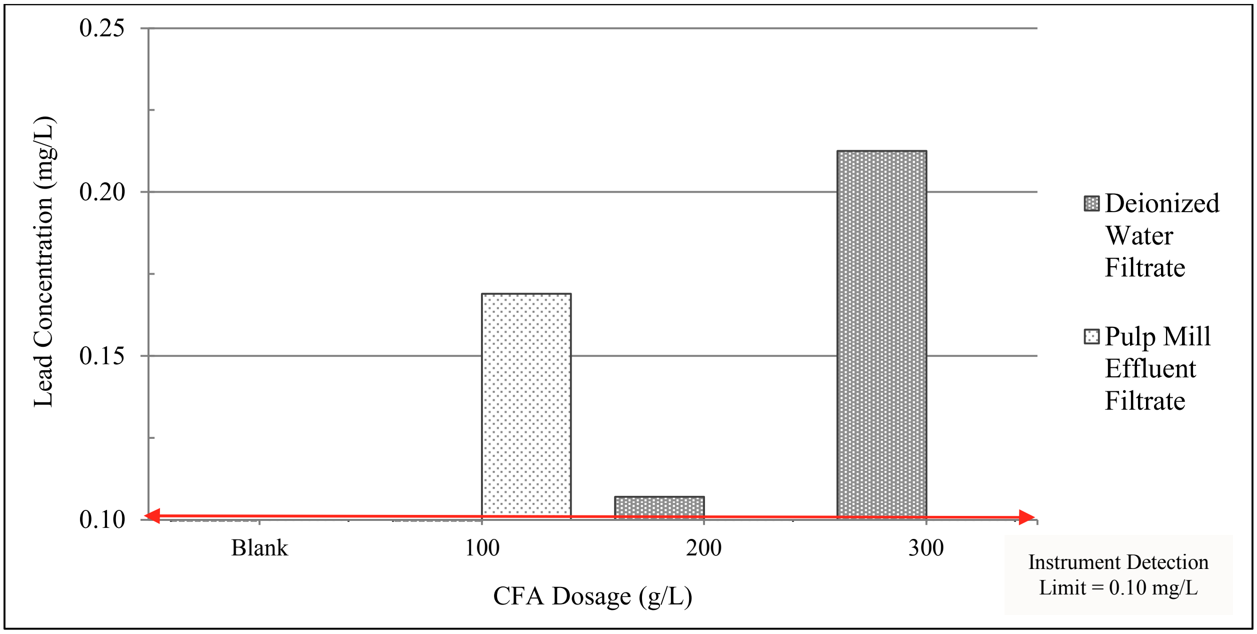

Figure 4-26: CFA Dosage vs Lead concentration in deionized water and pulp mill effluent.

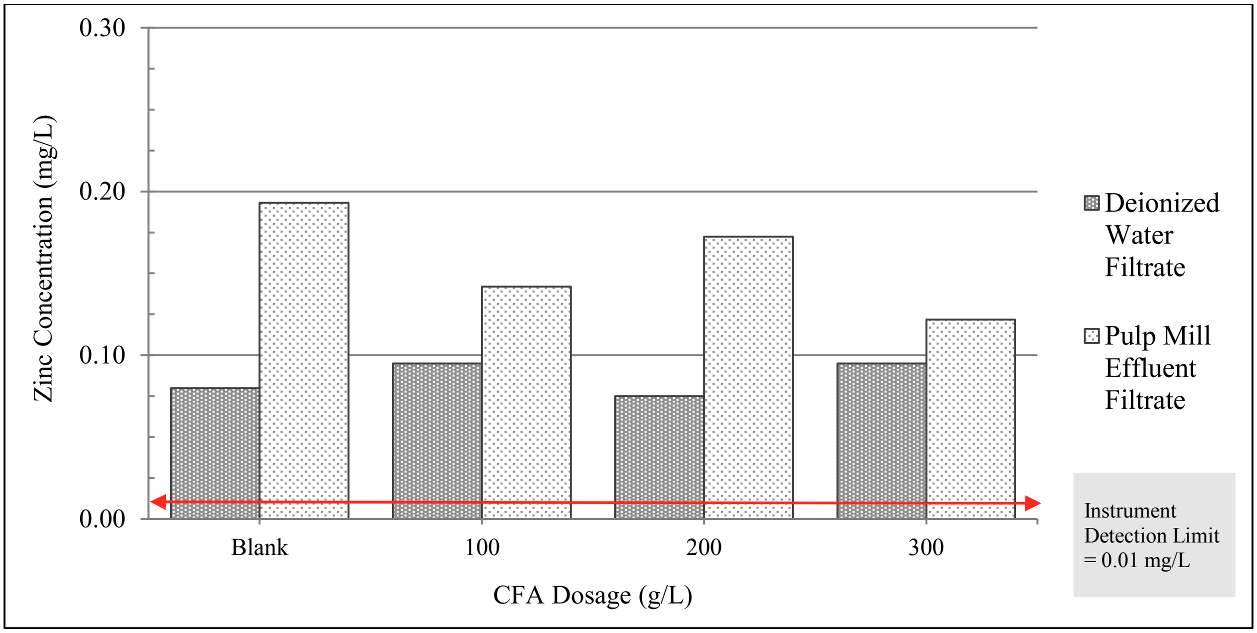

Figure 4-27: CFA Dosage vs Zinc concentration in deionized water and pulp mill effluent.

4.3.9 Comparison of PAC and CFA

The effect of PAC dosage on pulp mill effluent color removal was studied at dosages of 2.5, 5, 7.5, and 10 g/L. For comparison, the color removal and adsorption capacity data for CFA from the isotherm study is listed in **Table 4-11**. Color removal from the pulp mill effluent exhibited a fairly linear relationship with increasing PAC dosages, as shown in **Figure 4-28**. In addition, the average PAC adsorption capacity at an initial effluent color concentration of 1114 mg/L Pt-Co was determined to be 34.59 mg/g. For CFA, the average adsorption capacity observed at the same initial effluent color was 2.85 mg/g; less than 10% of the value for PAC.

