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Direct White Sugar Production: optimization and chemical regeneration of fixed-bed activated carbon adsorbers

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DIRECT WHITE SUGAR PRODUCTION:
OPTIMIZATION AND CHEMICAL REGENERATION OF
FIXED-BED ACTIVATED CARBON ADSORBERS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and Agricultural and Mechanical College
in partial fulfillment of the
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in
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by
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Nomenclature

Symbol	Description	Units
a	Total interfacial area of adsorbent per unit volume	m^2/m^3
A	Column cross sectional area	m^2
Brix, °Bx	Approximation of sucrose content. Measures total dissolved solids.	
BV	Bed volume(s)	-
BV/hr	Bed volumes per hour	-
C	Concentration in bulk fluid	IU
C^*	Concentration of fluid in equilibrium with adsorbent	IU
C_0	Feed concentration	IU
I_0	Modified Bessel function of the 1st kind and zero order	-
ICUMSA	International Commission for Uniform Methods of Sugar Analysis	-
IU	ICUMSA units	IU
K	Linear partition coefficient	-
k_L	Film mass transfer coefficient	m/min
k_La	Effective mass transfer coefficient	min^{-1}
q	Concentration on solid phase	IU
Q	Volumetric flow rate	m^3/min
t	Time	min
T	Temperature	°C
Vo	Superficial velocity	m/min
V	Interstitial velocity	m/min
V_{bed}	Bed volume for void fraction determination (includes voidage)	ml
V_{H2O}	Water volume for void fraction determination	ml
V_{carbon}	Carbon volume for void fraction determination	ml
V_T	Total volume for void fraction determination	ml
z	Bed depth	m

Greek Symbols

β	Variable of integration	-
ε	Void fraction	-
τ	Dimensionless time	-
ζ	Dimensionless distance	-
θ	Relative time	min

Abstract

A system for the direct production of white sugar from clarified sugar cane juice in a raw sugar factory has been developed at the Audubon Sugar Institute. This Direct White Sugar Production (DWiSP) system employs a series of columns packed with adsorbent media. Activated carbon is used in the first column(s) as a filter and bulk decolorizer. Ion exchange resins are then used to remove ash and remaining color.

Batch testing was performed in order to determine equilibrium parameters. An analytical model was utilized in conjunction with column loading tests to determine dynamic characteristics of the carbon adsorber for use in determining design parameters. Ion exchange columns were investigated to determine deashing and decolorization properties. The use of hydrogen peroxide pretreatment was also investigated. Chemical regeneration of carbon was also investigated.

Batch test indicated a decrease in the carbon's adsorptive capacity when the feed was pretreated. Column tests indicated that residence time has a significant effect on carbon column performance and film mass transfer was related to superficial velocity as is described in previous work. The ion exchange system performed consistently over seven cycles and was able to produce a low color, low ash product for approximately 15 bed volumes, after which exhaustion set in rapidly. Exhaustion was indicated by a sharp increase in conductivity of the final column product. Evaluation of a New Regeneration Process (NRP) for chemical regeneration of carbon showed it to be effective in returning the carbon to 70-85% of its virgin capacity. The NRP solution was also compared to a regenerant solution of sodium hydroxide. The NRP solution was twice as effective as a 2% sodium hydroxide solution, but costs more than twice as much.

Chapter 1. Introduction

1.1.   Traditional Production of Refined White Cane Sugar

White cane sugar is currently produced in three steps. The first step occurs in the sugar cane plant, where the sugar (sucrose) is produced. In the second step, raw sugar, which has a light brown color, is produced in a sugar factory (also referred to as a mill). The factory is ideally located in close proximity to the cane fields in order to minimize degradation and transportation costs. The third step occurs at a refinery, where the raw sugar is transported and processed to remove color and other impurities.

Figure 1.1 is a flow diagram of a raw sugar factory. Sucrose is extracted from cane with water by means of either counter-current milling or diffusion. The juice is screened, heated to boiling, and flashed. The juice is then clarified, where milk of lime (calcium hydroxide) is used to precipitate colloidal materials and suspended solids. The clarified juice is evaporated to a concentration of approximately 65 percent total dissolved solids in a multiple effect evaporator train. A three stage crystallization process is used to produce the sugar crystals, which are separated from the mother liquor by centrifuges after each stage. The raw sugar is sent to a refinery where it is processed into white sugar.

1.2.   Direct White Sugar Production

The development of a system to produce white sugar directly in the sugar factory is motivated by increasing factory revenue. Three areas where profitability may be increased are increased recovery during processing, improved quality of the sugar and value added from higher quality molasses (Fechter et al., 2001). Refineries are relatively low cost and simple operations. The greatest costs are from transportation of raw sugar, energy expenditures and losses during

refining. By producing the white sugar directly, these costs can be avoided, or at least minimized.
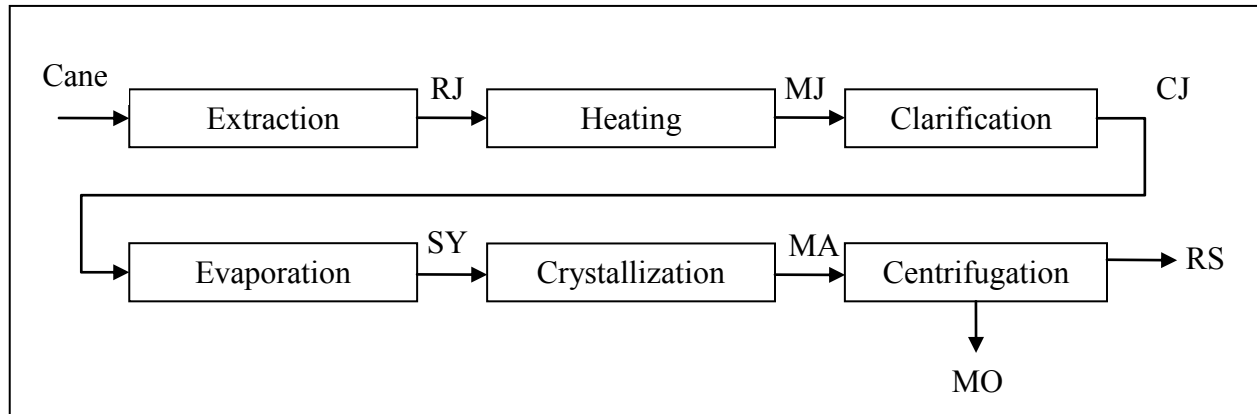
Figure 1.1. Raw Sugar Factory. RW = Raw Juice, MJ = Mixed Juice, CJ = Clarified Juice, SY = Syrup, MA = Massecuite, RS = Raw Sugar, MO = Molasses.

A system to produce white sugar directly in the raw factory has been proposed and developed at the Audubon Sugar Institute (Rein et al., 2006). The Direct White Sugar Production process (DWiSP) was designed to be a simple yet effective system involving the use of adsorbent media in packed bed columns and bleaching pretreatment. The system is intended to be incorporated into an existing sugar factory. The system may be installed after either the clarifier or the 1st effect evaporator (figures 1.2 and 1.3).

Juice from the clarifier or first stage evaporator is first pretreated with an oxidizing agent, such as hydrogen peroxide (H_2O_2). The pretreated juice is then passed through columns containing granular activated carbon (GAC) for decolorization. The first column acts as a guard column, where fines and suspended solids are removed. The juice is then cooled to 10°C before passing through a bed of strong acid cationic (SAC) resin, which causes a significant drop in pH. At low pH, sucrose breaks down to glucose and fructose by the process of inversion. Cooling the juice prevents this from occurring.
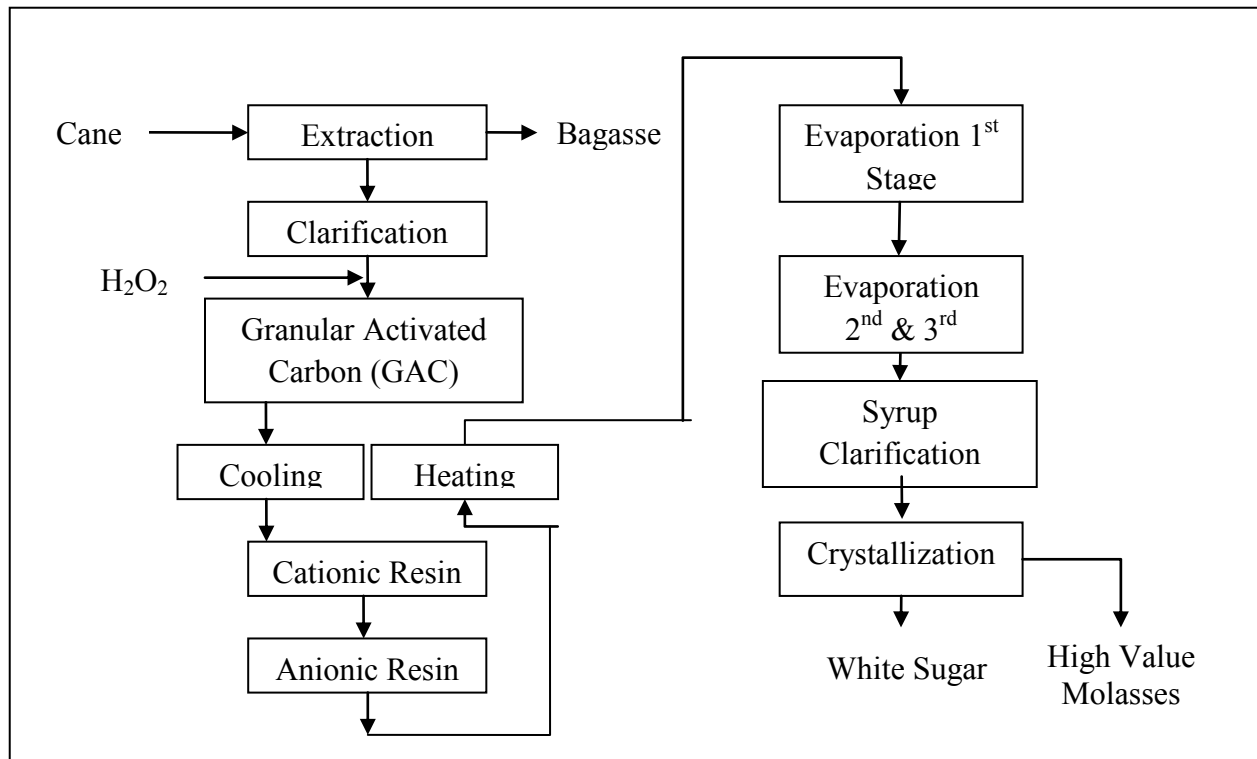
Figure 1.2. Direct White Sugar Production flow diagram for installation after clarifier
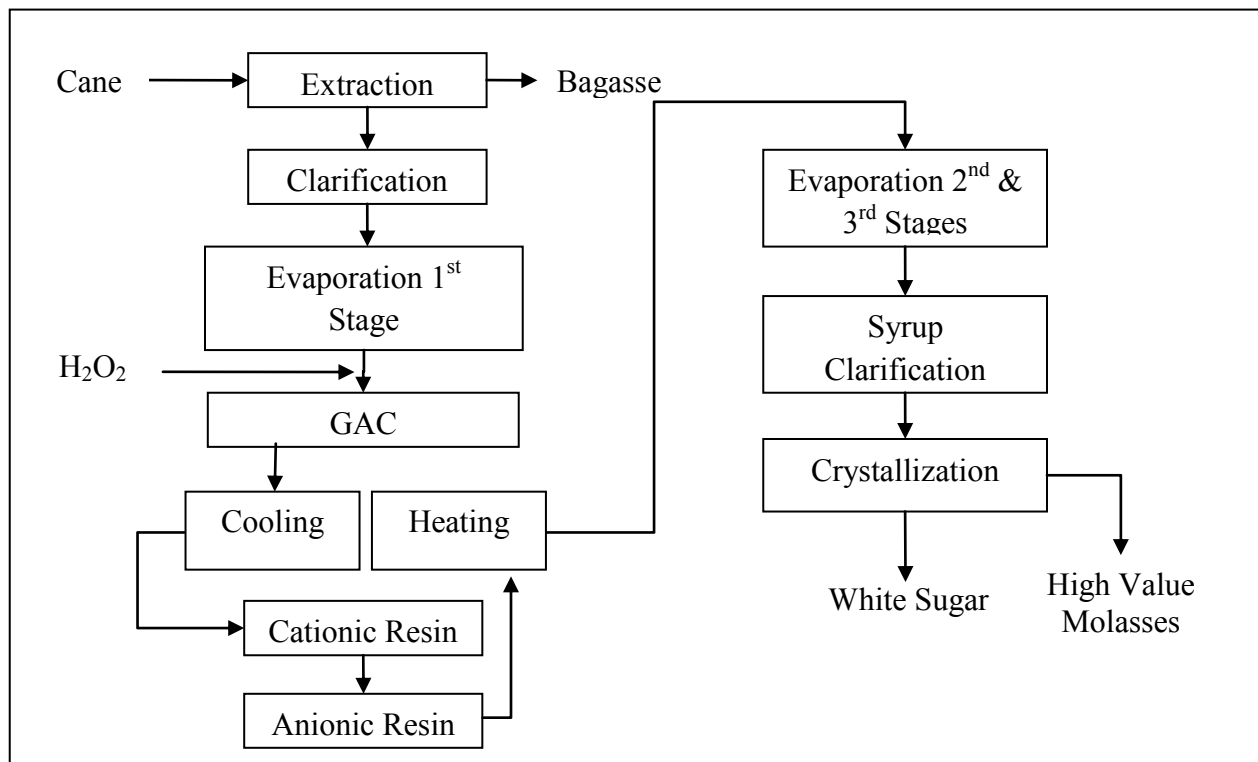
Figure 1.3. DWiSP installation after 1st effect evaporator

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After passing through the SAC resin, the juice is then sent to a weak base anion (WBA) resin column. This combination of resins removes most of the inorganic impurities present in the juice (demineralization or de-ashing) and some organic compounds. Most of the remaining colorants are also removed.

The juice is then reheated and sent to the evaporators, where it is concentrated to syrup of approximately 65% total dissolved solids. Clarification of the syrup is done to reduce turbidity, which is an undesirable effect of the DWiSP process. After this step, the syrup is handled as in a typical factory.

Another key element of the process is the use of chemical regeneration of the carbon columns. While chemical regeneration is the standard method for ion exchange resins, carbon is normally regenerated by means of heating in a kiln. The use of chemical regeneration avoids the expense of constructing and operating a furnace and losses that occur during handling of the carbon. A novel chemical regeneration system, referred to as the New Regeneration Process (NRP), has been developed at the Audubon Sugar Institute that has been shown to effectively remove adsorbed colorant from granular activated carbon.

The benefits of this process are:

- Increased yield

- Increased quality

- Decreased scaling of heat transfer surfaces

- Increased value of molasses

1.3.   Research Objectives

Granular activated carbon has been used in refineries for decolorization. Implementing the DWiSP process in a factory requires a different approach, since flow rates are higher and the liquor contains more color. Optimization of design parameters of the system's components will maximize performance and minimize construction and operating costs. The use of mathematical modeling allows for the determination of optimal design parameters.

In order to determine the optimal design parameters for the adsorber columns, mathematical modeling may be used. Models have been developed for packed bed adsorbers used to decolorize refinery liquors. The methods and principles employed in earlier investigations into decolorization can be used to investigate the performance of activated carbon on cane juice decolorization.

Since the chemical regeneration of carbon involves a novel process, it is necessary to investigate its effectiveness relative to other methods. The specific objectives of the research are:

- Determine and implement a suitable mathematical model for the evaluation of the performance of a granular activated carbon packed bed adsorber column

- Perform batch tests to determine equilibrium parameters for the model

- Conduct bench scale column loading experiments and determine mass transfer parameters from the model

- Investigate the feasibility and optimal dosing for hydrogen peroxide pretreatment

- Determine the effectiveness of the New Regeneration Process and compare to other regeneration methods

- Use model parameters to determine design specifications for a full scale system

Chapter 2. Background

2.1. Cane Juice Colorants

The primary objective of sugar refining is the removal of color, among other impurities, in order to produce as pure and low color a crystal as is feasible. Color determines the grade of sugar - raw or white - and is the main concern of buyer and consumers (Ellis, 2004). It follows then that significant effort has gone into the research of the nature of color, prevention of its formation and methods of its removal.

2.1.1. Natural colorants (Present in cane)

Colorants can fall into one of two categories: natural and those formed during production. *Plant pigments*: Plant pigments are inherent in the structure of the cane plant. They have been described as being primarily flavonoids and phenolics (Davis, 2001; Bento, 2003). They can comprise as much as two thirds of color in raw sugar. Flavonoids can be a considerable problem for sugar production, as they may account for 30% of the coloration of raw sugar at pH 7 (Mersad, 2003). Bento (2003) reports that, due to their solubility, flavonoids can pass through the sugar production process without being removed. The inclusion of a glycoside in their structure causes an affinity for sugar crystals. Phenolics are generally uncolored until they undergo reactions with compounds such as amines or iron. Both phenolics and flavonoids undergo enzymatic oxidation reactions, which lead to process-formed colorants, described later.

Plant pigments tend to have molecular weights of less than 1000 Daltons (Da). They are highly ionized, which gives them a high indicator value (IV, ratio of the absorbance at 420 nm of a sample at pH 9 to pH 4). They are readily removed during refining, but are also easily incorporated in the sugar crystal.

2.1.2. Colorants Formed During Production

Melanins: Melanins have been categorized by Davis (2001) as a subdivision of melanoidins. They are formed by enzymatic oxidation of phenolic compounds in quinones by polyphenoloxidases (PPO) to produce indole polymers (Mersad, 2003). They form at temperature between ⁻18 °C and 55 °C and at pH between 4.5 and 8. These conditions are descriptive of cutting and milling, and these activities create contact between the PPO and its substrates. Further reactivity with amines may lead to the formation of melanoidins.

Melanoidins: Mersad (2003) describes these colorants as the products of Maillard reactions (non-enzymatic browning), which are condensation reactions of a carbonyl compound, such as a reducing sugar, with amino acids, proteins or ammonia. They form at ambient temperatures, but the reaction is advanced by temperature rise. Their formation is also advanced by high brix and low purity.

Melanoidins develop slowly in acidic media and intensify in basic media. Formation peaks during evaporation and continues through crystallization. Their molecular weight is typically greater than 2500 Da. They have a slightly negative charge at neutral pH, but are positively charged in acidic conditions. They are insensitive to pH, and have a low IV.

Caramels: Caramels are of considerable interest to the food industry. Their composition can vary greatly, depending on formation conditions. The principal interest of the sugar industry concerns those which are formed from the thermal degradation of sucrose (Mersad, 2003). They possess a high molecular weight, which increases over time due to continued polymerization (Davis, 2001). They are slightly charged, and are not pH sensitive.

Invert Degradation Products: These colorants are referred to as hexose alkaline degradation products (Mersad) and alkaline degradation products of fructose (Davis, 2001). They are

produced by decomposition of monosaccharides in alkaline media. They tend to be brown in color, acidic (which can cause inversion), and, therefore, form more degradation color products. Since they are produced by high temperatures, their production is continuous throughout the sugar process, particularly on heated surfaces.

2.2. Removal of Color - Traditional Methods

White sugar is currently produced by refineries, which are usually independent of the raw sugar plant. Several refining techniques are employed – affination, carbonatation, sulphitation, crystallization and adsorptive decolorization.

Affination involves washing the adhering film of molasses from the surface of the raw crystal and is the first step in traditional refining. The separation involves mixing of raw sugar with heavy syrup (75 brix), then purging the mixture in centrifugals and washing with hot water after the syrup has been spun off (Chen, 1985).

Carbonatation is used for the removal of insoluble matter that contributes to the turbidity of the sugar liquor, but also provides a degree of decolorization. It consists of precipitating calcium carbonate in the washed raw liquor by adding lime and bubbling in carbon dioxide under controlled conditions of temperature and alkalinity. Crystalline calcium carbonate is formed, which traps much of the insoluble matter, as well as a portion of the ash and colored substances (Chen, 1985).

Phosphatation is similar to carbonatation except that it uses lime and phosphoric acid. Filtration of the calcium phosphate floc produced is difficult, so air flotation is commonly used to remove the floc from the liquor. Phosphatation produces similar color reduction to carbonatation – about 25-50% - but clarity of the carbonatation liquor is slightly better because the final liquor is pressure filtered (Chen and Chou, 1993).