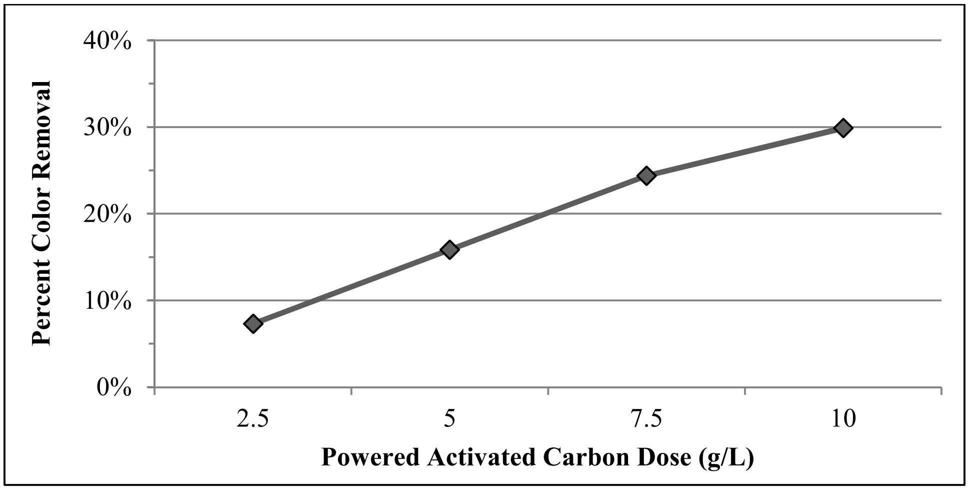

Figure 4-28: Color removal vs. PAC Dosage at an initial effluent color concentration of 1,114 mg/L Pt-Co, Mixing Speed = 150 RPM, Contact Time = 24 hours, Initial Effluent pH = 8.37.

Table 4-11: Adsorption capacities of PAC and CFA at an initial pulp mill effluent color concentration of 1,114 mg/L Pt-Co.

PAC Dosage (g/L)	Percent Color Removed	Adsorption Capacity (mg/g)	CFA Dosage (g/L)	Percent Color Removed	Adsorption Capacity (mg/g)
			150	42.4%	2.93
2.5	7.3%	32.86	200	60.7%	3.15
5	15.8%	35.91	250	71.7%	2.97
7.5	24.4%	36.18	300	78.1%	2.70
10	29.9%	33.40	350	84.8%	2.51
	Average:	34.59		Average:	2.85

4.4 Cost Analysis

The premise for using CFA to remove color from pulp mill effluent in lieu of traditional powdered activated carbon (PAC) treatment is the reduced procurement cost of CFA. Therefore, a cost analysis was completed in order to compare the cost of treating effluent with CFA versus PAC. For effluent requiring relatively high doses of PAC, the preferred adsorbent delivery method is a slurry-feed system, wherein water and PAC are mixed to form a slurry, which is then fed into the effluent stream. Spent PAC is then removed by sedimentation or filter beds. The spent PAC cannot be regenerated like granular activated carbon, and has to be disposed of (US EPA 2015). Because PAC and CFA have the same bulk particle size (below 45 µm), CFA could substitute for PAC in the process described above.

Several assumptions about the color removal process were made in order to estimate the costs of treatment, which are listed in **Table 12** below. First, the volume of pulp mill effluent requiring treatment was assumed to be 1 million gallons per day (MGD). Second, the percent color reduction goal of the process was set at 60%. The initial/final effluent color values were borrowed from Section 4.3.9, as were the adsorbent dosages necessary to achieve the target color removal goal. These input values were then used to calculate the mass of CFA/PAC required for treatment, in addition to annual material procurement costs. A review of the available literature provided the approximate unit costs for bulk CFA/PAC. The analysis showed that the mass of CFA required is ten times the mass of PAC required to achieve the target color reduction. However, using CFA to treat the same daily volume of pulp mill effluent would be a third of the cost of using PAC.

Table 4-12: Estimated costs of utilizing CFA versus PAC to remove color from pulp mill effluent in an industrial application.

Adsorbent	Effluent Volume	Percent Color Removal	Adsorbent Dosage	Adsorbent Mass Needed		Cost of Adsorbent Material	
	(gal/day)		(g/L)	(tons/day)	(tons/yr)	($/ton)	($/yr)
CFA	1,000,000	60%	200	8,347	3,046,585	50	152,329,228
PAC	1,000,000	60%	20	835	304,658	1,500	456,987,683

4.5 Column Study

The observed breakthrough data for pulp mill effluent color adsorption by CFA is shown in **Figure 4-30**. The plot shows that breakthrough occurs rapidly; after approximately 10 minutes, the outlet/inlet concentration ratio of the effluent (C_{out}/C_{in}) reached 0.15. At 30 minutes C_{out}/C_{in} reached 0.5, corresponding with a throughput volume of 24 mL (0.32 bed volumes). The column was considered exhausted when C_{out}/C_{in} reached 0.8, which occurred after 60 minutes of continuous flow at 0.8 mL/min (0.63 bed volumes).

The behavior of color removal from pulp mill effluent under column adsorption was further analyzed using the Thomas model. The breakthrough data for the column was fitted to the model by non-linear regression. Thomas equation constants and statistical parameters returned by the regression analysis are listed in **Table 4-13**. **Figure 4-30** shows the prediction curve of the Thomas model for effluent color adsorption by CFA. The studies by Prasad and Srivastava (2009) and Andersson et. al. (2012) reported values for the Thomas constants k_{Th} and q_0 that disagree with those found in the present research. For the adsorption of color from spent distillery wash onto CFA in a column study, Prasad and Srivastava (2009) determined the Thomas constants to be 0.0209 mL/min•mg (k_{Th}) and 414.72 mg/g (q_0). Likewise, Andersson et. al. (2012) reported the value of the Thomas constants as 0.04 mL/min•mg (k_{Th}) and 9.8 mg/g (q_0) for CFA.

While conducting the column study, it was discovered that raw pulp mill effluent does not readily flow through a CFA bed when it is packed into a column. As noted in the discussion of the sieve analysis, the CFA obtained in this research had an extremely fine particle size, and thus, low permeability. Unfortunately, this limits practical applications for unaltered CFA on an industrial scale. However, there are several methods available for immobilizing the fine particulate matter of CFA into bead/pellet form, which is the preferred form factor for continuous adsorption operations. Several options for further research into color removal from pulp mill effluent by CFA are discussed in greater detail in Section 5.2.

Table 4-13: Non-linear Thomas Model constants and statistical parameters.

Untreated Effluent Color	Statistical Parameter	Non-Linear Model	
		k_{Th} (mL/min•mg)	q_0 (mg/g)
C_{in} = 1,008 mg/L	Estimate	0.0000629	2208.6
	Std. Error	0.00001	113.6
	t statistic	6.29	19.4
	p-value	0.000028	0.00001

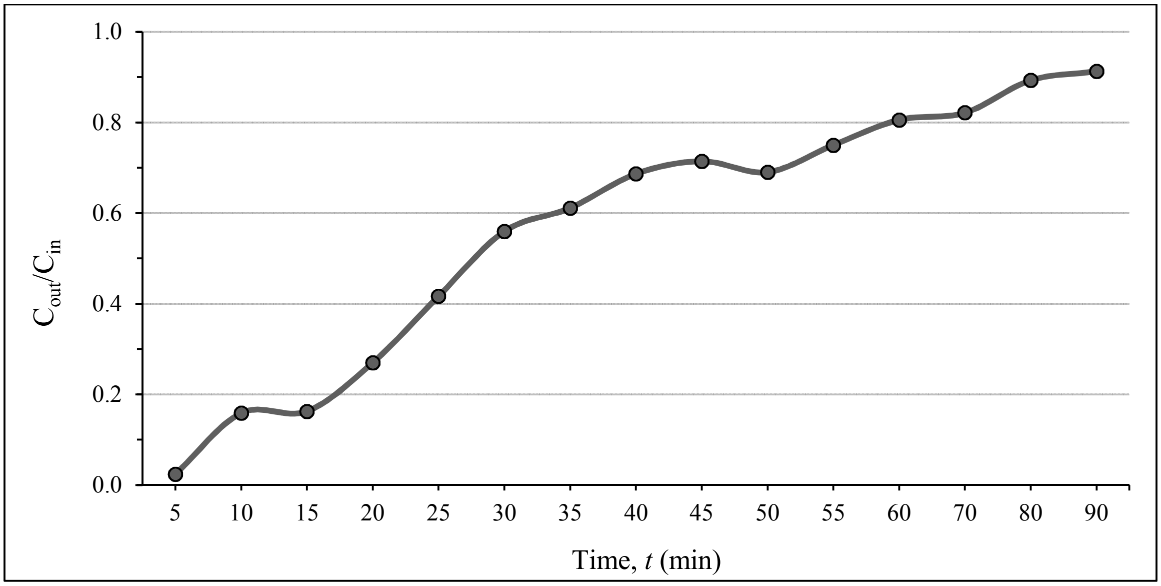

Figure 4-29: Time elapsed vs outlet/inlet concentration ratio (*C_{out}/C_{in}*) of effluent color in a CFA adsorption column.

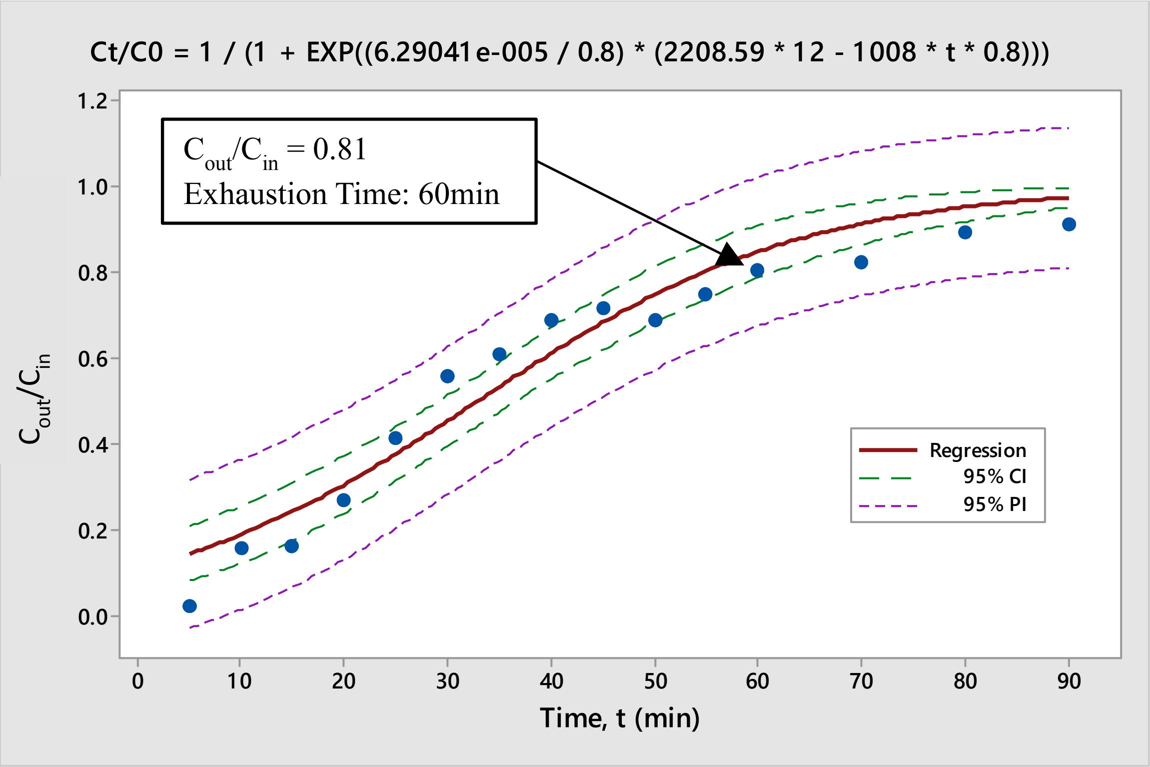

Figure 4-30: CFA column breakthrough data plotted with the non-linear prediction curve of the Thomas model. CI and PI here denote the confidence interval and prediction interval.t

CHAPTER 5:

CONCLUSION

5.1 Research Findings and Implications

In this research project, extensive batch studies and a brief column adsorption study were conducted to determine whether CFA can effectively remove color from pulp mill effluent in a laboratory setting.