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Sulfitation is a process that is employed in the production of factory-made white sugars. Sulfitation processes are subject to several variations, but the fundamental principles involve the use of sulfur dioxide in conjunction with lime to remove color and color forming products. The mechanism of color removal has been described as more of a suppression of color formation than as a removal of color already present (Davis, 2001). The inhibition is further detailed as being brought about by the combination of the sulfite group with reducing sugars, which blocks the formation of caramels and melanoidins. Sulfitation is also known to inhibit Maillard-type reactions.

Crystallization is perhaps the most effective method for the removal of colorant. Up to 95% of the color in cane sugar liquor is removed during crystal formation (Godshall, 1999).

2.3. Activated Carbon

Activated carbon is carbon that has been made porous by preparation with various gases (steam, CO_2, N_2) at high temperatures. It is typically derived from coal or biomass. The activation process increases surface area by the formation of these honeycomb-like pores (500-2000 m^2/g).

Activated carbons function via adsorption- Van der Waals forces cause solute particles to be pulled out of solution and adhere to the carbon surface. The undesired particle has a greater affinity for the carbon than for the solution.

The non-polar characteristic of carbon allows for adsorption of similar compounds, but polar compound are not typically adsorbed. However, chemisorption may occur due to oxygenated functional groups that remain from the activation process. This allows for polar molecules to also be removed from the solution. Activated carbons have been reported to be highly effective for phenol and flavonoid removal (Davis, 2001). The weakly acidic nature of

colorants allows for electrostatic linkage to the adsorbent surface, while the neutral sugar remains unaffected (Ellis, 2004). Therefore, an 80% typical colorant removal can be achieved when filtering clarified sugar juice.

There are three important characteristics for sugar color removal:

1. Distribution of pore volume among the three sizes - micropores are less than 20 Å, mesopores range from 20 to 500 Å, and macropores are greater than 500 Å. (Chiang et al suggest 20-200 Å as range for mesopores).

2. Distribution of surface area between micropores and external surface area

3. Chemical reactivity of the carbon surface

In a study evaluating the efficacy of carbons derived from agricultural by-products, Pendyal et al (1999) found a relationship between the various sizes of pores that characterized efficient color removal. The best decolorizers exhibited a pore volume distribution of 60-75% micro, 20-30% meso, 4-5% macro. It was also determined that the best decolorizers have a micropore surface area comprising 80-90% and an external surface area of 10-20% of the total. The effectiveness of these distributions was attributed to the larger pores serving as avenues for rapid diffusion of the colorants to the smaller pores, where they are adsorbed. These distribution factors are more significant in colorant adsorption than total surface area.

2.3.1. Regeneration of Carbon

The traditional method of regenerating exhausted activated carbon involves the use of kilns to thermally remove the colorants from the carbon granules or particles at temperatures reaching 800°C. This method is effective at regeneration, but requires a large amount of energy and expensive equipment. It also results in a typical loss of 5-10% of the carbon from attrition, excessive burnoff and washing during each cycle (Leng and Pinto, 1996). Therefore, the

alternative method of chemical regeneration may be used. Chemical regeneration has a number of advantages (Leng and Pinto, 1996):

1. It can be done *in situ,* thus avoiding unloading, transport and repacking of the adsorbent

2. Loss of carbon from thermal desorption is eliminated

3. Recovery of valuable adsorbates is possible

4. Chemical regenerants can be reused with proper subsequent treatments.

2.3.2. Chemical Regeneration of Carbon

Several factors must be considered when selecting a regeneration technique for activated carbon. The selection of regenerant is critical to the regeneration efficiency (Chiang et al., 1997). Leng and Pinto (1996) emphasized the determination of adsorbate and adsorbent characteristics - solubility, pH effects, reactivity - as key elements in predicting efficacy of the regenerant used. They concluded that addressing these factors in combination leads to higher regeneration efficiency. Chiang et al. (1997) also found that chemical properties of the regenerant should facilitate affinity/solubility.

It is interesting to note that both studies mentioned the use of alcohols as part of their procedure. Chiang et al. used ethanol as the regenerant, achieving a regeneration efficiency of 81.11% for phenols, while Leng and Pinto used methanol as a means of determining extraction efficiency, but still reported regeneration data for methanol (88.1%).

Many chemicals have been researched as potential regenerants. The use of acid-base sequences for regeneration has been investigated by several studies. The base, typically NaOH, is used as the regenerant, and the acid as a neutralizing agent. Newcombe and Drikas (1993) report a 94% removal of organic compounds after regeneration with NaOH followed by HCl neutralization. Their study was nonspecific for the identity of the organic compounds. However,

since low pH will result in sugar inversion (conversion of sucrose to its component monosaccharides), the use of an acid wash is not recommended, as is discussed below.

Srivastava and Tyagi (1995) used several chemicals to determine the regeneration potential for activated carbon derived from fertilizer waste slurry after exhaustion with various phenols as the adsorbate. The results of their experiments using NaOH as the regenerant are not as promising as are those of other research, but it must be emphasized that they used a novel carbon, and they did not follow a procedure of acid neutralization. (They did, however, find that excellent regeneration can be achieved for 2-4-6-trinitrophenol with acetone (88-92%), acetic acid (90-96%), and methanol (86-90%)).

Leng and Pinto achieved 71.9% regeneration with a solution of 1% NaOH for phenols using Kureha MP spherical activated carbon (Kureha Chemical Co., New York). Phenols react with NaOH to produce soluble salts, thus enabling desorption. The 1% solution gave better results for desorption of phenols than a 4% solution. They attribute this to the adsorption of OH^- ions, which hindered desorption. Moodley et al. (2000) found similar results when they increased solution strength from 2% to 4%. Leng and Pinto also did not use acid neutralization (but did conduct trials with acid as a regenerant).

Several studies have been conducted on activated carbons developed by Norit Carbon for chemical regeneration have been conducted (Moodley et al, 2000; Barker and Davis, 2002; Barker et al., 2004). In each experiment, the carbon was evaluated in terms of its color removal capacity after successive regenerations.

In the Moodley study (2000), it was determined that calcium fouling diminished the adsorptive capacity of the carbon, and hence, color removal. Regeneration efficiency was also affected negatively, so an acid prewash was performed before regeneration. Citric acid

neutralization after regeneration was also performed, in order to prevent the formation of colorants formed at high pH, as mentioned above. When this system was used, a 60 to 80% decolorization was achieved with regenerated carbon.

Subsequent experiments were performed on a new Norit carbon, developed to have faster adsorption kinetics (Barker and Davis, 2002; Barker et al., 2004). Since calcium fouling was such a problem, a prefilter was used in the 2002 study. This eliminated the need for an acid prewash. The use of acid neutralization was also eliminated, since it was determined that color formation was preferred to sucrose loss. Rinsing with water was done until effluent pH was approximately 9. Removal of the neutralization step appeared to have no effect on color removal.

2.4.   Ion exchange resins

Ion exchange resins have been used for over fifty years in the sugar industry. However, early resins, based on styrenic polymers in the chloride form, were limited in the level of syrup color they could effectively process. If color levels were too high, the regenerants would eventually fail to desorb the color bodies, and the resins would be rendered useless. Therefore, they were used primarily as polishers, following traditional color removal methods of bone char and granular activated carbon.

With the advent of macro-reticular resins in the 1960's, and acrylic resins in the 1970's, ion exchange became the principal decolorizer in a number of plants. These resins are capable of withstanding higher color loading and exhibit qualities of high stability and, in the case of acrylic resins, ease of regeneration.

Adsorption of color molecules by the resins is not actually ion exchange in character. Fries (1982) describes the mechanism of adsorption as a facilitation by the resins' functional groups that make the resin hydrophilic, which allows the sugar solution and color bodies to reach

the hydrophobic backbone of the polymeric resin. Bento (1998) describes the resin as acting via two mechanisms: ionic bonding between the anionic functional group of the resin to the anionic color molecule, and hydrophobic interaction between the apolar parts of colorant and the styrenic divinyl-benzenic matrix.

While some refineries use only one type of resin, it has been demonstrated (Fries, 1982) that a combination of styrenic and acrylic resins provide greater decolorization capability and less sensitivity to color loading. Acrylic resins remove aromatic, high molecular weight (HMW) colorants that foul styrenic resins.

2.4.1. Ion Exchange Chemistry

Ion exchange chemistry varies, depending on the type of functional groups used. The use of ion exchangers in sugar decolorization is well documented, and the use of various combinations of resin types has been explored. Remco Engineering (1981) provides a concise and sufficient explanation of basic ion exchange chemistry. By describing the functionality of the various resin types, a better understanding of the mechanisms of color and ash removal can be ascertained.

Strong Acid Cation (SAC): These resins behave as do strong acids, having the ability to be highly ionized in both the acid and salt forms. They function by the following representative reaction:

$(R\text{-}SO_3H) + NaCl \rightarrow (R\text{-}SO_3)Na + HCl$
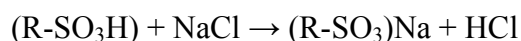
Regeneration is done with a strong acid, such as HCl, to return them to the hydrogen form. A salt solution can also be used, if the desire is to convert the resin to the sodium form (softening).

Weak Acid Cation (WAC): In weak acid cationic resins, the functional group is typically a less ionizable carboxylic acid:

$$2(R\text{-}COO^-H^+) + Ca^{2+}(HCO_3^-)_2 \rightarrow (R\text{-}COO)_2Ca + 2H_2CO_3$$
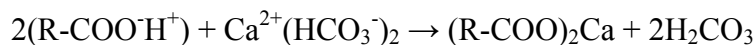
These resins have a higher affinity for H+ ions than do the strong acid type, which allows for regeneration with less acid solution. However, they are pH sensitive, and have limited capacity below pH 6.0.

Strong Base Anion (SBA): Strong base anion resins are analogous to the strong acid resins. They are highly ionizable, and can be used over the entire pH range. Regeneration is done with NaOH, which returns it to the hydroxide form. The characteristic reaction is:

$$R\text{-}NH_3OH + HCl \rightarrow R\text{-}NH_3Cl + H_2O$$
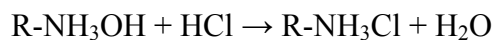
Weak Base Anion (WBA): These resins are used for the adsorption of acids as they cannot split salts. They require less regenerant than SBA resins. The reaction is described by:

$$R\text{-}NH_2 + HCl \rightarrow R\text{-}NH_3Cl$$

2.5. Oxidants in Sugar Decolorization

The use of oxidizing agents in sugar production has been discussed in several studies (Moodley, 1992; Mendoza, 2002; Bento, 2004). Hydrogen peroxide and ozone have both been used as decolorizing agents in refineries and mills. Bento (2004) describes the mechanism of decolorization. Peroxide cleaves unsaturated double bonds, forming carboxylic acids. Davis (2001) states that bleaching occurs via free radical addition at allylic site and double bonds, with eventual decomposition to acids and alcohols. The action of the oxidants decreases color and molecular weight, increasing efficacy of ion exchange. Bento also states that peroxide used in conjunction with ion exchange resins to decolorize sugar solutions can produce several benefits. Those applicable to this research include:

1. Less contaminated resin

2. Extension of resin cycles by 3-5 times

3. Less effluent of a lower color produced

4. Decreased consumption of chemicals and utilities

5. Decreased costs

2.6. Modeling

Several studies into the use of mathematical models to describe the phenomena occurring in packed bed adsorbers have been performed, with varying degrees of efficacy. The most significant limitations of the models employed involve assumptions made in order to apply the model. The assumptions include (Cheremisinoff and Ellerbusch, 1978):

- Uniform carbon particle size

- Ideal isotherm

- Dilute solutions

- Single component

- Adsorbate molecule too large to enter pore, so film diffusion controlling

- Flow rate too high, so pore diffusion controlling

- Comparison of actual to predicted data made on early part of breakthrough curve before carbon was exhausted

- Systems with relatively short mass transfer zones were studied

While these limitations may lead to discrepancies between actual and theoretical findings, complete accounting of all real world conditions in a mathematical model is difficult, if not impossible. The use of modeling is still an effective and valuable tool for the design of process operations and equipment.

Most of the model studies conducted with regard to cane sugar solutions involve the use of ion exchange resins and refinery liquors. Bagster (1972) investigated the use of small columns to predict the performance of larger ion exchange columns for refinery liquor decolorization. An attenuation index similar to the ICUMSA method was used for color measurement. A constant linear isotherm determined from batch testing was used for modeling purposes. It was determined that the Schumann model (1929) was applicable when long residence times were employed or if the media was uniformly pre-loaded, but at shorter residence times diffusion became a factor. The use of an internal diffusion model confirmed this.

Morley (1988) performed a detailed study of decolorizing ion exchange packed bed columns, utilizing a model similar to the Schumann model. The ICUMSA method was used for color measurement. Batch tests were used to determine that adsorption on ion exchange resin is best described by the Langmuir isotherm, but in the range being considered a linear isotherm was applicable. An average coefficient of determination (r^2) of 0.91 was reported for parameters determined from regression analysis of the experimental data.

A comprehensive examination of ion exchange decolorizers was conducted by Broadhurst (2002) which involved the use of finite element analysis to model colorant adsorption. Gel permeation chromatography was used to separate colorants into pseudo components of similar molecular weights. A linear isotherm was used to describe adsorption, but the linear partition coefficient (slope of the linear isotherm, described later) used in the modeling was determined by regression, and did not agree with that derived from isotherm tests. This work was confirmed and expanded by Ellis (2004).

Chapter 3. Mathematical Model

Adsorption by activated carbon is controlled by both film mass transfer and internal diffusion (Rice, 1982). The model used is the classic solution to packed bed adsorption where film transfer is controlling (Schumann, 1929, Bagster, 1978, Rice, 1982). It was selected for its simplicity and ease of implementation. The model is also adaptable for use in cases where diffusion is significant (Rice, 1982, Rice and Do, 1985). For this research, the model is modified by assuming K, the linear partition coefficient, to be a function of retention time (explained in Ch. 5). The derivation below is a summary of the complete derivation found in Rice and Do (1995).

Consider a section of a packed column (fig. 3.1) of length Δz, cross sectional area A, volumetric flow rate Q, concentration C and porosity ε.
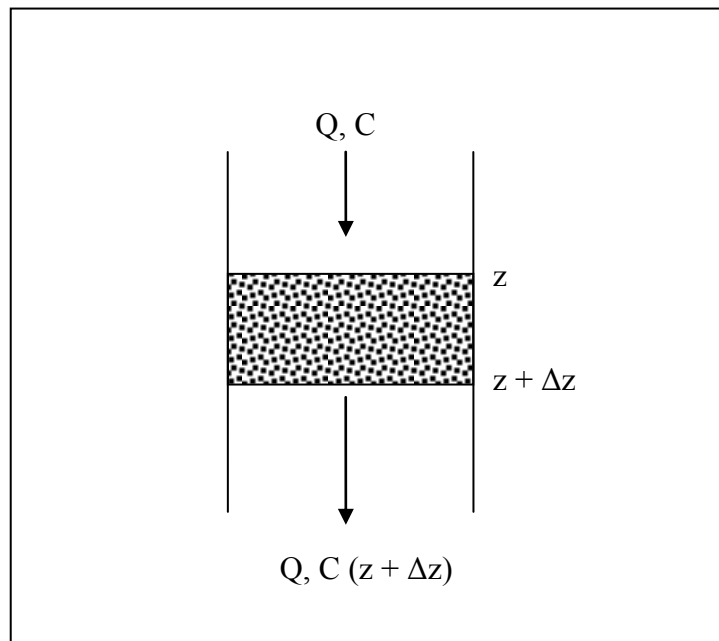

Figure 3.1. Differential slice of packed bed adsorber

Plug flow is assumed, which gives a flat fluid velocity profile. If the height of the bed is greater than 50 times the adsorbent particle diameter, axial dispersion effects may be ignored (Carberry and Wendel, 1963). Isothermal conditions are also assumed.

A linear adsorption isotherm is used to determine the ultimate adsorption capacity of the carbon.

$$q = KC^*$$

(3.1)

where q is the average concentration in ICUMSA units (IU) on the solid phase, C^* is the solute concentration (IU) which would exist at equilibrium and K is the linear partition coefficient.

A mass balance on the liquid phase gives the equation

$$V_0 A C(z,t) - V_0 A C(z + \Delta z) = \varepsilon A \Delta z \frac{\partial C}{\partial t} + (1 - \varepsilon) A \Delta z \frac{\partial q}{\partial t}$$

(3.2)

where V_0 denotes superficial velocity, ε is the void fraction or interstitial void volume and (1-ε) is the fractional volume made up of the solid phase.

A balance on the solid phase yields

$$A(1 - \varepsilon) \Delta z \frac{\partial q}{\partial t} = \Delta R = k_L a (C - C^*) A \Delta z$$

(3.3)

where ΔR is the rate of accumulation, C is the composition of the fluid phase, and $k_L a$ is the volumetric transfer coefficient. This equation simply states that rate of accumulation is equal to the rate of transfer to the solid.

Dividing **(3.2)** and **(3.3)** by AΔz and taking limits, one gets

$$-V_0 \frac{\partial C}{\partial z} = \varepsilon \frac{\partial C}{\partial t} + (1 - \varepsilon) \frac{\partial q}{\partial t}$$

(3.4)

$$(1 - \varepsilon) \frac{\partial q}{\partial t} = k_L a (C - C^*)$$

(3.5)

Eliminating q by substitution of KC^*, we arrive at the partial differential equations (PDEs)

$$V_0 \frac{\partial C}{\partial z} + \varepsilon \frac{\partial C}{\partial t} + (1 - \varepsilon) K \frac{\partial C^*}{\partial t} = 0 \qquad (3.6)$$

$$(1 - \varepsilon) K \frac{\partial C^*}{\partial t} = k_L a (C - C^*) \qquad (3.7)$$

In order to find an analytical solution to the system of PDEs, the initial conditions are

$$C(z,0) = 0 \qquad \text{and } C^*(z,0) = 0 \qquad (3.8)$$

and the boundary condition at the entrance is

$$C(0,t) = C_0 \text{ (constant inlet composition).} \qquad (3.9)$$

After the application of combination of variables (similarity transforms) and Laplace transforms, the analytic solution is achieved (Rice and Do, 1995):

$$C(\tau, \zeta) = C_0 \left[1 - \int_0^\zeta e^{-\beta} \exp(-\tau) I_0 (2\sqrt{\beta\tau}) d\beta \right] \qquad (3.10)$$

where:

$\zeta = (k_L a / \varepsilon)^*(z/V)$ – dimensionless distance

$\tau = (k_L a / (K(1-\varepsilon)))^*\theta$ – dimensionless relative time

$\theta = t - z/V$ – relative time (minutes)

$k_L a$ = effective mass transfer coefficient (min^{-1})

k_L = mass transfer coefficient (m/min)

a = total interfacial area of adsorbent per unit volume (m^2/m^3)

K = linear partition coefficient (-)

I_0 = modified Bessel function of the 1st kind and zero order

V_0 = superficial velocity (meters/minute)

V = interstitial velocity = V_0/ε (meters/minute)

z = bed height (meters)

ε = void fraction (-)

t = time (minutes)

β = variable of integration.

The solution is programmed into an Excel spreadsheet and regressed on the carbon outlet color data using Excel Solver. The modified Bessel function is a built-in function of the Excel Analysis ToolPak add-in. The integration was performed using the Gaussian Quadrature numerical integration technique with n = 6. The linear partition coefficient is allowed to vary during calculation in order for the regression to reach a non-trivial solution.

Chapter 4. Materials and Methods

4.1. Sample Analysis

Color: Samples were analyzed for color using the ICUMSA (International Commission for Uniform Methods of Sugar Analysis) method as described in ICUMSA method GS1/3/7 (2002). This procedure was selected as it is the current industry standard for color measurement. Other methods for color measurement are described in the literature (Clarke, et al. 1985, for example) and advanced techniques have been implemented to determine more detailed information regarding the nature of the colorants (Bento 1995, Broadhurst 2002).

Samples were diluted to a light yellow color to give an absorbance reading between 0.1-0.9. The pH was then balanced with HCl and NaOH solutions to 7.0 ± 0.05, which is less tolerant than the ICUMSA value of ± 0.1. Balancing pH can be quite difficult, particularly with deashed samples, since they have little buffering capacity. They were then filtered through a cellulose nitrate 0.45μm filter. The absorbance was then measured using a Spectronic Genesys 2 spectrophotometer at 420nm. Cell length was 10mm for higher color samples, and 50mm for lighter color samples. The brix value of the samples was then measured using a refractometer. The color was then calculated using the formula

$$ICUMSA\ (420nm) = \frac{[Abs(420nm) \times 10{,}000]}{[Conc.(g/ml] \times [Cell\ Length(mm)]} \tag{4.1}$$

The concentration term was determined using the data from Table 8 in the SASTA laboratory manual. An equation can be derived from this data, which has a correlation coefficient of 1 for the range of 1-20 brix:

$$Concentration(g/100ml) = 0.0042 \times \{Brix\ \%\}^2 + 0.9969 \times \{Brix\ \%\} \tag{4.2}$$

pH: The pH of each sample was measured using an Orion Model 520A pH meter.