- In the course of the batch adsorption studies, the effective observed CFA dose was 100 g/L, given an initial effluent color concentration of 900 mg/L Pt-Co or less. For effluent color concentrations above 900 mg/L Pt-Co, the effective CFA dose was 250 g/L.
- Experimentation revealed that the most effective mixing speed at which to agitate the CFA/pulp mill effluent mixture was 150 RPM. This mixing speed provided the best balance between maximum color removal and economical operation.
- The most effective initial effluent pH for color removal was found to be the unaltered pH of the raw pulp mill effluent, which fell within a range of 8.3 to 8.7. Only slight increases in color removal were observed at altered initial pH values. These increases were not significant enough to warrant the effort and expense of pH adjustment prior to treatment by CFA.
- The most effective CFA particle size for effluent color removal fell within the range of 0.15 mm – 0.297 mm. However, the mass of the ash at this size only constituted 1.68 % of the total CFA mass. Therefore, sieve separation of CFA for this specific particle size is not a cost-effective option.

- The equilibrium time for the adsorption of pulp mill effluent color onto CFA was determined to be after 24 hours of continuous contact. In addition, it was observed that most of the color removal occurs rapidly, within the first 15 minutes. Modeling the adsorption rate led to the conclusion that the Ho et. al. pseudo-second order kinetic model best describes the adsorption studied in this research.
- Adsorption capacity (q_e) of CFA was found to be dependent on both the initial concentration of color (C_0) in the effluent and the CFA dosage used. In addition, the adsorption system was successfully modeled by the Langmuir and Freundlich isotherms. Of the two, the Langmuir isotherm better describes the adsorption of effluent color onto CFA.
- Color removal from pulp mill effluent by CFA was observed to coincide with the removal of both DOC and COD. This suggests that CFA may suitable for the removal of other organic compounds from pulp mill effluent.
- No significant increases in effluent concentrations of lead or zinc were observed following treatment with CFA. Zinc concentrations decreased a small amount following CFA treatment.
- The breakthrough point of CFA column, where C_{out}/C_{in} equaled 0.8, occurred after 60 minutes of continuous operation. The Thomas model was found to not adequately explain the column adsorption phenomena observed.

5.2 Recommendations for Future Research

One area of the current research that deserves further study is the removal of organic compounds from pulp mill effluent by CFA. Due to the focus on color removal, organic compound adsorption was only addressed secondarily in this project. There are several existing studies that support this assertion. Estevinho, et al. (2007) reported that CFA columns exhibited a 99.9% removal efficiency for 2,4-dichlorophenol and pentachlorophenol. Kao, et al. (2000) also observed effective removal of 2-chlorophenol and 2,4-dichlorophenol from aqueous solutions by CFA. CFA was successfully used to remove dissolved organic matter from the secondary effluent of a municipal wastewater treatment plant (Wei, et al. 2011). However, no literature was found that investigated removal of similar compounds from pulp mill effluent specifically. Therefore, the next logical step along the path of the current research would be to fill this knowledge gap.

Another excellent topic for studies on color removal from pulp mill effluent by CFA would be the efficacy of immobilizing the ash particles. Given the difficulties encountered in this project due to the fineness of the CFA, immobilization of the ash in the form of synthetic zeolites or pellets would greatly enhance this material's applicability in an industrial setting. Creation of zeolites from CFA is well established procedurally in the literature (Querol, et al. 2002, Steenbruggen and Hollman 1998). To date, the studies investigating zeolitic CFA material have focused on the removal of dyes and heavy metals from aqueous solutions (Chunfeng, et al. 2009, Wang, Soudi, et al. 2006). One example is the work completed by Atun, et al. (2011). In their research two basic dyes (thionine ans safronine) were adsorbed onto CFA zeolites. The authors reported that the adsorption capacity of the zeolite was five times higher than that of unaltered

CFA. Other authors have taken this idea even further and successfully pelletized syntheic CFA zeolites (Rongsayamanont and Sopajaree 2007), and used the pellets for phenol removal from aqueous solutions (Jing 2013). Unfortunately, none of these lab-created CFA materials have been used to treat pulp mill effluent. Subsequent research into the removal of color and organics from pulp mill effluent by CFA should investigate the efficacy of these materials.

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APPENDIX A: SUPPLEMENTAL DATA

LIST OF TABLES

LIST OF FIGURES

Table A-1: Pt-Co Standard Solution concentrations used to prepare calibration curve for the method shown (8/10/13).

[a]Theo. Color Concentration (mg/L)	Hach Method 8025: Color		
	Deionized Water [b]Vol. (mL)	Standard Solution Vol. (mL)	[c]Exp. Color Concentration (mg/L)
500	-	10	500
300	4	6	308
200	6	4	207
150	7	3	159
100	8	2	106
50	9	1	54
30	9.4	0.6	34
10	9.8	0.2	13
0	10	0	3

[a] Theoretical
[b] Volume
[c] Experimental

Table A-2: Pt-Co Standard Solution concentrations used to prepare calibration curve for the method shown (5/24/2014).

Theo. Color Concentration (mg/L)	Hach Method 8025: Color		
	Deionized Water Vol. (mL)	Standard Solution Vol. (mL)	Exp. Color Concentration (mg/L)
500	-	10	508
300	4	6	308
200	6	4	206
150	7	3	156
100	8	2	103
50	9	1	52
30	9.4	0.6	31
10	9.8	0.2	12
0	10	0	0

Table A-3: CFA sieve analysis results.

Sieve #	Particle Size (mm)	[a]CFA Ret. (g)	[b]Cumul. Mass (g)	% Retained	Cumul. % Retained	% Finer
10	2	0.21	0.21	0.07	0.07	99.93
18	1	0.75	0.96	0.25	0.32	99.68
35	0.5	2.06	3.02	0.69	1.01	98.99
50	0.297	0.95	3.97	0.32	1.32	98.68
100	0.15	5.03	9	1.67	3.00	97.00
325	0.044	69.62	78.62	23.18	26.18	73.82
PAN	0.01	221.7	300.32	73.82	100.00	0.00

[a] CFA Retained

[b] Cumulative Mass

Table A-4: Effect of CFA dosage on effluent color removal for Effective Dosage Study B.1.