Conductivity: Conductivity was measured using a Fisher Scientific Accumet® Basic Model AB30. Conductivity gives an indication of the ash in each sample. The meter was calibrated using a potassium chloride standard with known conductivity of 362 μS at 25 °C.

Conductivity Ash % on Brix: Two runs were analyzed for conductivity ash % on brix as per ICUMSA method GS1/3/4/7/8-13 (1994).

4.2. Void Fraction Determination

Void fraction, ε, is an important parameter used in modeling the carbon column. Void fraction is determined by adding a small volume of prepared carbon (washed and oven dried) to a graduated cylinder and adding a measured volume of water (or other solvent) to it. The cylinder is then inverted several times to ensure complete mixing and filling of void spaces. The volumes of the carbon, water, and carbon-water mixture are then used to determine the void fraction by the equation

$$\varepsilon = \frac{V_{void}}{V_{bed}} = \frac{V_{bed} - V_{carbon}}{V_{bed}} = 1 - \frac{V_T - V_{water}}{V_{bed}} \tag{4.3}$$

where:

V_{bed} = volume of the packed carbon bed

V_{water} = volume of water added

V_T = total volume in cylinder

Several tests were done. The average was calculated and used in the modeling.

4.3. Batch Tests

Batch tests were conducted in order to determine equilibrium parameters from plots of adsorption isotherms. They were also used to find optimum temperature and hydrogen peroxide dosing for the column tests. In order to run the adsorption isotherm tests, the time to equilibrium was determined. Six beakers filled with equal amounts of carbon (10ml) and juice (200ml, 14° ±

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1° Bx) were placed in a Precision Scientific 360 Shaker Bath at 70 °C. One beaker was removed and sampled at one-hour intervals and the samples analyzed for color remaining in solution.

The isotherm tests were done at temperatures of 65, 75 and 85 °C. Carbon doses of 0.05, 0.1, 0.5 1.0, 1.5, 2.0 and 3.0 grams were added to 400ml beakers. 200ml of juice at 14.0° ±1.0° brix was then added to each beaker and stirred to ensure wetting. An eighth beaker was used as the control, containing no carbon. After the prescribed temperature was reached, the beakers were placed in the bath, covered and gently agitated. The tests were allowed to run overnight to ensure equilibrium was reached. Samples from each beaker were drawn and analyzed for ICUMSA color. Isotherms were also produced with hydrogen peroxide dosing of 500, 1000 and 2000 mg/kg solids at the same temperatures.

After analyzing the samples the data were plotted using Microsoft Excel spreadsheet software. Curve fitting via nonlinear regression was then done using Excel Solver to determine the degree of agreement with the linear isotherm equation,

$$q = KC^*$$ **(4.4)**

where q = concentration of color on carbon at equilibrium (IU), C^* = equilibrium concentration of color remaining in solution (IU), and K is the linear partition coefficient (see Appendix A for details).

4.4. Column Loading Tests

Column loading tests were conducted in order to determine mass transport parameters. Two identical jacketed columns were packed with 150ml of prepared virgin carbon. The carbon investigated was Calgon Carbon Cane Cal® 12X40, which includes 5-8% magnesite ($MgCO_3$) as a pH buffer. Preparation of the carbon was done by rinsing with deionized water to remove fines and any contaminants that may have been present. Carbon was then oven dried at 105°C for 24

hours. After packing, the columns were rinsed to remove any remaining fines. The columns were left full of water for 24 hours to ensure complete wetting.

Juice was prepared by diluting syrup with deionized water to $22 \pm 1°$ brix. A higher solids concentration was used in order to simulate conditions after the first effect of the evaporator train, which is a likely location for implementation of the system. The juice was filtered through a 250µm mesh screen. It was then fed to the columns at various flow rates in order to compare performance as a function of superficial velocity. Seventy five bed volumes were fed through each column at flow rates varying from 9 to 53 ml/minute. Samples were collected at one hour intervals. Column products were collected in order to compare bulk decolorization. Nine tests were conducted. Collected samples were then analyzed for ICUMSA color and the data regressed on the model.

4.5. Regeneration Efficiency

Chemical regeneration of the carbon is a significant feature of the DWiSP process. Regeneration involves the use of a solution and procedure developed at the Audubon Sugar Institute, and is referred to as the New Regeneration Process (NRP) (Bento and Rein, 2007). The NRP solution used was composed of 5% (w/v) NaOH, 0.2% (v/v) H_2O_2, and 25% (v/v) ethyl alcohol. Application of the regenerant is precede and proceeded by 1 BV of 1% (v/v) HCl for neutralization and 1 BV of 2% (w/v) NaOH. All solutions used for regeneration were fed at 4 BV/hr. Testing was conducted using either 2 or 8 BV of NRP, which is discussed later.

It cannot be assumed that the chemical regeneration used on the carbon is completely efficient (all adsorbed color bodies desorbed). Therefore, it is necessary to determine the regeneration efficiency.

4.5.1. Regeneration Efficiency Batch Test

A 150ml bed of carbon was prepared and loaded into the carbon column. Cane juice produced via dilution of syrup was prepared at 15.5° ± 0.5° brix, with a color of approximately 20000 IU. The juice was then passed over the carbon as in the column tests (85° C) at 15 BV/hr for six hours (90 BV).

The carbon was then rinsed and regenerated as per the column tests. A 2 ml sample of carbon was then extracted from the carbon bed. To ensure a representative sample, the bed was stirred vigorously before sampling. The sample was washed and stored in deionized water. This was repeated for six runs.

After the runs were completed, all six carbon samples were dried in a vacuum oven at 70°C until dry. The temperature was kept low to avoid inadvertent thermal regeneration. The samples were weighed and their weights recorded.

Equal amounts by weight of the samples were then placed in 400 ml bottle flasks. 200 ml of molasses solution of 15.5° brix and 90000 IU color was added to each beaker. A beaker with virgin carbon was prepared as the control. The beakers were placed in the shaker bath at 85°C. A 5 ml sample of molasses was then drawn from each beaker at 3 hour intervals. This was repeated for 9 hours to ensure the adsorption had equilibrated. Samples were also drawn at 24 hrs.

The samples were then analyzed for ICUMSA color. The amount of color removed by the carbon was compared to the control. The color removed by control or sample was calculated by

$$Color\ removed = \frac{(molasses\ color - sample\ color)}{mass\ of\ carbon\ in\ sample} \qquad \textbf{(4.5)}$$

The efficiency was then calculated by

$$\%Efficiency = \frac{(color\ removed\ by\ control - color\ removed\ by\ sample}{color\ removed\ by\ control} \times 100\% \quad \textbf{(4.6)}$$

4.5.2. Regeneration Efficiency Dynamic Test

Further investigation into the efficacy of chemical regeneration was performed using data acquired from carbon column tests. Two jacketed columns were loaded with 150ml of virgin carbon each. Juice of approximately 11000 ICUMSA color at $22° \pm 1°$ brix was prepared from deionized water and factory syrup. The juice was fed to the columns at 15 BV/hr for 5 hrs. The columns were maintained at 85°C. An initial sample was taken at 15 minutes. Subsequent samples were taken at one hour intervals. The columns were then chemically regenerated using the NRP protocol. One column was regenerated using 2 BV of the NRP solution; the other used 8 BV. Column temperatures were maintained at 70°C. This cycle was repeated for 7 runs. The samples were then analyzed for ICUMSA color.

4.5.3. Regenerant Comparison

Comparison of the NRP solution to a simple solution of sodium hydroxide was conducted in the same fashion as the dynamic test. One column was regenerated using 2 BV of the NRP solution. The other was regenerated using an equal quantity of 2% (w/v) NaOH. Samples were again collected at one hour intervals after an initial sample at 15 minutes and analyzed for color.

4.6. Ion Exchange

Two columns were used to examine the performance of an ion exchange system to decolor and demineralize the product from a carbon column. The strong acid cation resin was Purolite C150, and the weak base anion resin used was Thermax Tulsion® A-2XMP. Both resins were soaked in deionized water for 24 hours to allow for swelling. 200 ml of SAC resin was

added to the first column, and 240 ml of WBA resin was added to the second column. Since the resins were in the inappropriate forms (Na^+ on SAC, Cl^- on WBA), they were converted to H^+ and OH^- forms with HCl and NaOH solutions, respectively.

The system was fed a juice mixture prepared from syrup produced at the Cora Texas Sugar Factory and deionized water. The color of the juice was raised from approximately 11000 IU to 22000 IU using final molasses from the same source. The juice had a final solids concentration of 18-20° brix. The carbon column was fed at rates of 15, 10, 6 and 3 bed volumes per hour (BV/hr), with the 15, 10 and 3 BV/hr runs repeated with hydrogen peroxide dosing of 1000 mg/kg on brix. The peroxide was allowed to react with the juice for at least 30 minutes. The temperature of the carbon column was maintained at 85°C by heated recirculating bath. The product of the carbon column was then fed to the ion exchange columns at a fixed rate of 3 BV/hr on the SAC column (200ml bed volume). The SAC column was maintained at 10°C to prevent inversion of the sucrose in low pH conditions. The feed to the ion exchange columns was partitioned so that 3 BV/hr were fed to the columns with the excess being drained away.

The media used in all three columns was chemically regenerated. Carbon was regenerated using the NRP system, with 8 BV of the NRP solution being used. Temperature of the carbon column was controlled at 70°C during regeneration. SAC resin was regenerated with 4 BV of 6% (v/v) HCl. BWA resin was regenerated using 4 BV 10% (w/v) NaOH. Resin column temperatures were not controlled.

Samples from all three columns were taken at fixed time intervals and analyzed for color, pH and conductivity. Carbon column data were regressed on the model. The color data from the ion exchange columns were not regressed since the feed color was not constant.

Chapter 5. Results and Discussion

5.1. Batch Tests

Contact time for the batch tests was determined to be in excess of 10 hrs. This illustrates the significance of internal diffusion on carbon adsorption. Data was regressed on equation 5.1, where t = time:

$$Color(IU) = 8271 \times (\exp(-0.583t)) + 2909 \qquad \textbf{(5.1)}$$
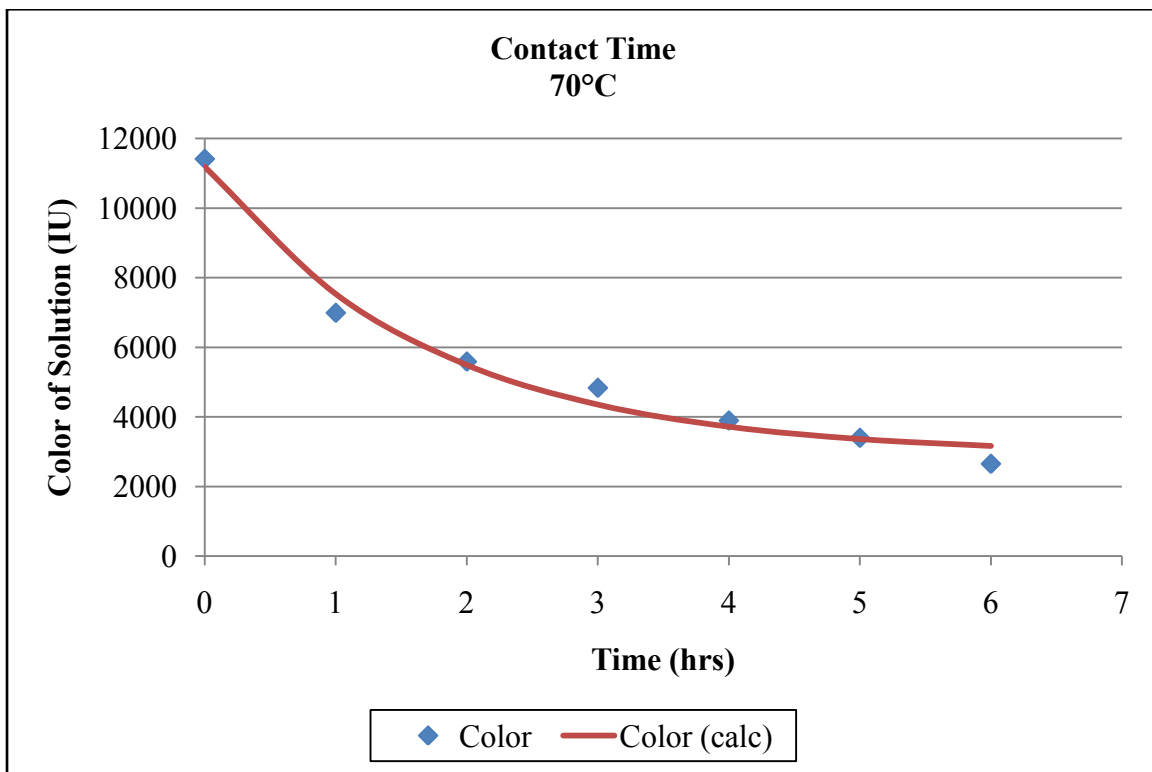
Figure 5.1. Contact time for equilibrium (saturation)

Batch test results give valuable information concerning the adsorptive properties of porous media. In the case of activated carbon, the most significant information ascertained is the fact that the isotherm is linear at 85°C and the value of the partition coefficient. The linearity of the isotherm indicates that the colorants are dilute and the use of multicomponent isotherms is unnecessary (Seader and Henley, 1998).
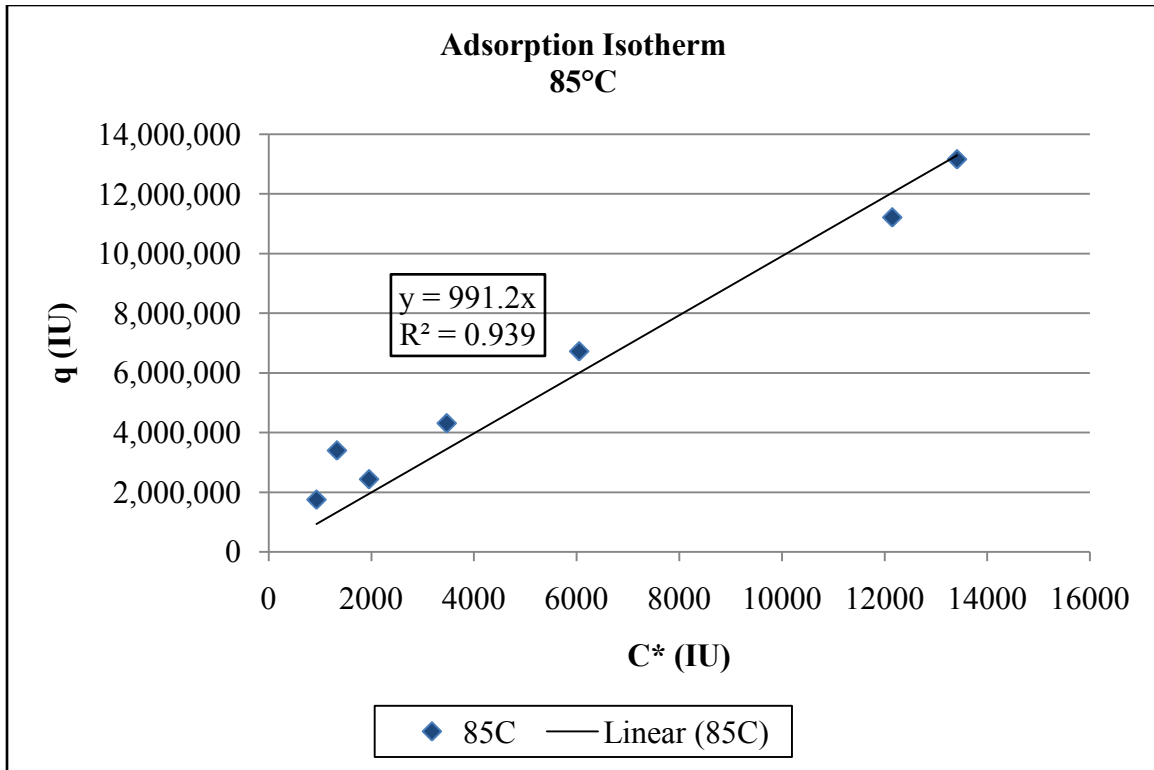
Figure 5.2. Linear adsorption isotherm

A significant aspect of the DWiSP process as developed by Rein et al. (2006) is the use of hydrogen peroxide as a pretreatment. This pretreatment method was included in the process based on work done by Bento (2004), which suggest that peroxide pretreatment extends the life of ion exchange resins, and Ellis (2004), which reports improved decolorization by carbon. Batch testing indicates that peroxide pretreatment actually decreased the adsorptive capacity of carbon. The discrepancy may be due to the fact that both Bento and Ellis adjusted the feedstock used in their experiments to an alkaline pH of 8.5, whereas the testing reported here was done at unadjusted pH of 6-7. Since the bleaching activity of peroxide is greatly enhanced by alkalinity, their results were more favorable. This, however, does not simulate factory conditions, where raw juice of pH 5-5.5 is adjusted to approximately pH 7.0 during clarification.
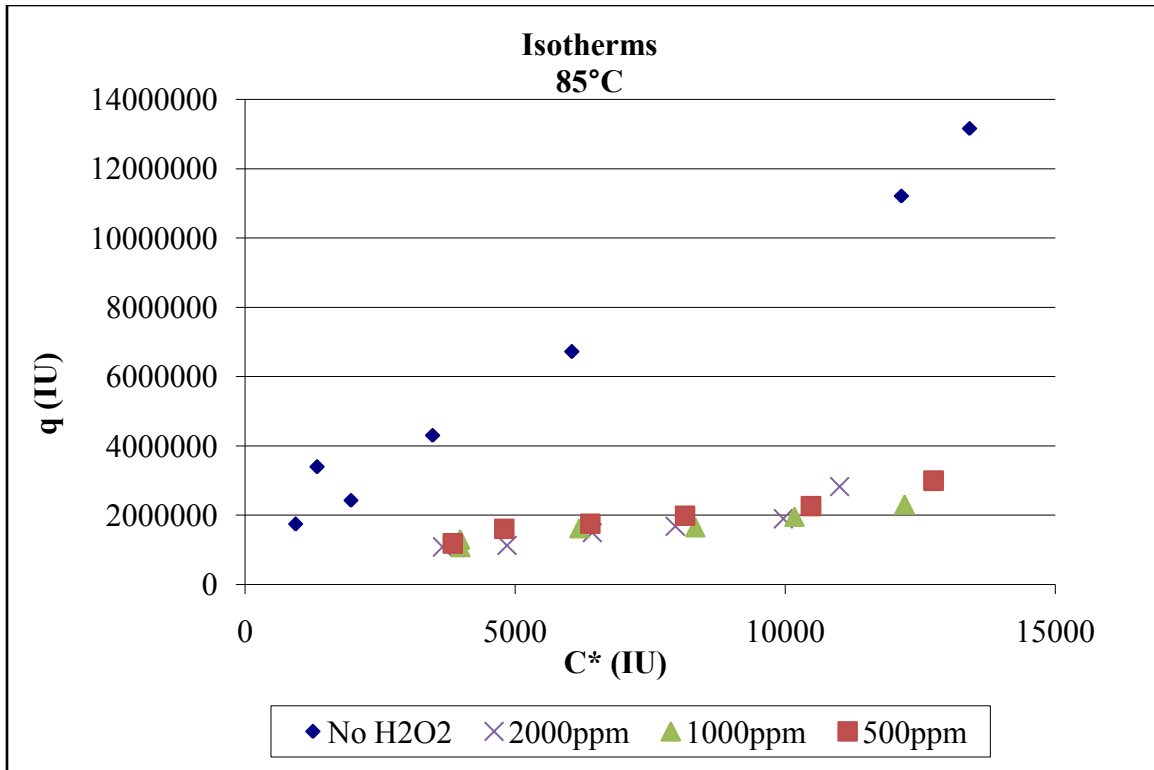
Figure 5.3. Isotherms demonstrating effect of peroxide treatment on adsorption

Figure 5.3 demonstrates the effect of peroxide pretreatment on adsorption. The slope of the isotherms conducted with pretreated feed was less steep (lower partition coefficient) than that of the untreated feed. Adsorption is also greater for the untreated test over the entire range of final concentrations (C^*). Similar results were obtained at 65°C and 75°C (see Appendix B). This suggests that the expense and difficulty of pretreatment can be spared (hourly dosing for a factory processing 400 m^3 of 14.5° brix juice per hour would be approximately 180 liters of 30% peroxide).

5.2. Column Loading Tests

5.2.1. Carbon Breakthrough Curve

Figure 5.4 shows a typical breakthrough curve for a carbon adsorber (results from additional runs are found in Appendix C & D). As can be seen, pH and conductivity remain

constant throughout the test. Five to eight percent Magnesite is added to the carbon by the manufacturer to act as a buffer against pH drop associated with sugar solution decolorization.
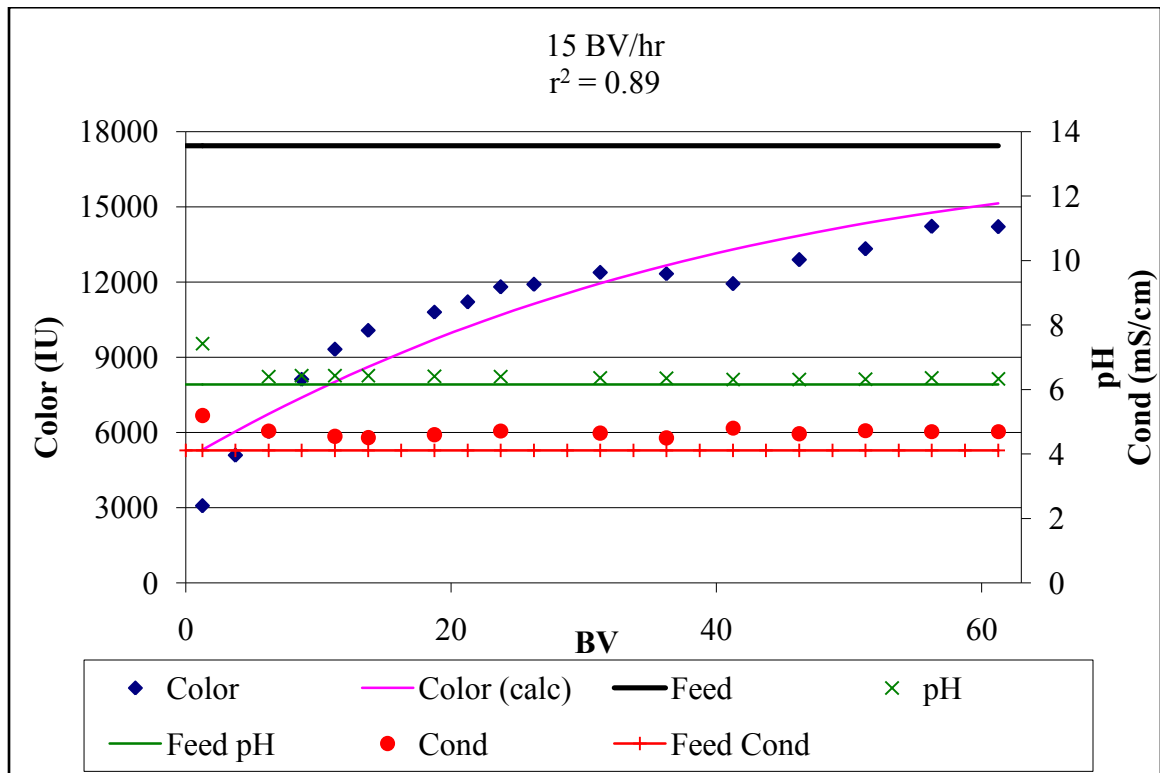
Figure 5.4. Typical breakthrough curve for carbon column

5.2.2. Effect of Coefficients K and k_La on Column Performance

Understanding the effects the coefficients derived from testing have on the performance of the column is essential for selecting optimum operating parameters. The effect of varying K, the linear partition coefficient, is shown in figure 5.5. It is clear that as K increases, with k_La held constant, decolorization is greater over an equivalent time interval. So K can be described as a measure of ultimate adsorptive capacity.
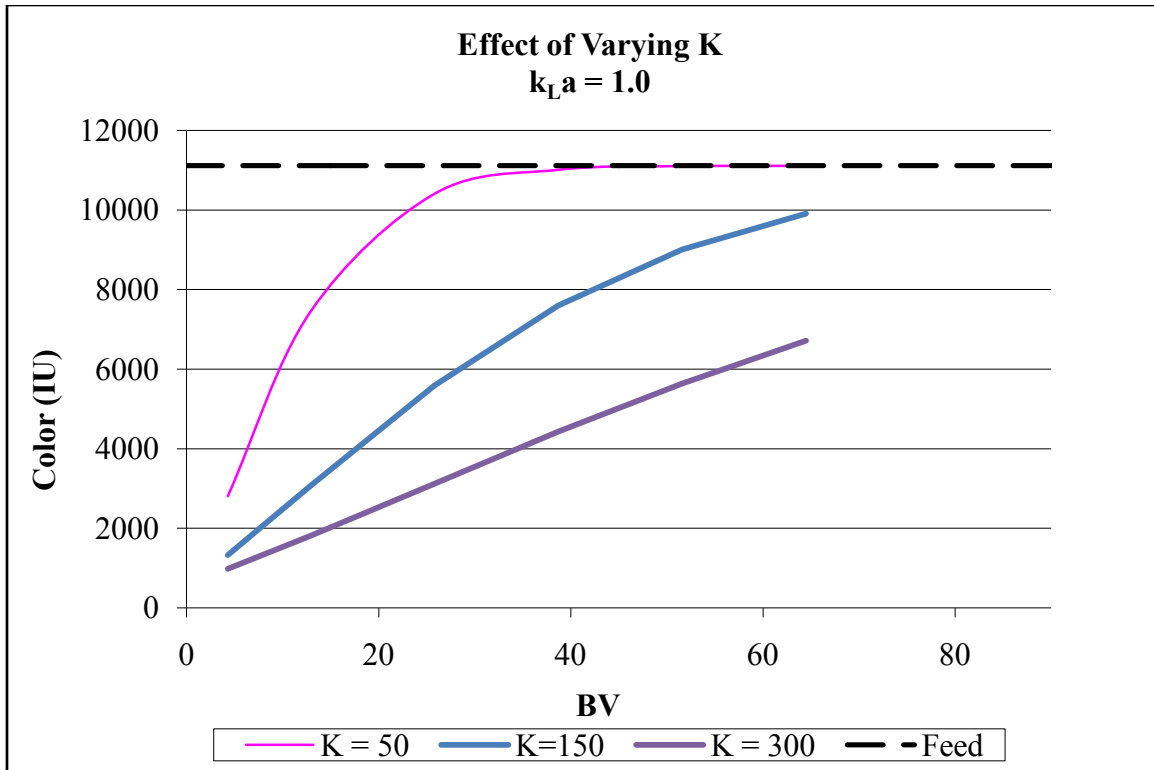
Figure 5.5. Effect of varying K with k_La held constant

Figure 5.6 shows the effect of varying k_La, the effective mass transfer coefficient, with constant K. As this value increases decolorization is more rapid, but breakthrough occurs sooner. The mass transfer coefficient describes the how quickly the colorant is taken up by the carbon, but as K is fixed, the maximum adsorbancy is reached sooner. So with a higher k_La value, over a shorter period of time, a lower color product can be produced.

5.2.3. Determination of Optimum Flow Rate

Previous studies have reported correlations between superficial velocity (V_o) and mass transfer coefficient. Broadhurst (2002) derived a correlation of

$$k_L \propto V_o^{1/3}, \qquad (5.1)$$

while Bagster (1972) determined a correlation of

$$k_L \propto V_o^{0.9}. \qquad (5.2)$$

33
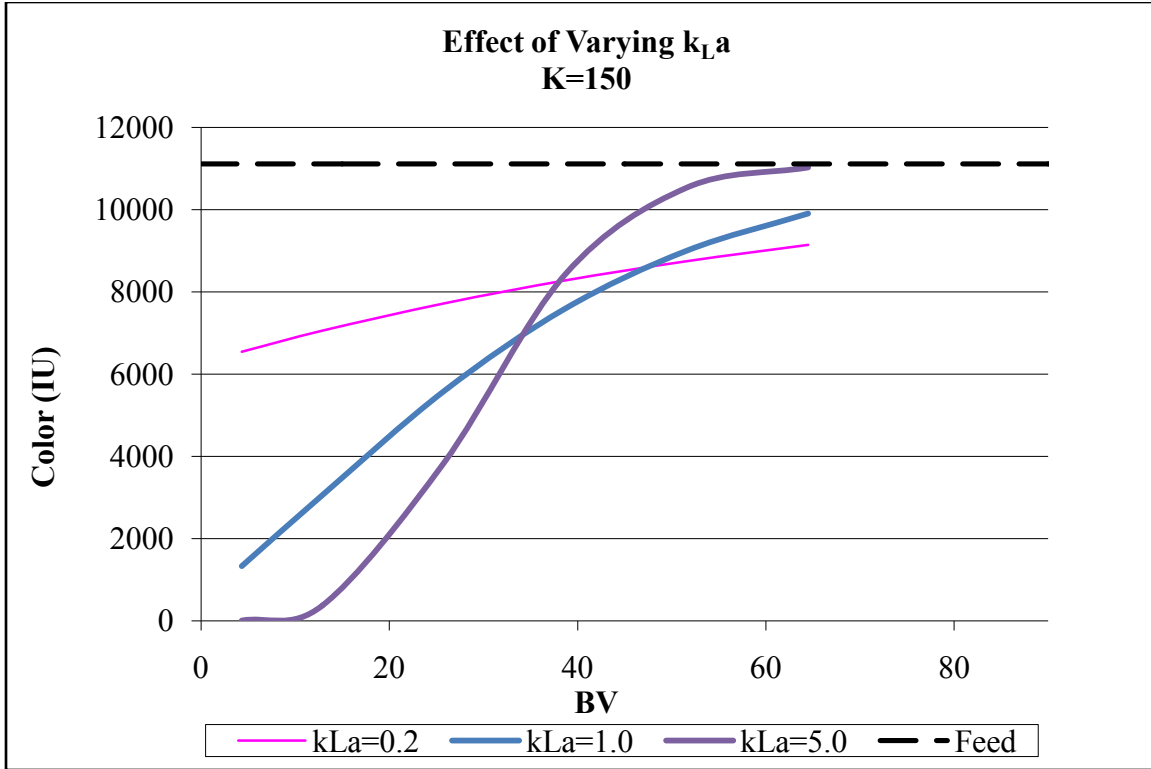
Figure 5.6. Effect of varying k_La with K held constant

Regression of the data found from the column experiments shows a similar correlation (figure 5.7). In this case, k_La (min^{-1}) was used, since the effective surface area per unit volume, a, is a constant and does not affect the correlation. The correlation is found to be

$$k_La = 0.892(V_o)^{0.294}, r^2 = 0.94. \qquad (5.3)$$

Typically, the partition coefficient (K) is supposed to be derived from isotherm testing and remain constant when using the Schumann model. However, both Broadhurst (2002) and Ellis (2004) report having to allow for K to vary in order for their models to converge to a solution. They also report a discrepancy between the value of K determined by isotherm and that calculated from regression analysis. This may be explained by considering the contact time needed to reach saturation of color on carbon, which is measured in hours. If an isotherm test were to be conducted such that samples were taken at short time intervals, such as every 30

minutes, and the results plotted, the K value should increase with time. This is exactly what Broadhurst observed. It follows, therefore, that K is a function of contact, or retention, time.

Effective Mass Transfer Coefficient (k_La)
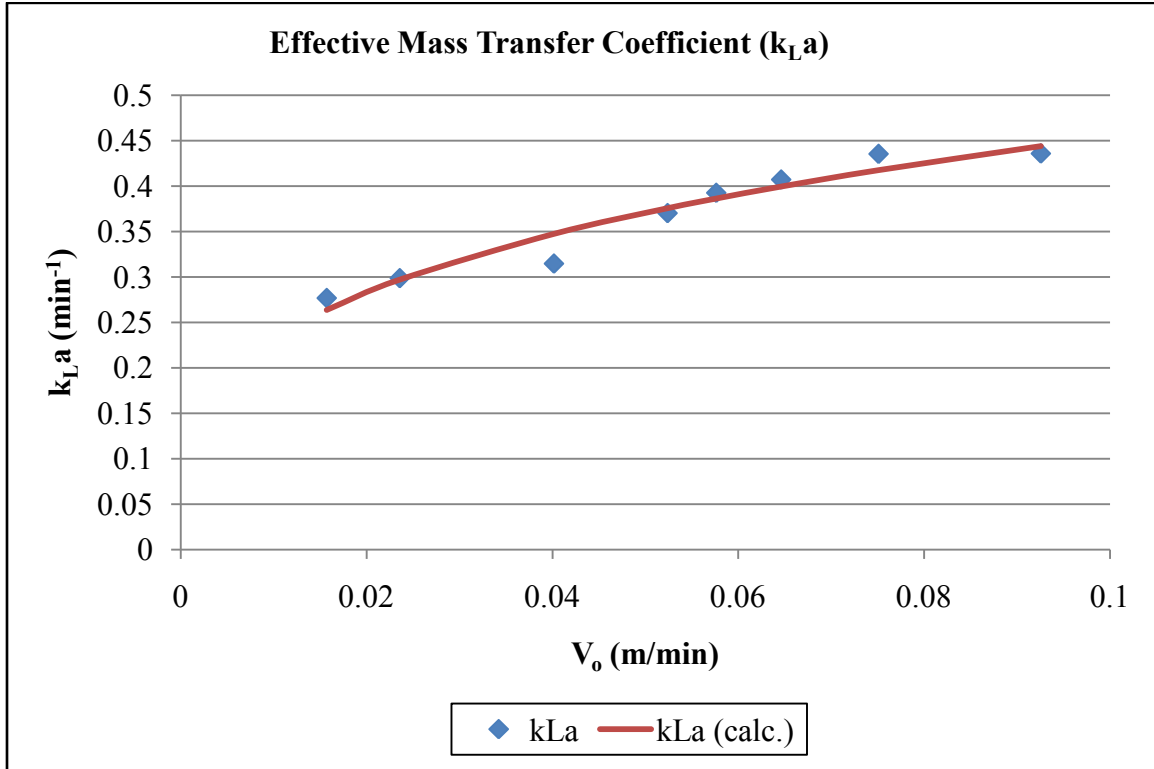
Figure 5.7. Effective mass transfer coefficient as a function of superficial velocity

Retention times in an adsorber are usually measured in minutes, unless extremely low flow rates are used. Contact time is equal to the inverse of the flow rate in bed volumes per unit time, so at 2 BV/hr, contact time is ½ hour. Figure 5.8 displays the relationship between K and retention time from the column tests. The data were regressed on a solution similar to that used for k_La. The correlation, with retention time (t_R) in minutes, is:

$$K = 99.56(t_R)^{0.232}, r^2 = 0.93 \qquad \textbf{(5.4)}$$
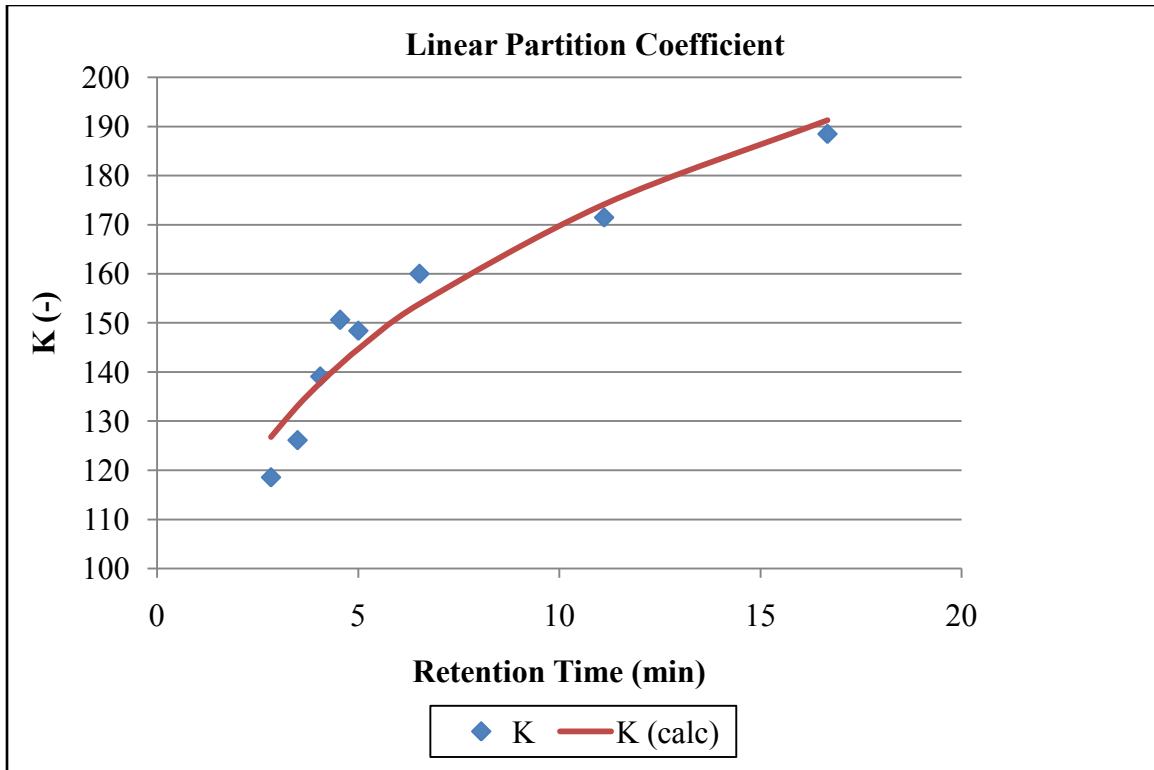
Figure 5.8. Linear partition coefficient as a function of retention time

Table 5.1 summarizes the results from the column tests. The product of the square of K and square root of $k_L a$ gives an approximate indication, or performance index (P.I.) of column performance (Figure 5.9). The square of K is used to give additional weight to it, since it is more significant to column performance.

Table 5.1. Regression parameters from column tests

BV/hr	V_0(m/min)	$k_L a$(min^{-1})	t_R(min)	K	$K^2 * \sqrt{(k_L a)}$ (x10^3)	r^2
3.6	0.0157	0.277	16.667	188.49	18.697	0.999
5.4	0.0236	0.299	11.111	171.50	16.076	0.993
9.2	0.0402	0.315	6.522	136.92	10.518	0.969
12	0.0524	0.370	5.000	148.43	13.407	0.976
13.2	0.0576	0.393	4.545	150.58	14.209	0.950
14.8	0.0646	0.407	4.054	139.11	12.349	0.971
17.2	0.0751	0.435	3.488	126.12	10.497	0.880
21.2	0.0926	0.436	2.830	118.57	9.281	0.852
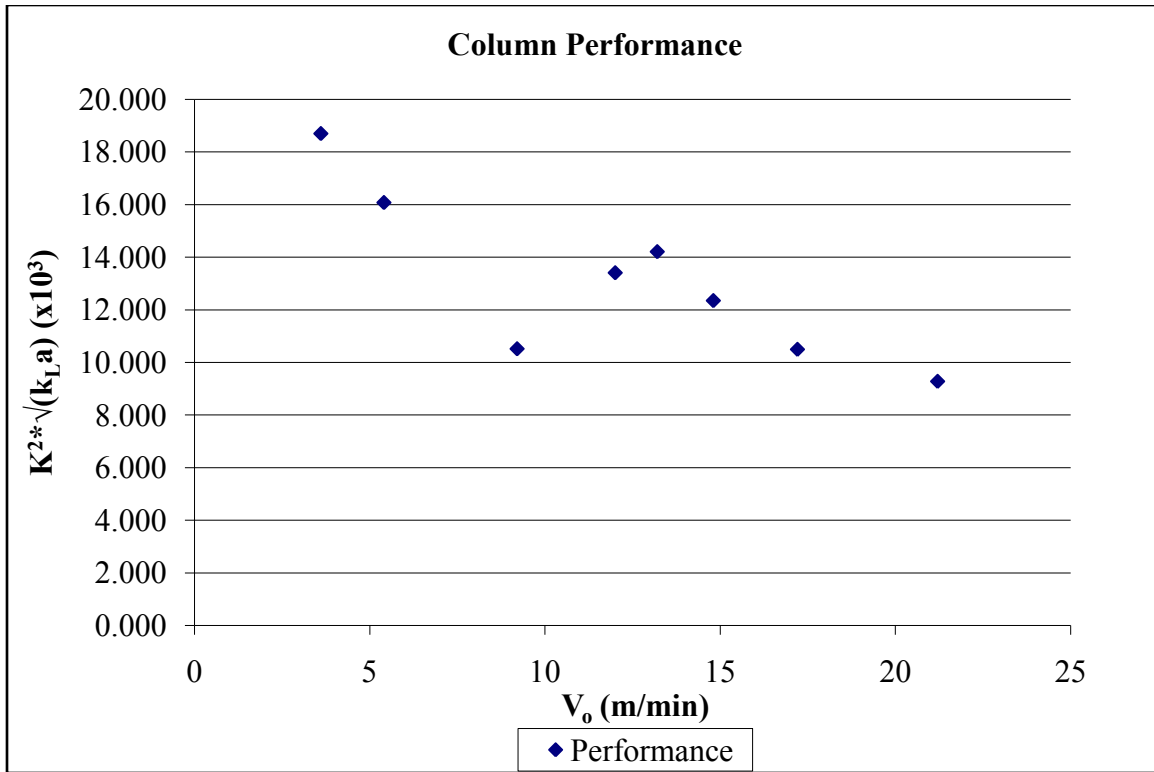
Figure 5.9. Column performance. Higher value indicates better performance.