Date	**CFA Dosage (g/L)**	**Measured Dosage (±0.001g)**	**Sample A Color (mg/L)**	**Sample B Color (mg/L)**	**Average Filtrate Measurements**		
					pH	Color (mg/L)	Color Removal
8/11/13	0	0.0000	286	286	7.958	286	-
8/11/13	2	0.2003	266	275	7.795	272	4.86%
8/10/13	1	0.0996	282	286	7.829	279	2.62%
8/10/13	0.5	0.0500	282	288	8.016	284	0.56%
8/10/13	0.3	0.0300	288	288	8.044	288	-0.73%
8/10/13	0.2	0.0197	283	285	8.022	284	0.70%
8/10/13	0.1	0.0102	284	280	8.116	282	1.33%
8/11/13	0.05	0.0049	289	288	7.872	289	-0.91%
8/11/13	0.02	0.0019	296	281	7.863	289	-0.87%

Table A-5: Effect of CFA dosage on effluent color removal for Effective Dosage Study B.2.

Date	CFA Dosage (g/L)	Measured Dosage (±0.001g)	Sample A Color (mg/L)	Sample B Color (mg/L)	Average Filtrate Measurements		
					pH	Color (mg/L)	Color Removal
8/24/13	0	0.0000	284	284	7.985	284	-
8/24/13	20	2.0040	197	201	7.998	199	29.9%
8/24/13	10	1.0016	225	224	8.033	225	21.0%
8/24/13	5	0.5039	241	241	8.097	241	15.1%
8/24/13	3	0.3020	245	244	8.073	244	14.0%
8/24/13	2	0.2014	275	275	8.051	275	3.3%
8/24/13	1	0.1002	269	269	8.057	269	5.4%
8/24/13	0.5	0.0507	274	275	8.079	274	3.5%
8/24/13	0.3	0.0311	273	272	8.085	272	4.1%
8/24/13	0.1	0.0102	270	269	8.154	269	5.2%

Table A-6: Effect of CFA dosage on effluent color removal for Effective Dosage Study B.3.

Date	CFA Dosage (g/L)	Measured Dosage (±0.001g)	Sample A Color (mg/L)	Sample B Color (mg/L)	Average Filtrate Measurements		
					pH	Color (mg/L)	Color Removal
9/6/13	0	0.0000	257	258	8.095	258	-
9/6/13	20	1.9960	208	210	8.102	209	18.9%
9/6/13	10	0.9998	237	237	8.143	237	8.1%
9/6/13	5	0.5012	255	255	8.120	255	1.2%
9/6/13	3	0.3002	256	259	8.138	258	0.0%
9/7/13	2	0.2011	262	264	8.137	263	-2.0%
9/7/13	1	0.0998	267	268	8.152	267	-3.8%
9/7/13	0.5	0.0504	265	266	8.327	265	-2.9%
9/7/13	0.3	0.0308	263	262	8.165	262	-1.7%

Table A-7: Effect of CFA dosage on effluent color removal for Effective Dosage Study B.4.

Date	CFA Dosage (g/L)	Measured Dosage (±0.001g)	Sample A Color (mg/L)	Sample B Color (mg/L)	Average Filtrate Measurements		
					pH	Color (mg/L)	Color Removal
9/7/13	0	0.0000	260	260	8.217	260	-
9/7/13	100	10.0008	50	51	8.030	51	80.50%
9/7/13	75	7.5136	97	96	8.051	97	62.80%
9/7/13	50	4.9978	114	116	8.126	115	55.80%
9/7/13	30	2.9978	167	169	8.162	168	35.30%
9/14/13	20	2.0013	192	194	8.135	193	25.70%
9/14/13	10	1.0033	240	241	8.194	240	7.40%
9/14/13	5	0.4986	253	253	8.204	253	2.70%
9/14/13	3	0.3047	260	261	8.221	260	-0.30%

Table A-8: Effect of CFA dosage on effluent color removal for Effective Dosage Study B.5.

Date	CFA Dosage (g/L)	Measured Dosage (±0.001g)	Sample A Color (mg/L)	Sample B Color (mg/L)	Average Filtrate Measurements	
					Color (mg/L)	Color Removal
9/8/13	0	0.0000	248	240	244	-
9/8/13	100	10.0010	38	40	39	84.10%
9/15/13	75	7.5017	60	60	60	75.50%
9/15/13	50	5.0002	103	99	101	58.80%
9/15/13	30	3.0082	151	150	151	38.30%

Table A-9: Effect of CFA dosage on effluent color removal for Effective Dosage Study B.6.

Date	**CFA Dosage (g/L)**	**Measured Dosage (±0.001g)**	**Sample A Color (mg/L)**	**Sample B Color (mg/L)**	**Average Filtrate Measurements**	
					Color (mg/L)	Color Removal
9/7/13	0	0.0000	278	280	280	-
9/7/13	100	10.0114	60	63	61	78.0%
9/7/13	75	7.5320	92	90	91	67.6%
9/7/13	50	5.0030	130	129	129	53.8%
9/7/13	30	3.0209	172	171	171	38.6%
9/7/13	20	2.0024	209	209	209	25.2%
9/7/13	10	1.0101	233	234	234	16.3%
9/7/13	5	0.5063	265	263	263	5.4%

Table A-10: Effluent color and pH after pH adjustment and after CFA treatment for Effective pH Batch Study C.1.

Nominal Initial pH	After pH Adjustment		CFA Dosage (±0.001g)	After CFA Treatment			
	pH	Color (mg/L)		pH	Sample A Color (mg/L)	Sample B Color (mg/L)	[a]Avg. Color (mg/L)
4	4.00	344	9.9953	8.71	139	110	125
6	5.98	429	9.9995	8.74	135	134	134
7	7.02	573	9.9990	8.72	186	193	189
8	8.03	512	10.0120	8.91	216	206	212
10	10.00	575	10.0060	9.50	225	222	223
12	12.10	523	10.0110	10.64	198	196	197

[a] Average

Table A-11: Effluent color and pH after pH adjustment and after CFA treatment for Effective pH Batch Study C.2.

Nominal Initial pH	After pH Adjustment		CFA Dosage (±0.001g)	After CFA Treatment			
	pH	Color (mg/L)		pH	Sample A Color (mg/L)	Sample B Color (mg/L)	Avg. Color (mg/L)
4	4.08	380	2.0058	6.33	191	191	191
6	6.00	519	1.9993	8.13	397	485	441
7	7.01	584	2.0051	8.39	512	496	504
8	8.00	599	2.0015	8.89	494	501	498
10	10.18	602	2.0073	9.58	516	548	532
12	11.95	558	2.0033	11.13	467	489	478

Table A-12: Effluent color and pH after pH adjustment and after CFA treatment for Effective pH Batch Study C.3.