5.3. Predictive Tests

In order to verify the results from column testing, three predictive runs were performed on a different column. The diameter of the column was 51 mm, about twice that of the columns used in the dynamic tests.

All predictive runs were run under the same conditions as those done during column testing. The bed volume for run 1 was 250 ml and feed brix was 22°. Flow rate was set at 12 BV/hr. Runs 2 and 3 used a bed volume of 200 ml and 14.5° brix feed. Figure 5.10 through 5.12 give the results for the three runs. In order to determine the correct K for runs conducted at other than 22° brix, the value obtained from the correlation equation must be multiplied by the ratio of feed brix to 22. This is a curious finding and may be due to the linear driving force term from the model (equation 3.5).

Table **5.2** is a comparison of the regressed parameters versus predicted values.
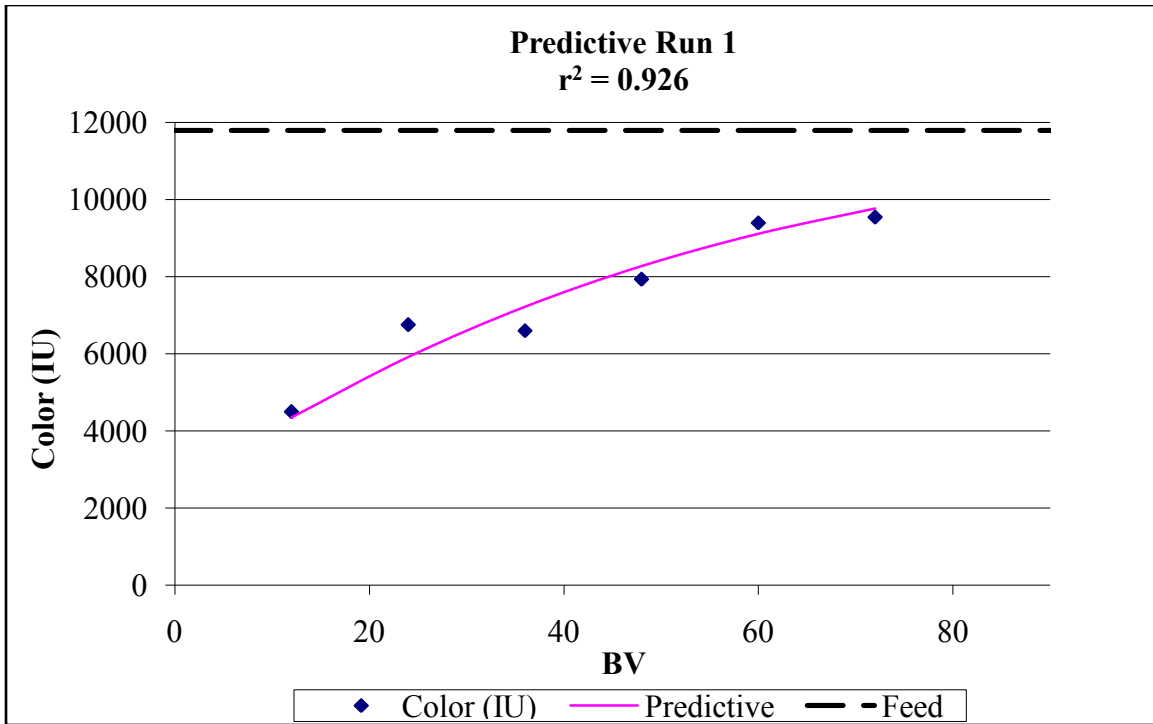
Figure 5.10. Predictive run 1
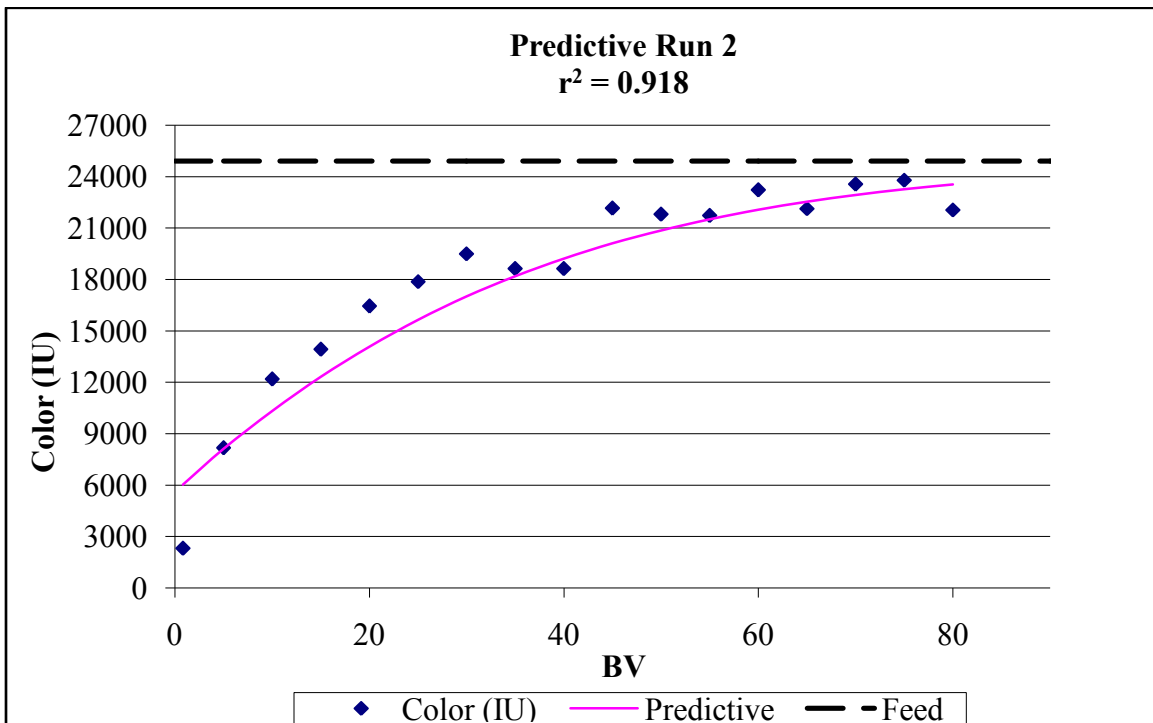
Figure 5.11. Predictive run 2
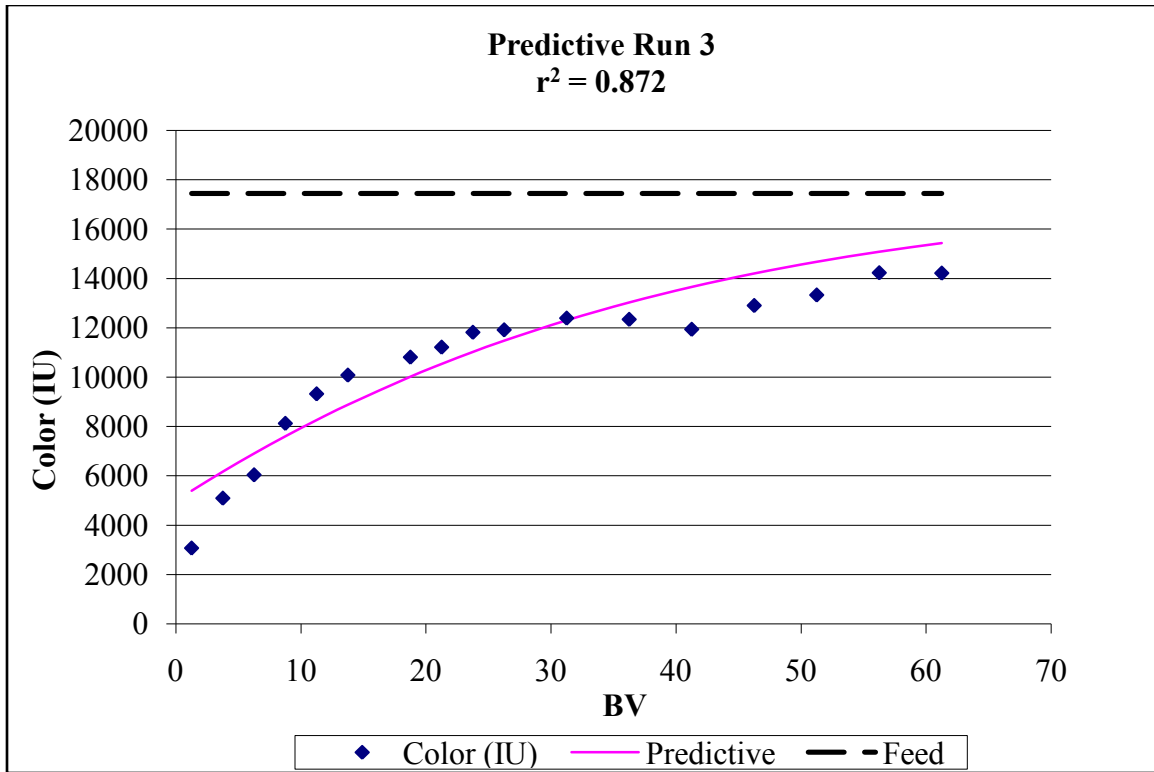
Figure 5.12. Predictive run 3

Table 5.2. Parameters from predictive runs

		Regressed			Predicted		
	BV/hr	k_La	K	r^2	k_La	K	r^2
Run 1	12	0.265	149.653	0.937	0.300	144.626	0.926
Run 2	10	0.266	82.853	0.948	0.246	99.440	0.918
Run 3	15	0.301	100.447	0.879	0.300	93.634	0.872

5.4. Ion Exchange System

After the juice passes through the carbon column, ash and remaining color are removed by the ion exchange columns. The SAC resin acts to remove positive ionic impurities while also adsorbing some residual color. The pH of the juice drops significantly (below 1.5) as hydrogen ion concentration of the SAC product increases significantly. Figure 5.13 shows a breakthrough curve for the SAC column. The pH of the SAC product is low until the resin becomes exhausted,

after approximately 15 BV have passed. This was found to occur consistently throughout testing (see Appendix D).

As described in chapter 2, the WBA resin functions by removing acids (more a capture than an exchange). The WBA column will become ineffective as the SAC pH rises. This is evident in the WBA breakthrough curve in Figure 5.14.

Seven cycles were performed for the ion exchange tests. Regardless of the flow rate of the carbon feed or cycle number, the performance of the ion exchange columns remained consistent until exhaustion (Figure 5.15). The ion exchange columns are only effective for 12-15 BV (onset of exhaustion), then experience a rapid decrease in performance.
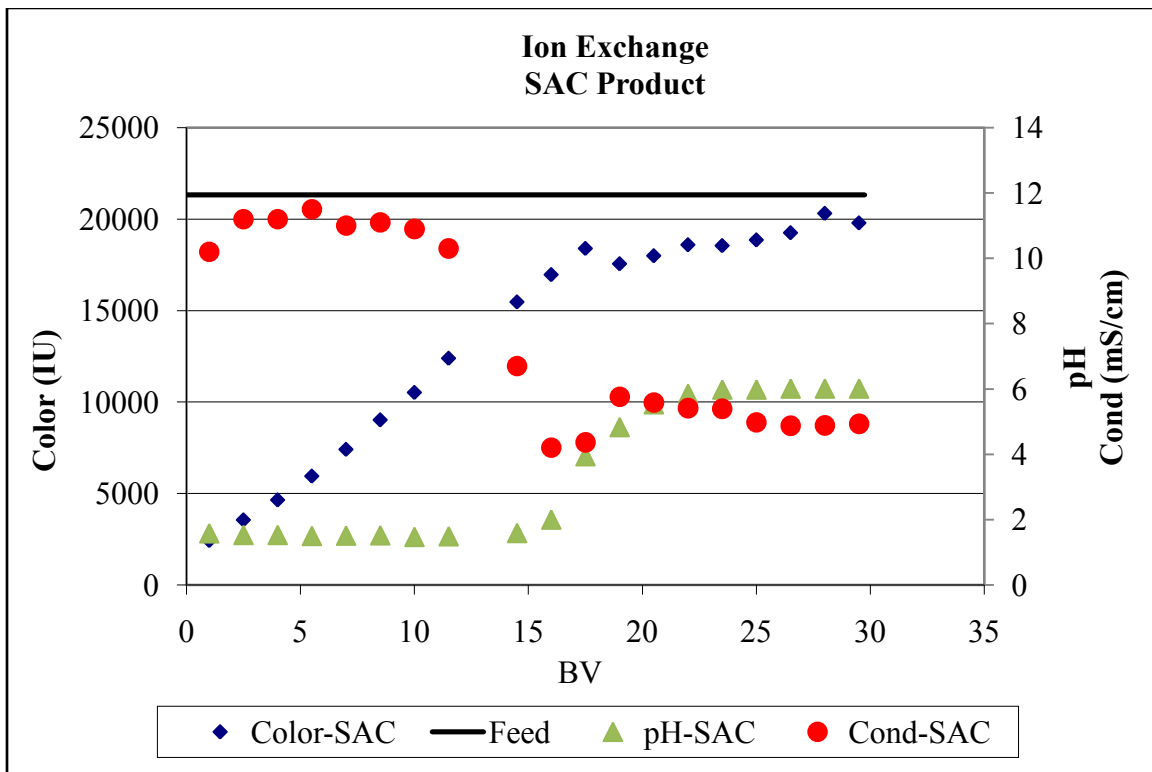
Figure 5.13. SAC breakthrough curve
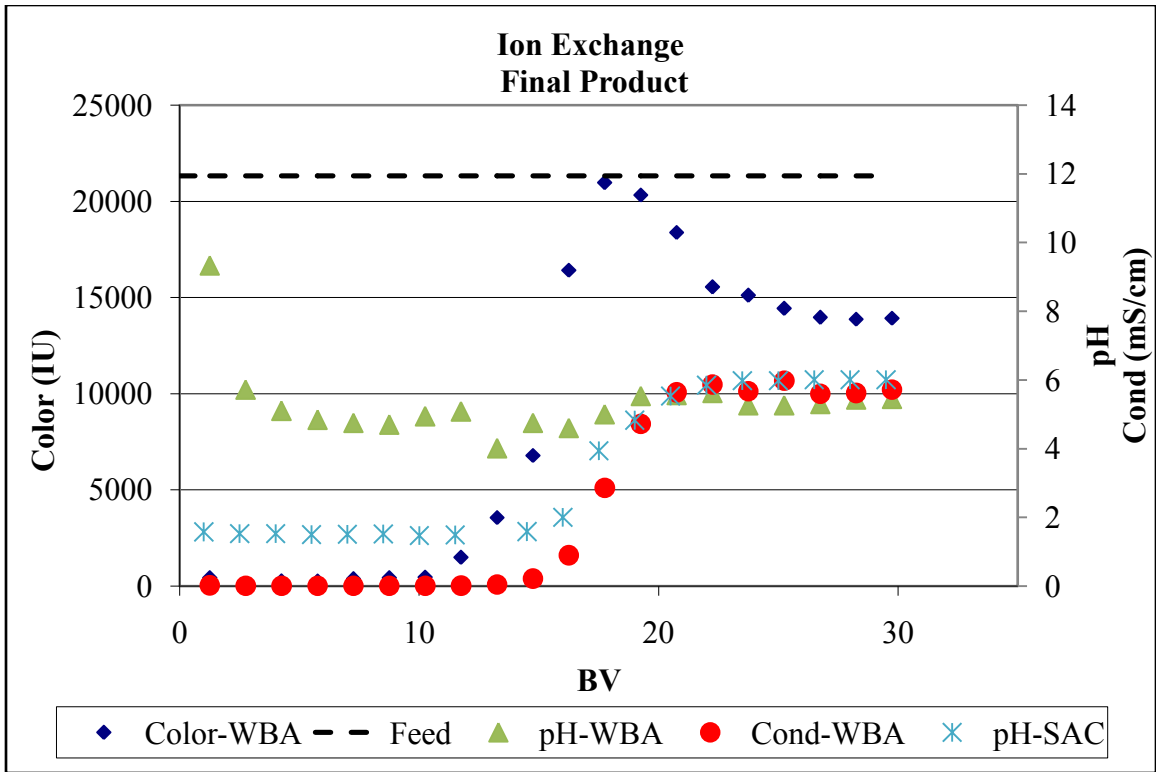
Figure 5.14. WBA breakthrough curve
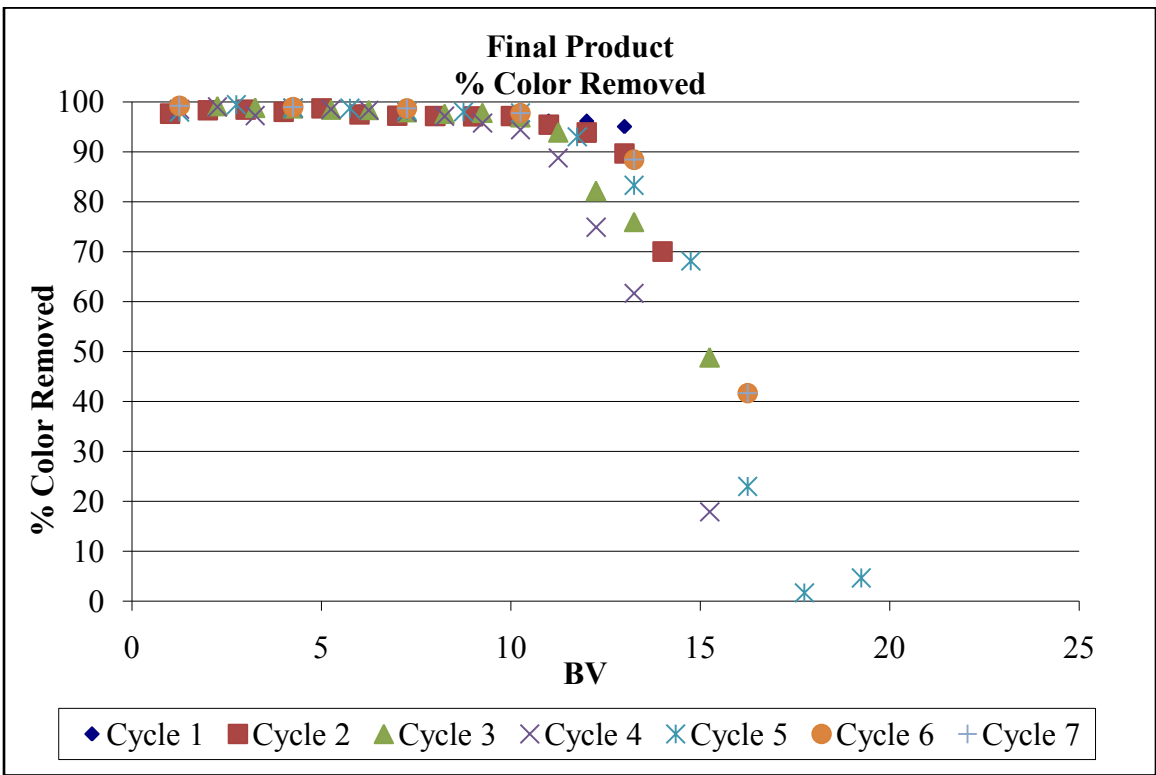
Figure 5.15. Final product (WBA) percent color removed as compared to original feed

5.5. Regeneration Tests

5.5.1. Regeneration Efficiency Test (Batch Test)

The high color of the molasses used in conjunction with the small amount of carbon collected prevented better characterization of the results. Figure 5.16 shows the regeneration efficiency as determined by the batch method.

5.5.2. Regeneration Efficiency Dynamic Test

Analysis of the data collected in the dynamic test yielded two conclusions. The first is that after the second run the performance of the carbon becomes consistent. This is evident from Table 5.3 and Figure 5.17, which display the parameters derived from regression on the analytical model. Second, while performance of the column regenerated with 8 BV of NRP solution is better than that of the column regenerated with 2 BV of regenerant, the increased performance is not proportional to the abundance of solution used. Figure 5.18 and Figure 5.19 display results from the column tests. A curious occurrence is the dip in performance after the first regeneration, as is evident from the lower K value. Performance improves again after the second regeneration. This also occurs in the regenerant comparison test (section 5.5.3.). Figure 5.20 shows the results of a second test used to confirm this phenomenon and to eliminate the possibility of experimental error. The 2 BV regeneration regime was used in this confirmation test.
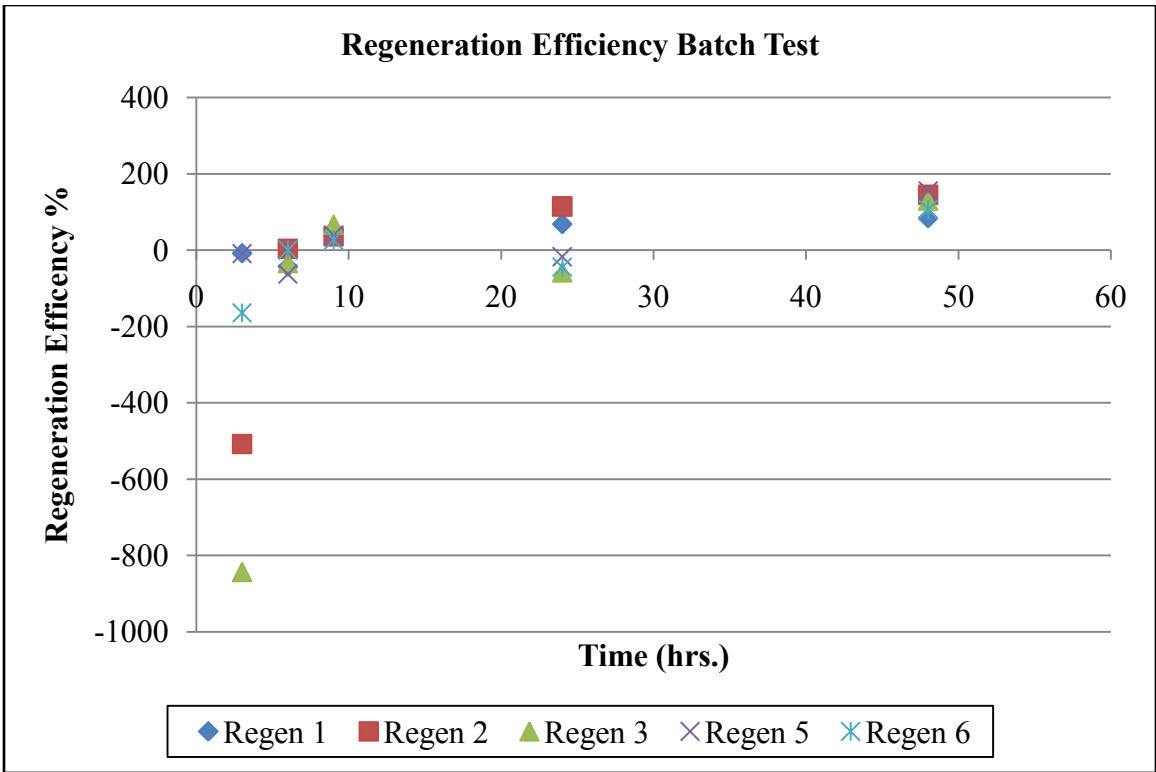
Figure 5.16. Regeneration efficiency batch test
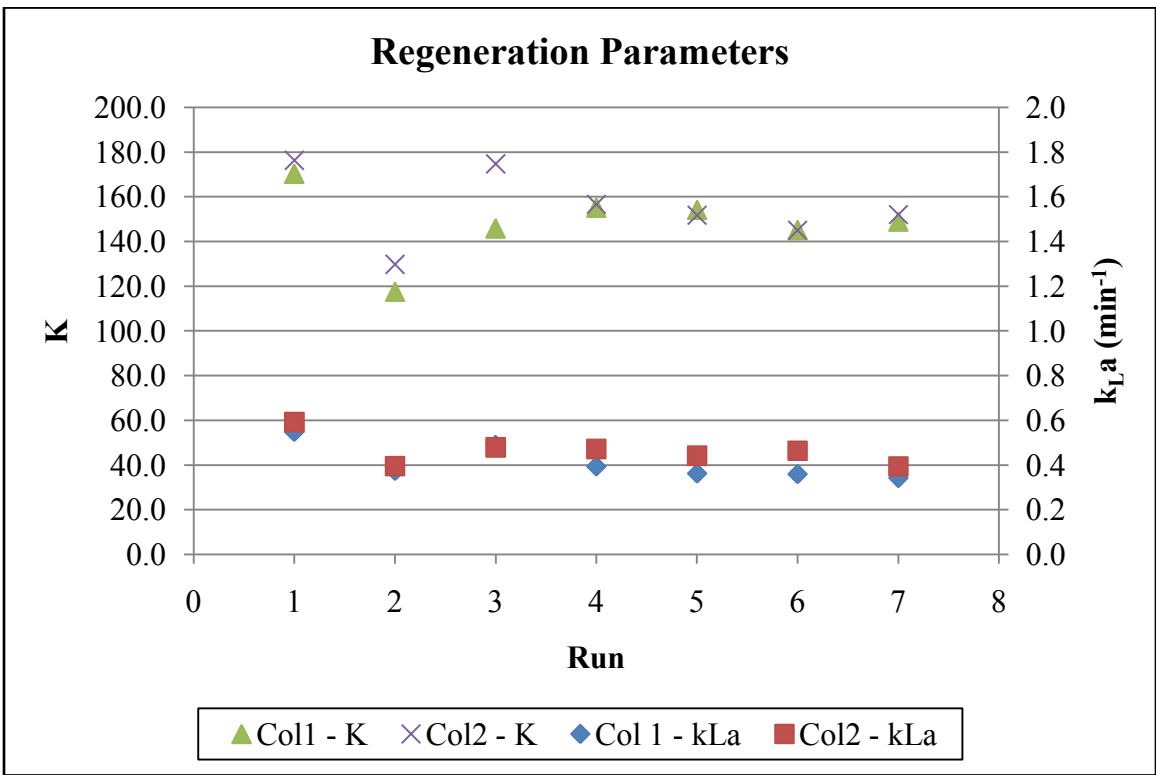
Figure 5.17. Regeneration parameters

Table 5.3. Regeneration efficiency test regression parameters

				2BV NRP	
Run	k_La (min^{-1})	K	r^2	Efficiency of k_La	Efficiency of K
1	0.549	170.32	0.94	-	-
2	0.373	117.51	0.91	68.07	68.99
3	0.490	145.82	0.93	89.31	85.62
4	0.393	155.16	0.95	71.68	91.10
5	0.362	154.17	0.91	66.04	90.52
6	0.359	145.11	0.89	65.46	85.20
7	0.341	148.91	0.83	62.16	87.43
				8BV NRP	
Run	k_La (min^{-1})	K	r^2	Efficiency of k_La	Efficiency of K
1	0.592	176.32	0.95	-	-
2	0.395	129.77	0.94	66.74	73.60
3	0.479	174.75	0.91	80.91	99.11
4	0.472	156.69	0.95	79.72	88.86
5	0.441	151.80	0.92	74.59	86.09
6	0.463	145.02	0.92	78.30	82.25
7	0.394	152.07	0.86	66.53	86.25
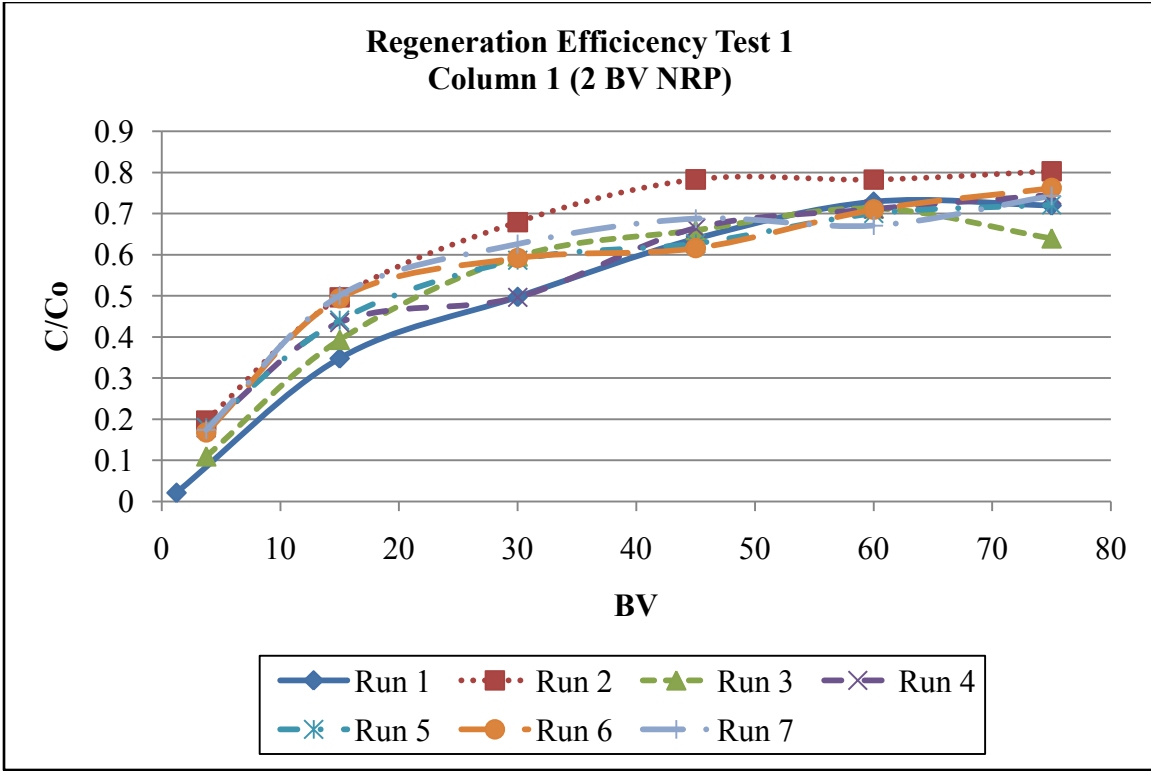
Figure 5.18. Results from regeneration efficiency test. Two BV of NRP were used.
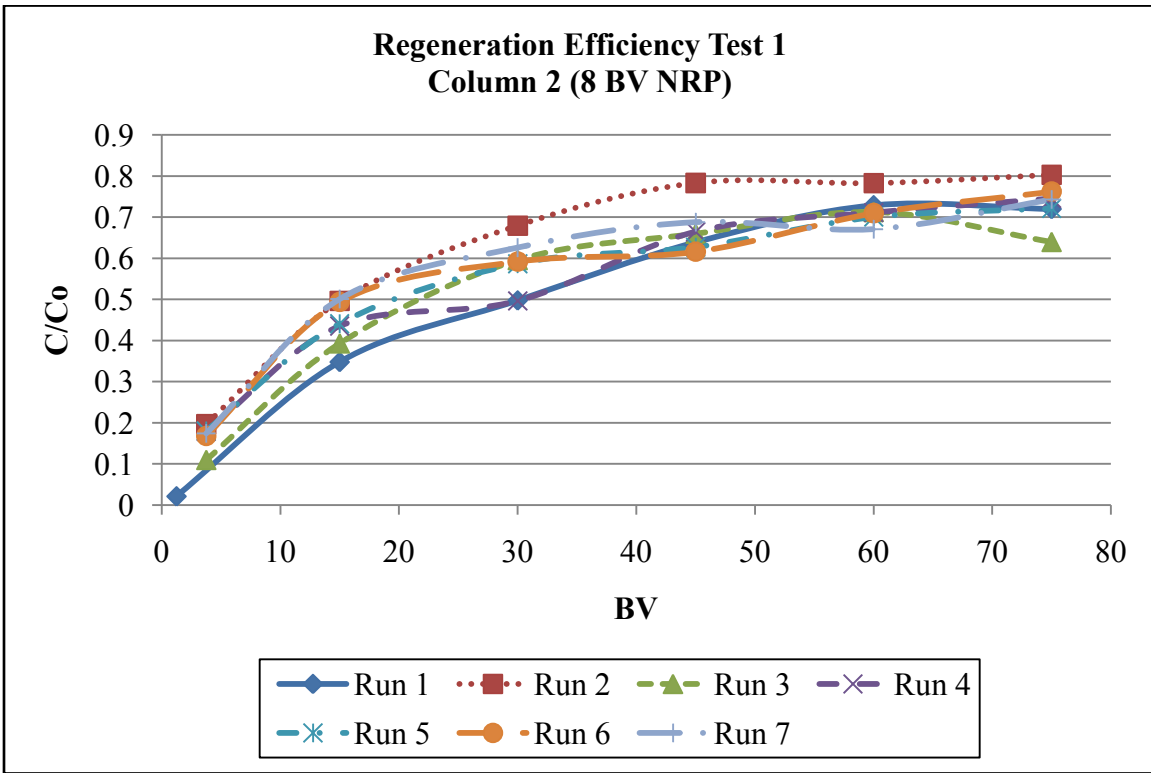
Figure 5.19. Results of regeneration efficiency test, column 2. Eight BV of NRP regenerant were used.
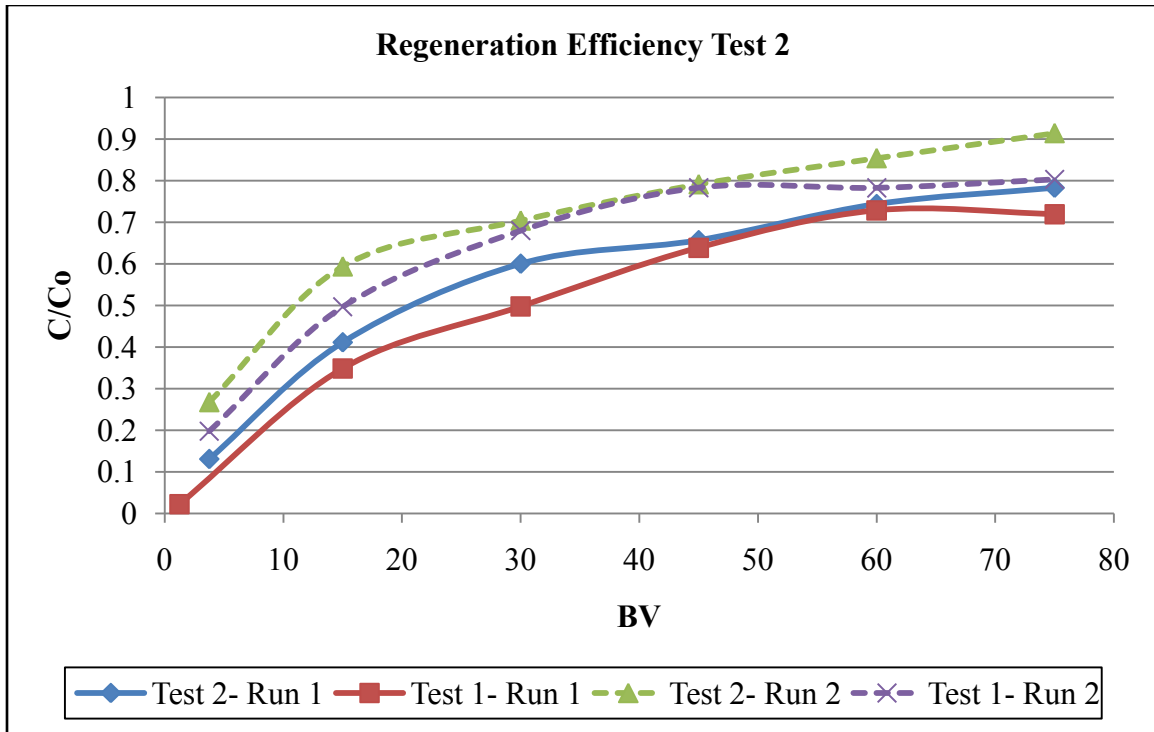
Figure 5.20. Regeneration Efficiency Test 2. Test was performed to confirm the dip in performance after 1st regeneration.

5.5.3. Regenerant Comparison

Results from the comparison test indicate that the NRP outperforms the sodium hydroxide solution for approximately the first 15 bed volumes. Performance of the carbon is similar for each column beyond this point. This can be seen in Figure 5.21. Figure 5.22 is a plot of the regression parameters in Table 5.4.

Table 5.4. Regenerant comparison regression parameters

		NaOH			NRP		
Run	Condition	$k_L a$	K	r^2	$k_L a$	K	r^2
1	Virgin	0.50	133.07	0.98	0.45	134.99	0.95
2	1st Regen	0.24	76.29	0.82	0.37	83.59	0.91
3	2nd Regen	0.21	91.31	0.90	0.29	92.93	0.87
4	3rd Regen	0.28	101.02	0.93	0.35	131.28	0.92
5	4th Regen	0.22	108.61	0.90	0.33	137.41	0.90
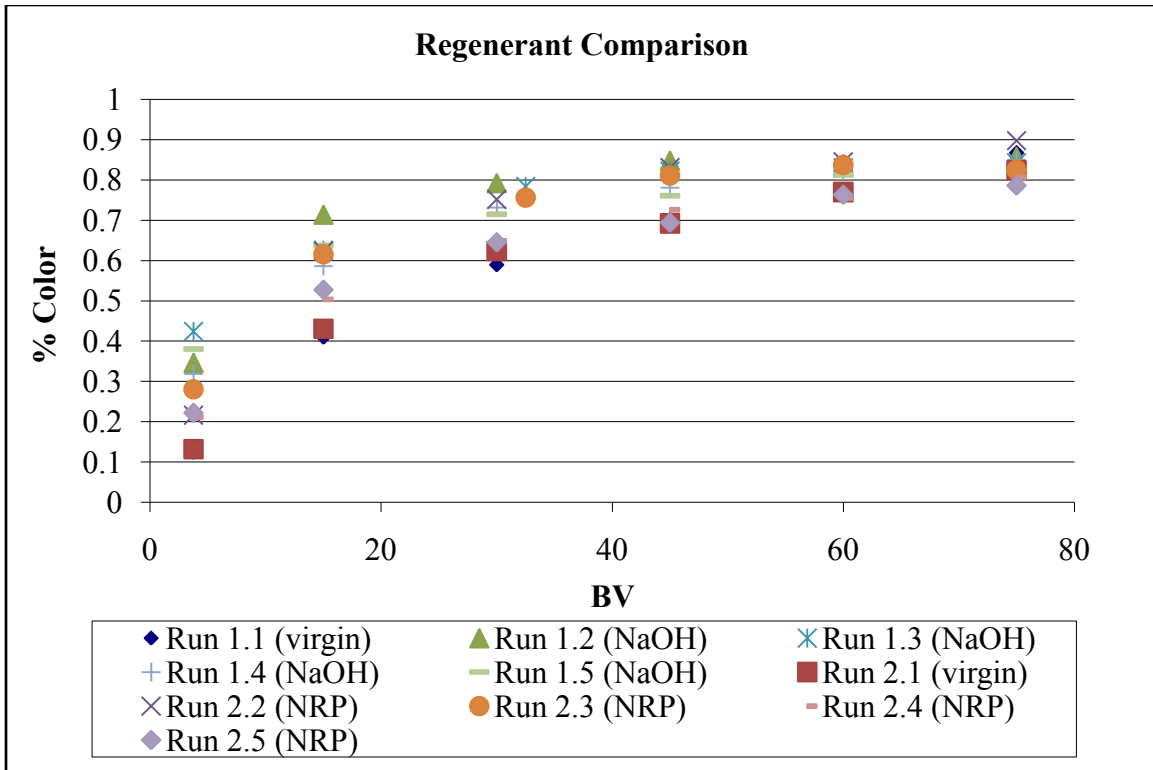
Figure 5.21. Regenerant comparison
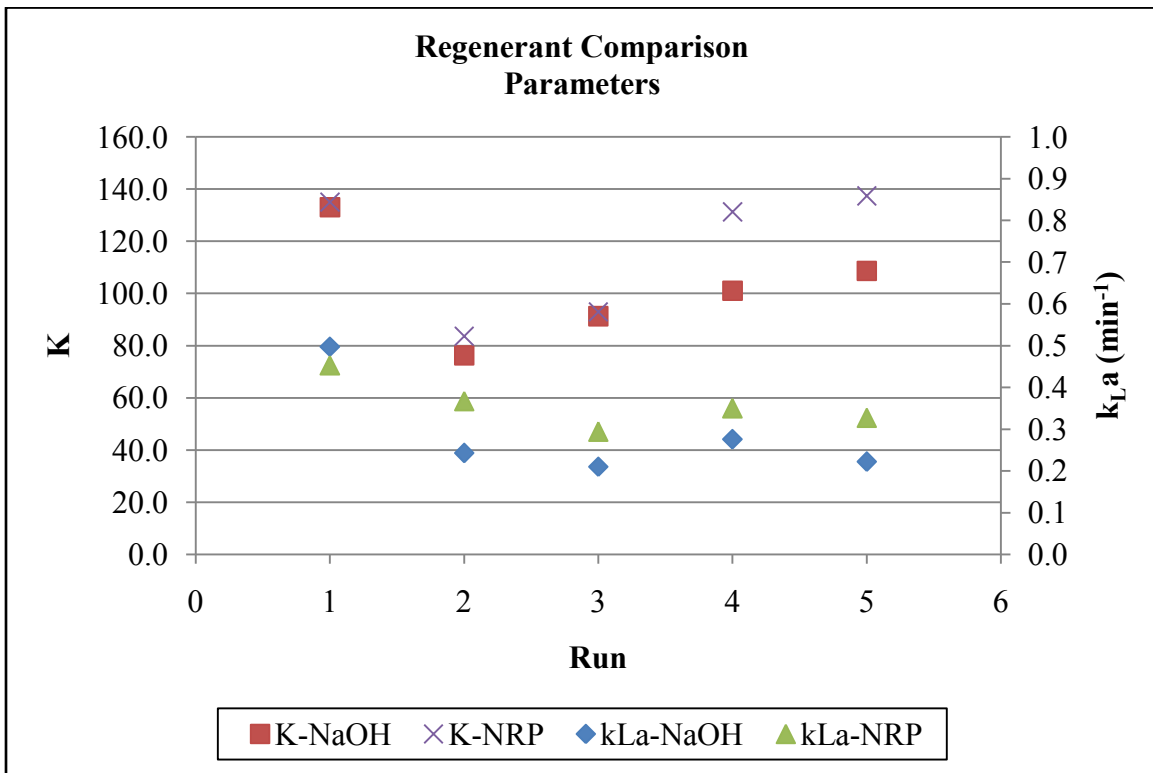
Figure 5.22. Regeneration comparison regression parameters