Nominal Initial pH	After pH Adjustment		CFA Dosage (±0.001g)	After CFA Treatment			
	pH	Color (mg/L)		pH	Sample A Color (mg/L)	Sample B Color (mg/L)	Avg. Color (mg/L)
4	4.01	515	14.9969	8.57	260	300	280
6	5.93	746	15.0008	8.84	331	329	330
7	7.01	838	14.9963	8.95	346	375	360
8	7.99	876	14.9994	9.29	393	395	394
8.3	8.34	880	14.9938	9.44	439	436	437
10	9.99	958	15.0012	9.35	435	463	449

Table A-13: Effluent color and pH after pH adjustment and after CFA treatment for Effective pH Batch Study C.4.

Nominal Initial pH	After pH Adjustment		CFA Dosage (±0.001g)	After CFA Treatment			
	pH	Color (mg/L)		pH	Sample A Color (mg/L)	Sample B Color (mg/L)	Avg. Color (mg/L)
4	4.01	724	24.9791	8.90	183	184	184
6	6.03	940	24.9932	9.45	211	220	216
7	7.01	1,076	24.9771	9.67	291	299	295
8.7	8.70	1,152	24.9705	9.63	361	363	362
10	9.98	1,196	24.9772	9.63	404	388	396
12	11.99	1,240	24.9841	10.38	456	508	482

Table A-14: Color removal measurements for varied CFA contact times with pulp mill in Kinetic Study E.1.

Date	**Contact Time (hours)**	**Measured Dosage (±0.001g)**	Sample A Color (mg/L)	Sample B Color (mg/L)	**Average Filtrate Sample Measurements**		
					pH	Avg. Color (mg/L)	Color Removal
12/11/13	0	0.000	570	572	9.338	571	-
12/11/13	0.5	9.996	387	411	8.969	399	30.0%
12/11/13	1	10.002	359	388	9.051	374	34.5%
12/11/13	1.5	10.006	392	366	9.108	379	33.5%
12/11/13	2	9.999	401	381	8.702	391	31.4%
12/11/13	3	9.997	377	357	8.387	367	35.6%
12/9/13	12	10.000	335	318	9.360	327	42.7%
12/9/13	24	10.004	312	295	9.432	304	46.8%
12/9/13	48	10.000	320	272	9.313	296	48.1%

Table A-15: Color removal measurements for varied CFA contact times with pulp mill in Kinetic Study E.2.

Date	**Contact Time (hours)**	**Measured Dosage (±0.001g)**	Sample A Color (mg/L)	Sample B Color (mg/L)	**Average Filtrate Sample Measurements**		
					pH	Avg. Color (mg/L)	Color Removal
1/20/14	0	0.000	882	892	9.097	887	-
1/20/14	0.25	24.979	237	279	9.138	258	70.9%
1/20/14	0.5	24.982	260	259	9.190	260	70.7%
1/20/14	1	24.971	270	256	9.278	263	70.3%
1/22/14	1.5	24.981	269	253	9.288	261	70.6%
1/22/14	2	24.969	228	230	9.337	229	74.2%
1/20/14	3	24.999	213	246	9.281	230	74.1%
1/20/14	4	24.977	206	210	9.374	208	76.6%
1/22/14	6	24.987	198	210	9.362	204	77.0%
1/22/14	8	24.967	203	231	9.336	217	75.5%
1/20/14	10	24.981	168	164	9.424	166	81.3%
1/20/14	12	24.959	158	174	9.471	166	81.3%
1/29/14	18	24.980	159	172	9.444	166	81.3%
1/20/14	24	24.964	152	156	9.526	154	82.6%
1/20/14	36	24.983	131	145	9.551	138	84.4%
1/28/14	48	24.983	136	143	9.377	140	84.3%

Table A-16: Color removal measurements for varied CFA contact times with pulp mill in Kinetic Study E.3.

Date	**Contact Time (hours)**	**Measured Dosage (±0.001g)**	Sample A Color (mg/L)	Sample B Color (mg/L)	**Average Filtrate Sample Measurements**		
					pH	Avg. Color (mg/L)	Color Removal
1/28/14	0	0.000	887	887	9.097	887	-
1/28/14	0.083	19.990	394	454	9.141	424	52.2%
1/29/14	0.167	19.969	415	418	9.256	417	53.0%
1/28/14	0.25	19.979	431	416	9.268	424	52.3%
1/29/14	0.333	19.965	395	391	9.353	393	55.7%
1/28/14	0.5	19.989	362	383	9.325	373	58.0%
1/28/14	1	19.982	346	345	9.428	346	61.0%
1/29/14	2	19.980	366	347	9.332	357	59.8%
1/30/14	5	19.981	294	299	9.455	297	66.6%
1/30/14	8	19.979	269	282	9.416	276	68.9%
1/29/14	12	19.959	247	261	9.621	254	71.4%
1/29/14	18	19.993	242	266	9.390	254	71.4%
1/28/14	24	19.963	225	216	9.609	221	75.1%

Table A-17: Color removal measurements for pulp mill effluent treated with varied CFA dosages in Isotherm Study F.1.

Date	**CFA Dosage (g/L)**	**Measured Dosage (±0.001g)**	Sample A Color (mg/L)	Sample B Color (mg/L)	**Average Filtrate Sample Measurements**		
					pH	Avg. Color (mg/L)	Color Removal
2/10/14	0	0.000	928	928	9.154	928	-
2/10/14	100	9.981	526	542	9.518	534	42.5%
2/10/14	125	12.504	488	487	9.464	488	47.5%
2/10/14	150	14.969	376	390	9.475	383	58.7%
2/10/14	175	17.500	289	313	9.456	301	67.6%
2/10/14	200	19.996	249	254	9.410	252	72.9%
2/10/14	225	22.503	212	225	9.410	219	76.5%
2/10/14	250	24.986	163	161	9.435	162	82.5%
2/10/14	275	27.500	108	123	9.392	116	87.6%
2/10/14	300	29.996	101	102	9.393	102	89.1%

Table A-18: Color removal measurements for pulp mill effluent treated with varied CFA dosages in Isotherm Study F.2.