Another way of comparing the performance of the regenerants is to compare the average bulk color of the products produced from the four post-regeneration runs. By averaging color of the four runs, the bulk color of the product can be estimated by taking the mean of two adjacent points (x_1y_1, x_2y_2) and multiplying it by the volume of juice passed through the column between the two points (x_2-x_1). This gives an approximation of the area under the color curve between x_1 and x_2. The average color of the bulk product solution up to any x_i is calculated by summing the areas up to x_i and dividing it by the total volume produced up to x_i.

Figure 5.23 shows the comparison of the average bulk colors of the four runs produced after regeneration. Each point indicates the average color of the bulk product that will have been produced at any x quantity of bed volumes. Brix is assumed constant for the test and not considered in the analysis.

These figures illustrate the difference in efficacy of the two regenerants. At the point where each column color output reaches 5000 IU, 15 BV have passed from the NaOH regenerated column, whereby 30 BV have been produced by the NRP column. While it is clear that the NRP regenerated carbon produces a lower color product, the NRP solution also contained 2.5 times more NaOH. Therefore, the price for twice the performance is more than 2.5 time greater.
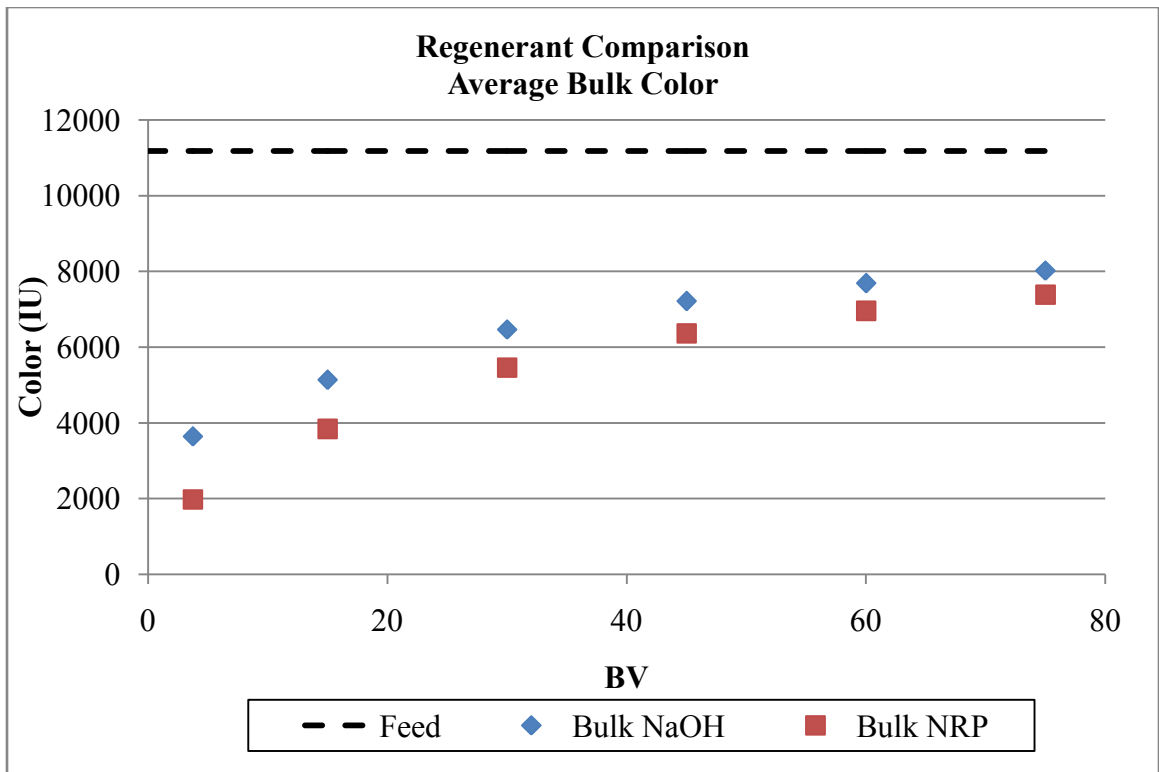
Figure 5.23. Average bulk color of product produced in comparison test

Chapter 6. Conclusions

6.1. Decolorization with Activated Carbon

The results from GAC testing revealed some interesting facts concerning adsorption dynamics. One of the most surprising is the effect of hydrogen peroxide on adsorptive capacity. Testing indicated that peroxide pretreatment reduces the adsorptive capacity of the carbon for cane juice colorants. It is possible that the peroxide changes the colorants in such a way as to affect their solubility and/or decrease the carbon's affinity for them. Peroxide may be beneficial to the DWiSP system at some other point in the stream. Further investigation is required.

Mass transfer parameters of the carbon used followed a discernible trend consistent with findings in the literature and seemingly independent of brix. Adsorption capacity, as determined by the partition coefficient, was not constant, and appeared to vary with residence time. It also appeared to be dependent on brix.

6.2. Chemical Regeneration of Activated Carbon

The use of chemicals to regenerate carbon provides an alternative to thermal regeneration. Performance of the carbon column decreased only slightly during the testing. The NRP regeneration solution was more effective at regenerating carbon than a solution of sodium hydroxide alone, but may be due to the additional sodium hydroxide in the NRP solution. The NRP solution was twice as effective, but cost more than twice as much on hydroxide alone. Losses normally associated with thermal regeneration were avoided. There was no loss of carbon observed during the investigation.

The use of chemical regeneration in industrial settings would not be without its difficulties. The effluent would have to be handled in an environmentally feasible manner.

Separation techniques can be employed to reclaim reusable material or potential value-added products. The alcohols used in the NRP solution can be distilled and reused or returned to the co-generation supply.

6.3. Ion Exchange System

The most significant finding from the ion exchange test was the consistency of performance over the cycles performed. Regardless of feed or regeneration condition of the carbon and resins, the performance before exhaustion was nearly identical. This is most likely due to the consistency of feed ion content, which is unaffected by the carbon column, and the high regeneration efficiency of ion exchange resins. The variation of color in the feed to the ion exchange columns does not appear to have as pronounced an effect on resin longevity.

Sizing of the ion exchange columns should be made on deashing requirements (Broadhurst, 2002, and Ellis, 2004). Operation of the columns may be governed by the product conductivity, which gives an indication of impending exhaustion. Unless it is shown that the columns are effective at higher flow rates, either large columns or a system of multiple smaller columns would have to be used.

6.4. DWiSP Design Parameters

A full scale implementation of the DWiSP system for a factory crushing 10,000 tons of cane per day would require processing of approximately 400 m^3/hr of clarified juice for a system installed after the clarifier, or 260 m^3/hr for installation after the first evaporator effect. Table 6.1 lists the design parameters of columns operating at 3, 6 and 12 BV/hr. If the system were installed after the 1st effect of the evaporator train, it would only have to handle 260 m^3/hr and columns of equal diameters would be 65% as tall. Table 6.2 lists the design parameters for such an installation.

Operating a column at such high flow rates would require superficial velocities considerably greater than those investigated in the column tests. According to the model results, this should improve the rate of mass transfer.

Table 6.1. DWiSP design parameters for installation after clarifier

BV/hr	BV (m^3)	r (m)	V$_o$ (m/min)	z (m)	t$_R$ (min)
3	133.33	1	2.12	42.44	20
6	66.67	1	2.12	21.22	10
12	33.33	1	2.12	10.61	5
3	133.33	2	0.53	10.61	20
6	66.67	2	0.53	5.31	10
12	33.33	2	0.53	2.65	5
3	133.33	3	0.24	4.72	20
6	66.67	3	0.24	2.36	10
12	33.33	3	0.24	1.18	5
3	133.33	6	0.06	1.18	20
6	66.67	6	0.06	0.59	10
12	33.33	6	0.06	0.29	5

Table 6.2. DWiSP design parameters for installation after 1st effect evaporator

BV/hr	BV (m^3)	r (m)	V$_o$ (m/min)	z (m)	t$_R$ (min)
3	86.67	1	1.38	27.59	20
6	43.33	1	1.38	13.79	10
12	21.67	1	1.38	6.90	5
3	86.67	2	0.34	6.90	20
6	43.33	2	0.34	3.45	10
12	21.67	2	0.34	1.72	5
3	86.67	3	0.15	3.07	20
6	43.33	3	0.15	1.53	10
12	21.67	3	0.15	0.77	5
3	86.67	6	0.04	0.77	20
6	43.33	6	0.04	0.38	10
12	21.67	6	0.04	0.19	5

6.5. Future Research Directions

Conducting more carbon column testing in the laboratory would increase the database of column performance over a larger range of flow rates and retention times. As mentioned in section 6.4, handling of such a high flow rate would require superficial velocities considerably higher than those investigated. The use of columns of various length-to-diameter ratios would facilitate testing at different combinations of superficial velocity to retention time.

While ion exchange resins have been researched extensively in sugar decolorization, continued investigation is warranted by the findings herein. Few studies have been conducted using low brix solutions. The work done by Broadhurst (2002) should be expanded, with a wider range of flow rates being investigated. Another consideration is the need for refrigeration of the SAC column. The DWiSP system would benefit from elimination of this requirement. The use of a strong base anionic resin before a cationic resin may provide a remedy to this situation.

Several aspects of the chemical regeneration procedure may also be investigated. Evaluation of the desorption characteristics can be used to optimize operating parameters. An increase in the flow rate would reduce the time required to complete regeneration and restore the column to service sooner. A relatively short retention time was used to load the carbon, which may not have loaded the carbon thoroughly enough. Increasing contact time during loading would provide a better indication of the regenerant's effectiveness.

The feasibility of the DWiSP system ultimately rests on its cost effectiveness. Rein et al (2007) reports the cost of regeneration to be roughly $0.50 for a color loading of 1 ton DS•IU/L of carbon per cycle, which translates into 0.20 cents per pound of sugar for regeneration cost. Ion exchange regeneration is estimated at 0.76 cents per pound sugar, which can be reduced with

regenerant reuse. Regenerant cost may also be offset by the reduction in chemicals necessary for evaporator cleaning. Further investigation into startup and operational cost is required.

Although pilot scale testing has been conducted in conjunction with the DWiSP project, the results have not been as informative as would be desired. Peroxide was used in studies conducted during the 2005 and 2006 seasons, which invalidated comparison to the data from the tests. The study conducted during the 2006 season was plagued with equipment malfunctions which prevented the production of syrup suitable for crystallization (see Appendix E). Therefore, a pilot plant study which employs the findings of this research would provide greater understanding of the process.

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Appendix A. Sample Calculations

A.1. ICUMSA Color

1. Set pH to 7.0 ± 0.05 and dilute sample to give a 420nm absorbance between 0.1 and 0.9 AU.

2. Measure 420nm absorbance, A = 0.243.

3. Cuvette length = 10mm.

4. Measure brix of sample in cuvette, b = 5.17.

5. Convert to concentration using equation 4.2:

$$\text{Concentration (g/100 ml)} = 0.0042*(5.17)^2 + 0.9969*(5.17)*(5.17)$$

$$= 5.27 \text{ g/100ml}$$

$$= 0.0527 \text{ g/ml}$$

6. Calculate ICUMSA color:

$$ICUMSA(420) = \frac{10000 \times Abs.}{Conc.(g/ml) \times Cell\ Length(mm)}$$

$$ICUMSA(420) = \frac{10000 \times 0.243}{0.0527 \times 10}$$

$$= 4609 \text{ IU}$$

A.2. Void Fraction Determination

The packed bed void fraction of the carbon used in the analytical model can be described by the following equation:

$$\varepsilon = \frac{Void\ Volume}{Bed\ Volume}$$

Expressing the above equation to measurable quantities:

$$\varepsilon = \frac{V_{bed} - V_{carbon}}{V_{bed}} = 1 - \frac{V_T - V_{H2O}}{V_{bed}}$$

where:

V_{bed} = Volume of the packed carbon bed (includes voidage)

V_{carbon} = Volume of carbon in bed

V_{H2O} = Volume of water added to bed in cylinder

V_T = Total volume of carbon and water in cylinder

Table A.1 lists the values used to determine the average void fraction.

Table A.1. Void fraction determination

Trial #	1	2	3	4	5	6	7
V_{bed}	5	7.5	10.5	10	15	25	6.5
V_{H2O}	10	10	20	20	20	30	10
V_T	11.2	11.8	23.0	22.5	24.0	36.0	11.5
ε	0.75204	0.75886	0.71429	0.75000	0.73333	0.76000	0.76923
ε_{avg}	0.74825						

A.3. Peroxide Dosing

1. Determine brix and temperature of juice to be used:

b = 14.5; T = 85°C

2. Required peroxide dosing:

1000 ppm = 0.001 kg/kg

3. Calculate juice density at temperature and brix using the correlation below (Bubnik et al., 1995):

$$\rho_{juice} = 1000 \left(1 + \left(\frac{b(b + 200)}{54000} \right) \right) \times \left(1 - 0.036 \left(\frac{T - 20}{160 - T} \right) \right)$$

$$\rho_{juice} = 1000\left(1 + \left(\frac{b(b+200)}{54000}\right)\right) \times \left(1 - 0.036\left(\frac{T-20}{160-T}\right)\right)$$

$$= 1024.60 \text{ kg/m}^3$$

4. Determine the volume of juice to be processed, calculate the mass of juice, then total dissolved solids:

V_{juice} = 15 * 200ml = 3000 ml = 3 L = 0.003 m^3

m_{juice} = 0.003 m^3 * 1024.60 kg/m^3 = 3.07 kg juice

m_{solids} = 3.074 kg juice * 0.145 = 0.4457 kg solids

5. Using the require peroxide dosage, find the mass of H$_2$O$_2$ to be added, then the volume, using a density of 1100 kg/m^3 for peroxide at 30%:

m_{H2O2} = 0.4457/1000 = 0.0004457 kg

V_{H2O2} = 0.0004457 kg/(1100 kg/m^3 * 0.30)/1x10^6 ml/m^3= 1.351 ml

A.4. Adsorption Isotherm Calculation

Isotherm tests were conducted overnight to allow for complete saturation of the carbon. The data gathered from the tests were:

V_{carbon} - volume of carbon used in each beaker

V_{juice} - volume of juice used; same for each beaker

C*   - color of juice in each beaker at end of test

C   - initial juice color

To determine color adsorbed by the carbon, the following equation is used:

$$q(IU) = \frac{(C - C^*)V_{juice}}{(1 - \varepsilon)V_{carbon}}$$

Appendix B. Batch Test Results

B.1. 65°C

Table B.1. Adsorption isotherm parameters, 65°C

Trial	K	r^2
No H_2O_2	324.06	0.868
500 ppm	230.72	-2.375
1000 ppm	299.01	0.531
2000 ppm	303.66	0.949
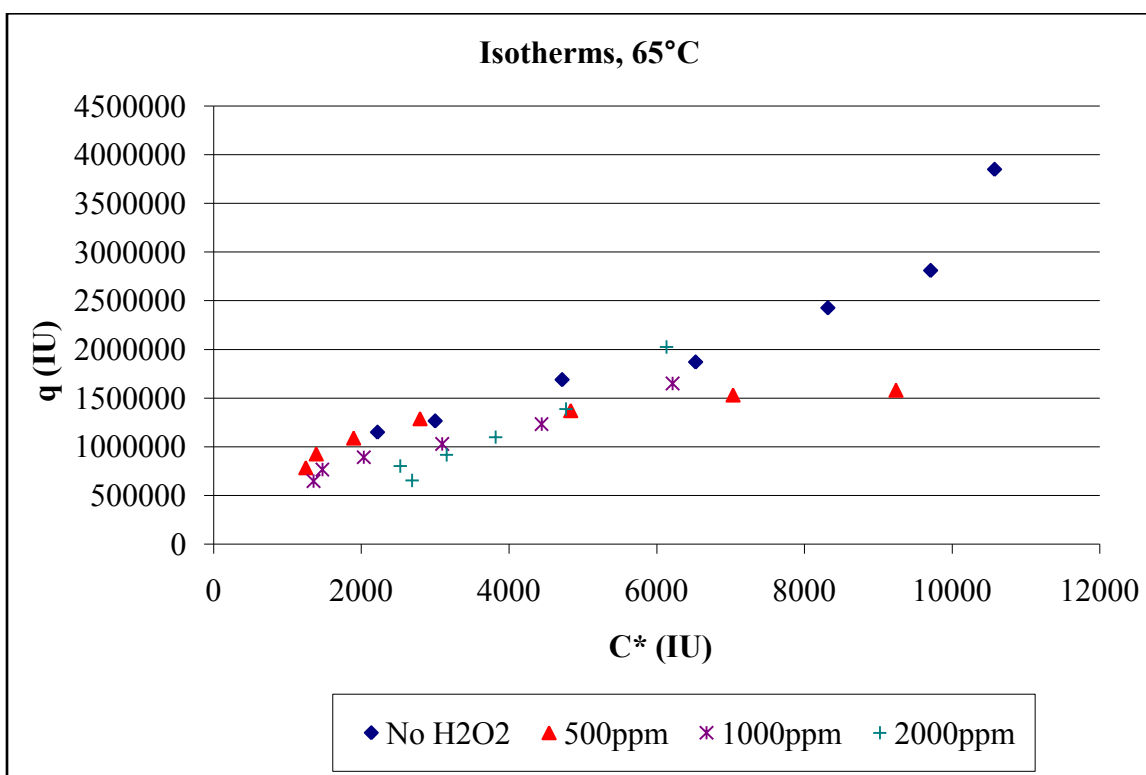
Figure B.1. Batch adsorption test results, 65°C