Date	**CFA Dosage (g/L)**	**Measured Dosage (±0.001g)**	Sample A Color (mg/L)	Sample B Color (mg/L)	**Average Filtrate Sample Measurements**		
					pH	Avg. Color (mg/L)	Color Removal
4/5/14	0	0.000	1,036	1,036	8.913	1,036	-
4/5/14	150	14.998	594	600	9.536	597	42.4%
4/5/14	175	17.499	500	494	9.555	497	52.0%
4/5/14	200	19.989	422	392	9.599	407	60.7%
4/5/14	225	22.502	370	374	9.588	372	64.1%
4/5/14	250	24.992	272	314	9.553	293	71.7%
4/5/14	275	27.498	250	251	9.565	251	75.8%
4/5/14	300	29.978	239	215	9.484	227	78.1%
4/5/14	325	32.509	186	190	9.530	188	81.9%
4/5/14	350	34.990	158	157	9.596	158	84.8%

Table A-19: Color and COD measurements for untreated pulp mill effluent.

Date	Raw Effluent Sample	Average Raw Effluent Sample Measurements			
		pH	Temp (°C)	Color (mg/L)	COD (mg/L)
9/21/2014	Raw #2	8.374	26.8	571	325
9/21/2014	Raw #3	8.416	26.8	928	410
9/21/2014	Raw #4	8.375	26.8	1,036	630

Table A-20: Color and COD measurements for pulp mill effluent treated with various CFA dosages.

Batch Study	CFA Dosage (g/L)	Measured Dosage (±0.001g)	Average Filtrate Sample Measurements					
			pH	Temp (°C)	Color (mg/L)	Color Removal	COD (mg/L)	COD Removal
Isotherm Study H.1	0	0.000	9.154	19.9	928	N/A	410	N/A
	100	9.981	9.518	19.7	534	42.5%	288	29.8%
	150	14.969	9.475	19.7	383	58.7%	289	29.5%
	200	19.996	9.410	19.7	252	72.9%	213	48.0%
	250	24.986	9.435	19.8	162	82.5%	231	43.7%
	300	29.996	9.393	19.8	102	89.1%	164	60.0%

Table A-21: Zinc concentration measurements for raw and treated pulp mill effluent.

Batch Study	Sample	Date	[a]V_{sample} (mL)	V_{acid} (mL)	Modifying Factor, MF	C_{zinc} sample (mg/L)	C_{zinc} corrected (mg/L)	C_{zinc} raw effluent (mg/L)	ΔC_{zinc} increase (mg/L)	ΔC_{zinc} increase (%)
Raw Effluent	Raw #2	6/1/2014	25	0.3	1.012	0.19	0.19	N/A	N/A	N/A
	Raw #3	6/1/2014	25	0.4	1.016	0.19	0.19	N/A	N/A	N/A
	Raw #4	6/1/2014	25	0.4	1.016	0.32	0.33	N/A	N/A	N/A
Isotherm Study, F.1	100 g/L CFA	6/1/2014	25	0.35	1.014	0.14	0.14	0.19	-0.05	-26.5%
	200 g/L CFA	6/1/2014	25	0.35	1.014	0.17	0.17	0.19	-0.02	-10.7%
	300 g/L CFA	6/1/2014	25	0.35	1.014	0.12	0.12	0.19	-0.07	-37.0%

[a] See **Table A-24** for definitions of all variables used in **Tables A-21 – A-23**.

Table A-22: Lead concentration measurements for raw and treated pulp mill effluent.

Batch Study	Sample	Date	C_{lead} reagent (mg/L)	C_{lead} sample (mg/L)	C_{lead} net (mg/L)	C_{lead} raw effluent (mg/L)	ΔC_{lead} increase (mg/L)	ΔC_{lead} increase (%)
Raw Effluent	Raw #2	5/18/2014	0.036	0.1	0.064	N/A	N/A	N/A
	Raw #3	5/17/2014	0.036	0.1	0.064	N/A	N/A	N/A
	Raw #4	5/17/2014	0.036	0.254	0.218	N/A	N/A	N/A
Isotherm Study, F.1	100 g/L CFA	5/18/2014	0.036	0.205	0.169	0.064	0.105	164.1%
	200 g/L CFA	5/18/2014	0.036	0.095	0.059	0.064	-0.005	-7.8%
	300 g/L CFA	5/18/2014	0.036	0.1	0.064	0.064	0.000	0.0%

Table A-23: Chromium concentration measurements for raw and treated pulp mill effluent.

Batch Study	Sample	Date	V_{sample} (mL)	V_{acid} (mL)	Modifying Factor, MF	C_{Cr} sample (mg/L)	C_{Cr} net (mg/L)	C_{Cr} raw effluent (mg/L)	ΔC_{Cr} increase (mg/L)	ΔC_{Cr} increase (%)
Raw Effluent	Raw #2	6/21/14	25	0.3	1.012	-0.06	-0.06	-	N/A	N/A
	Raw #3	6/21/14	25	0.4	1.016	-0.09	-0.09	-	N/A	N/A
	Raw #4	6/21/14	25	0.45	1.018	-0.08	-0.08	-	N/A	N/A
Isotherm Study, F.2	150 g/L	7/9/14	25	0.4	1.016	-0.03	-0.03	-0.09	0.06	66.7%
	250 g/L	7/9/14	25	0.3	1.012	0	0	-0.09	0.09	100.0%
	350 g/L	7/9/14	25	0.3	1.012	0.01	0.01	-0.09	0.10	111.1%

Table A-24: Definition of variables used in Zinc, Lead, and Chromium measurement tables.

Variable	Definition
V_{sample}	Volume of CFA-treated effluent sample.
V_{acid}	Volume of acid (1 M HCl) added to the sample to adjust the pH to 4, as specified by the test procedure.
Modifying Factor (MF)	Heavy metal concentration correction factor to account for acid additions to sample volume.
$[C_{zinc}, C_{lead}, C_{Cr}]_{sample}$	Heavy metal concentration in the effluent sample.
$[C_{zinc}, C_{lead}, C_{Cr}]_{corrected}$	Heavy metal concentration in the effluent sample, corrected for acid additions.
$[C_{zinc}, C_{lead}, C_{Cr}]_{raw\ effluent}$	Heavy metal concentration in untreated effluent sample.
$[\Delta C_{zinc}, \Delta C_{lead}, \Delta C_{Cr}]_{increase}$	Heavy metal concentration increase due to CFA treatment.

Table A-25: Color and COD measurements for pulp mill effluent treated with Pulverized Activated Carbon (PAC).

Date	**CFA Dosage (g/L)**	**Measured Dosage (±0.001g)**	Sample A Color (mg/L)	Sample B Color (mg/L)	**Average Filtrate Sample Measurements**				
					pH	Color (mg/L)	Color Removal	COD (mg/L)	COD Removal
8/14/14	0	0.000	1,084	1,144	8.374	1,114	N/A	422	N/A
8/14/14	2.5	0.250	1,036	1,028	8.443	1,032	7.3%	413	2.1%
8/14/14	5	0.496	972	900	8.438	936	15.8%	412	2.4%
8/14/14	7.5	0.752	836	848	8.416	842	24.4%	422	0.0%
8/14/14	10	1.000	796	764	8.375	780	29.9%	431	-2.1%

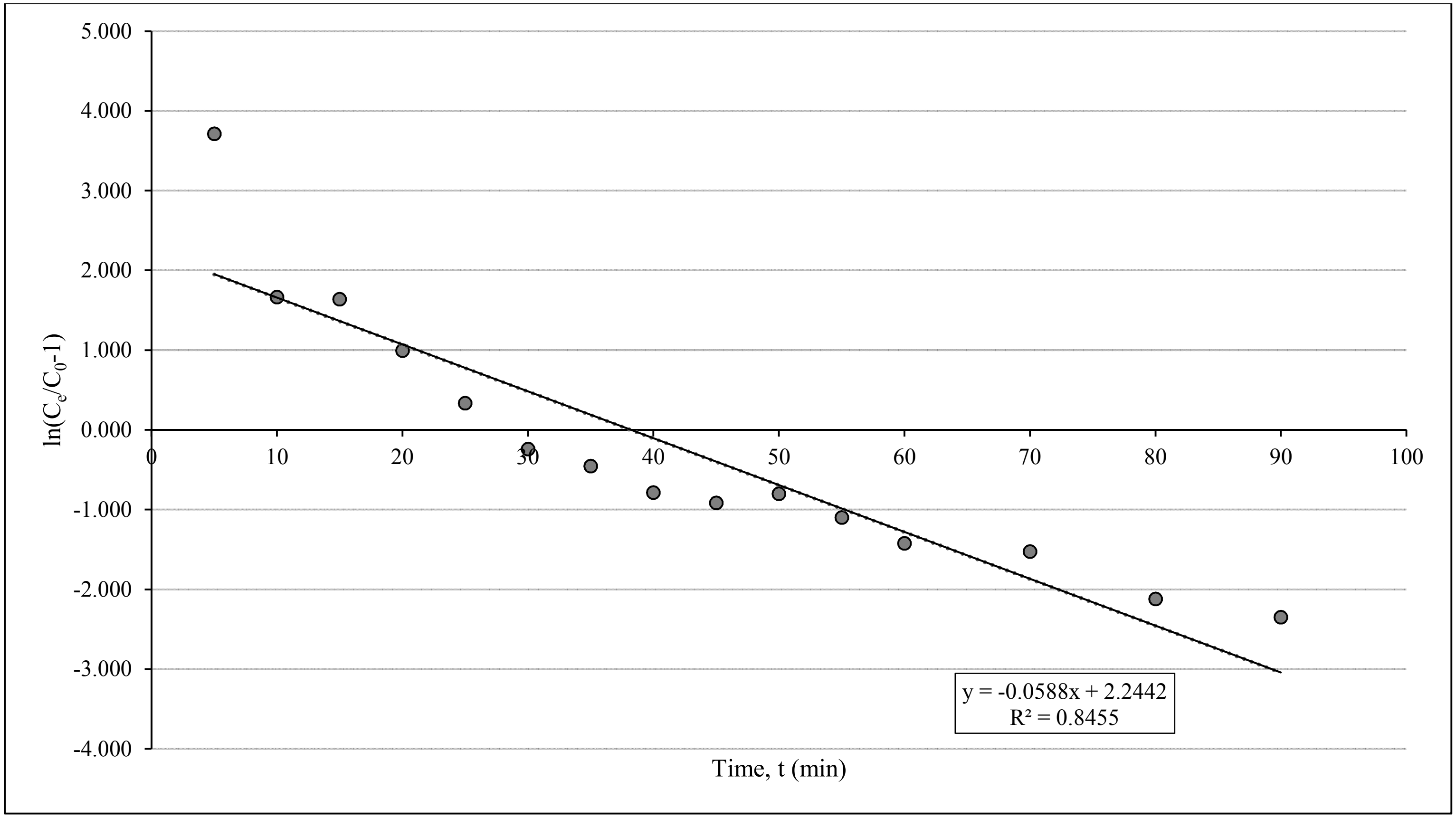

Figure A-1: CFA column breakthrough data plotted with the values predicted by the linear form of the Thomas model.

Table A-26: Color measurements for pulp mill effluent treated with 6g of CFA packed in an adsorption column.

Date	Time, t (min)	Thru-put volume (mL)	Measured Color	Dilution Factor	Color, C_{out} (mg/L Pt-Co)	C_{out}/C_{in}
9/21/2014	0	0	252	4	1,008	1
9/21/2014	5	4	6	4	24	0.02
9/21/2014	10	8	40	4	160	0.16
9/21/2014	15	12	41	4	164	0.16
9/21/2014	20	16	68	4	272	0.27
9/21/2014	25	20	105	4	420	0.42
9/21/2014	30	24	141	4	564	0.56
9/21/2014	35	28	154	4	616	0.61
9/21/2014	40	32	173	4	692	0.69
9/21/2014	45	36	180	4	720	0.71
9/21/2014	50	40	174	4	696	0.69
9/21/2014	55	44	189	4	756	0.75
9/21/2014	60	48	203	4	812	0.81
9/21/2014	70	56	207	4	828	0.82
9/21/2014	80	64	225	4	900	0.89
9/21/2014	90	72	230	4	920	0.91