B.2. 75°C

Table B.2. Adsorption isotherm parameters, 75°C

Trial	K	r^2
No H_2O_2	282.28	0.718
500 ppm	263.80	0.424
1000 ppm	188.23	0.950
2000 ppm	232.04	0.770
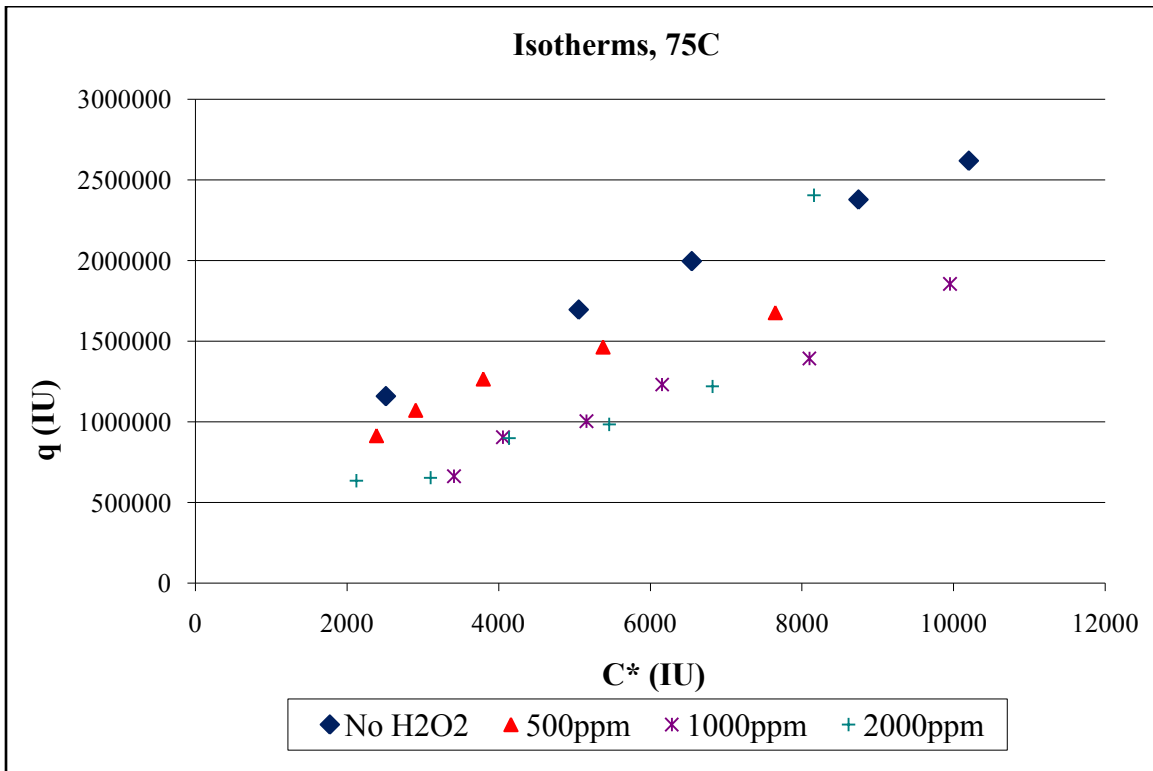
Figure B.2. Batch test results, 75°C

Appendix C. Column Test Results
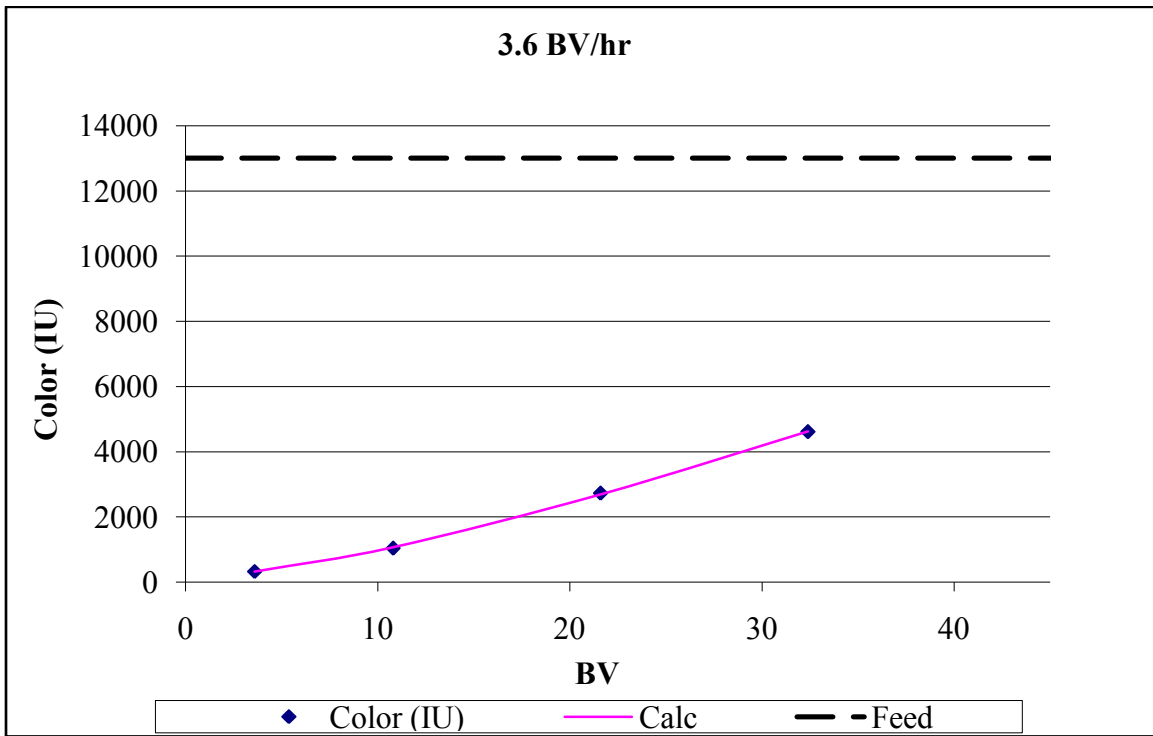
Figure C.1. Carbon 1 product color
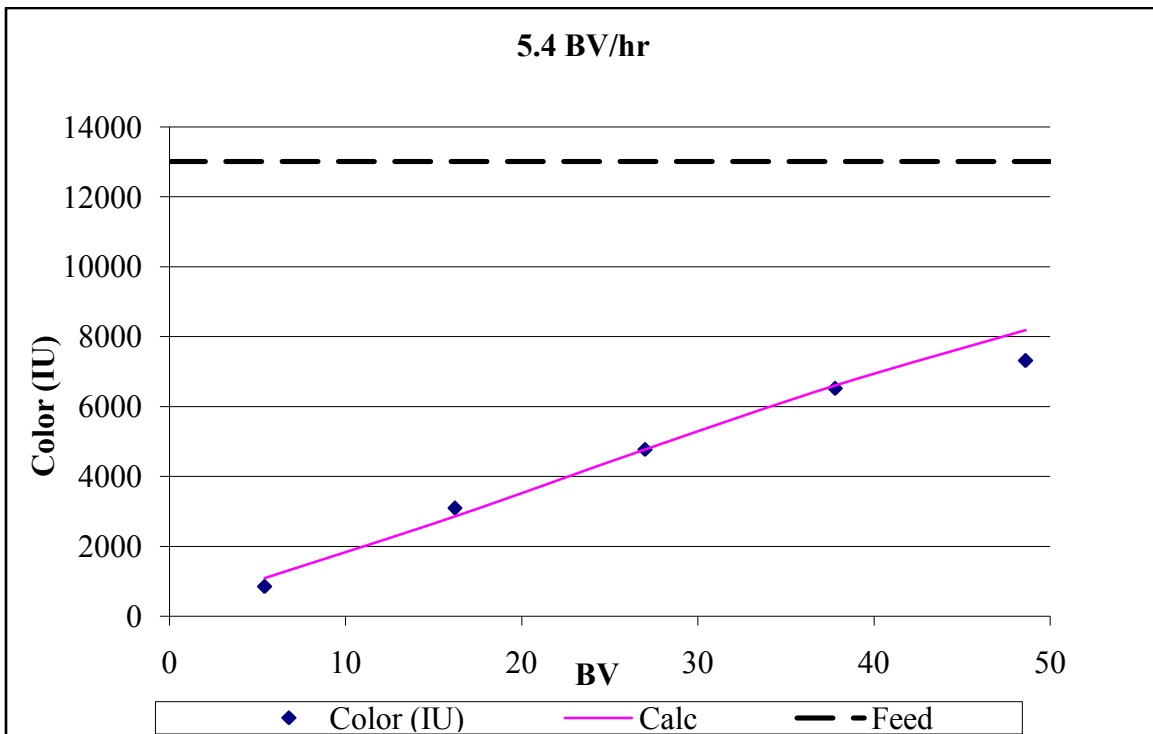
Figure C.2. Carbon 2 product color

Figure C.3. Carbon 3 product color

Figure C.4. Carbon 4 product color

Figure C.5. Carbon 5 product color

Figure C.6. Carbon 6 product color

Figure C.7. Carbon 7 product color

Figure C.8. Carbon 8 product color

66
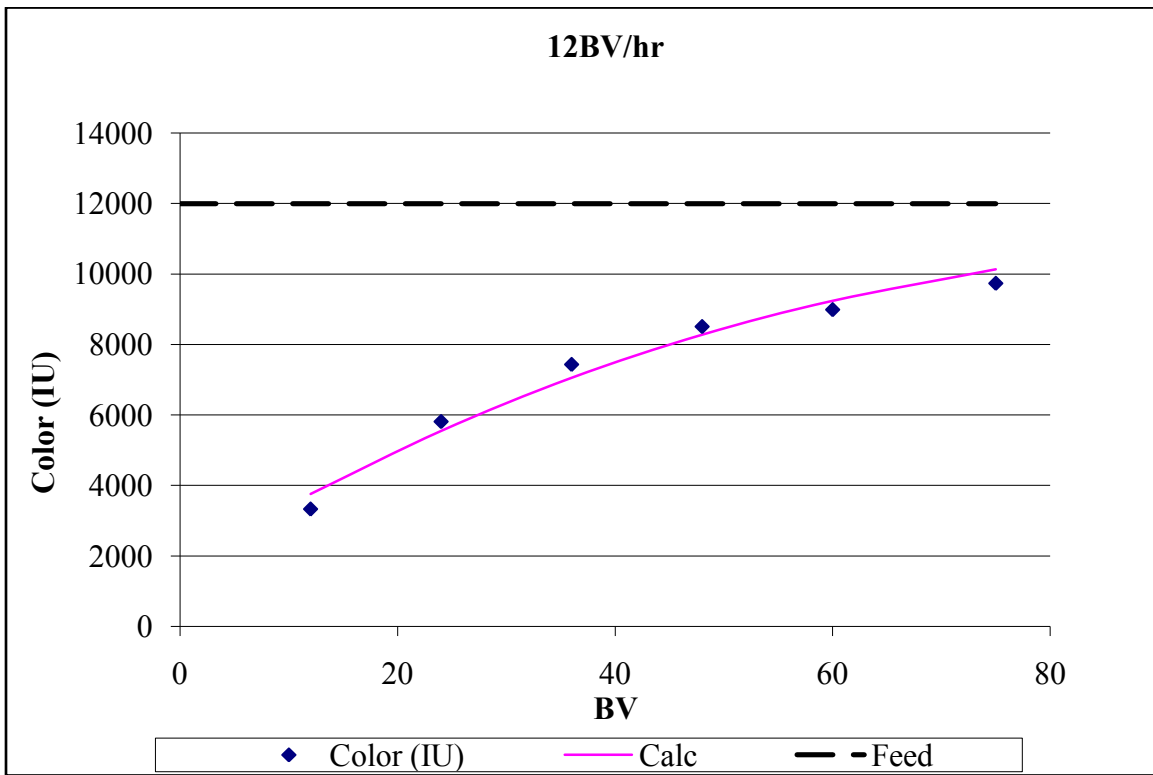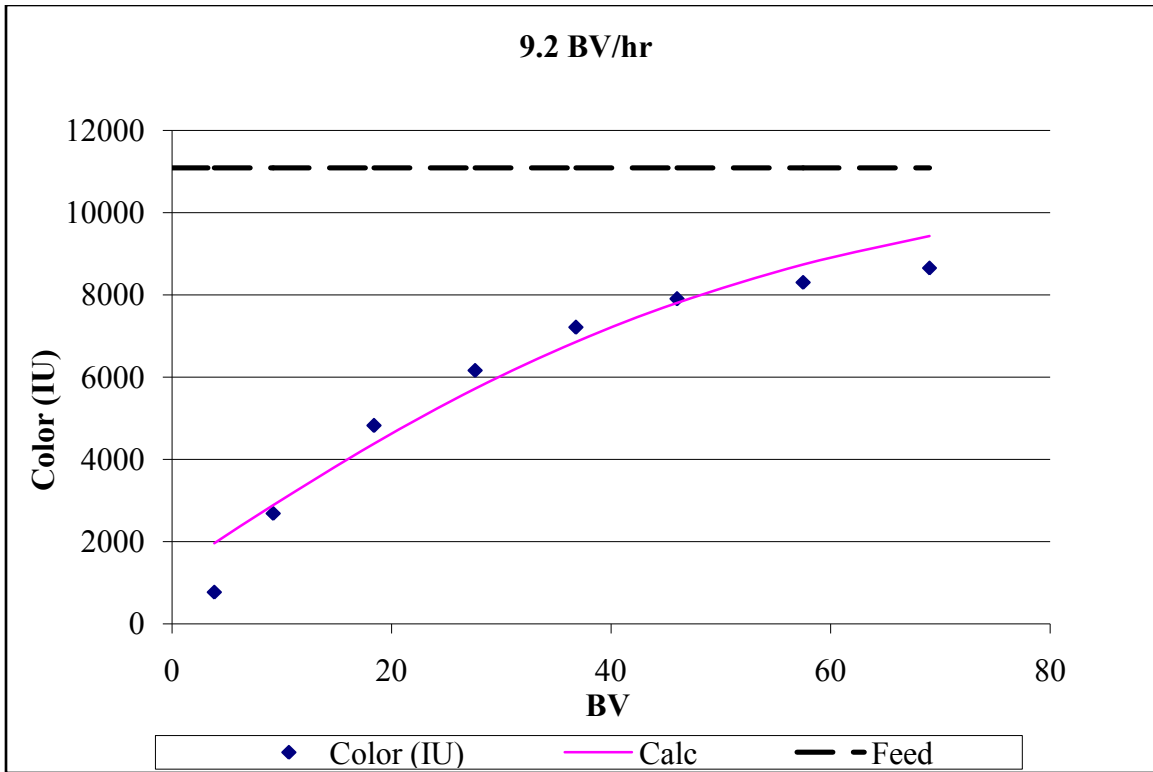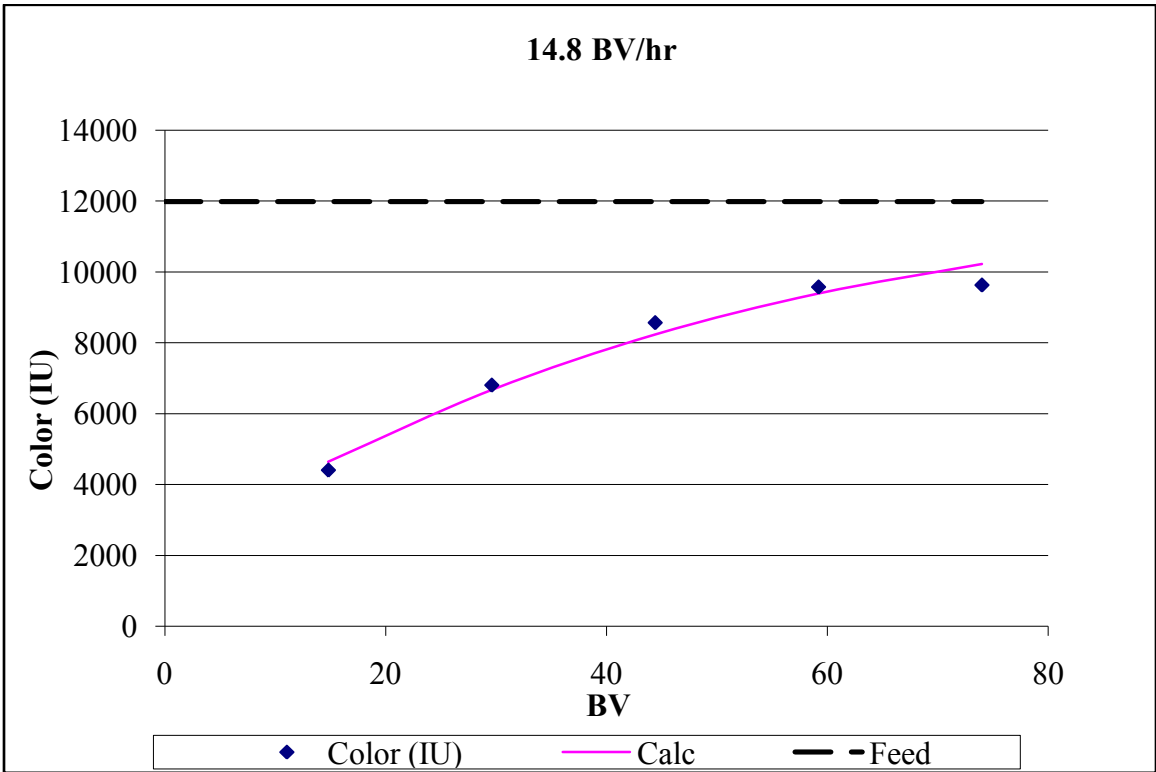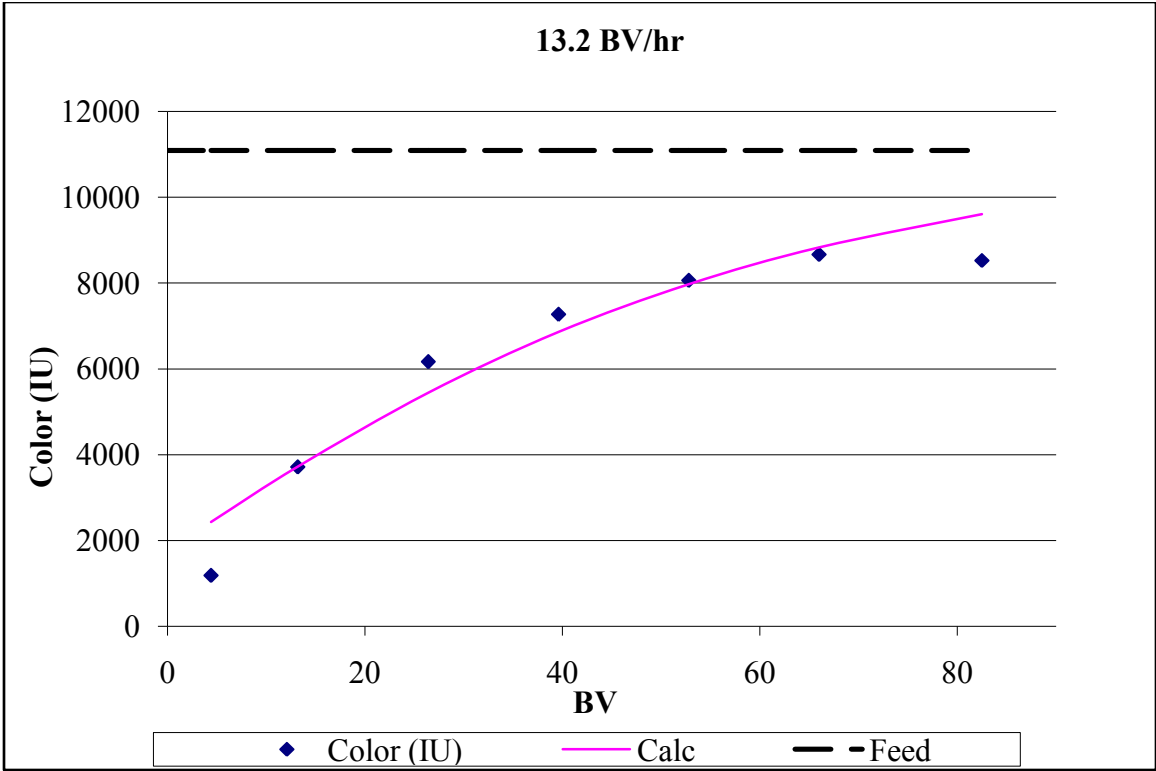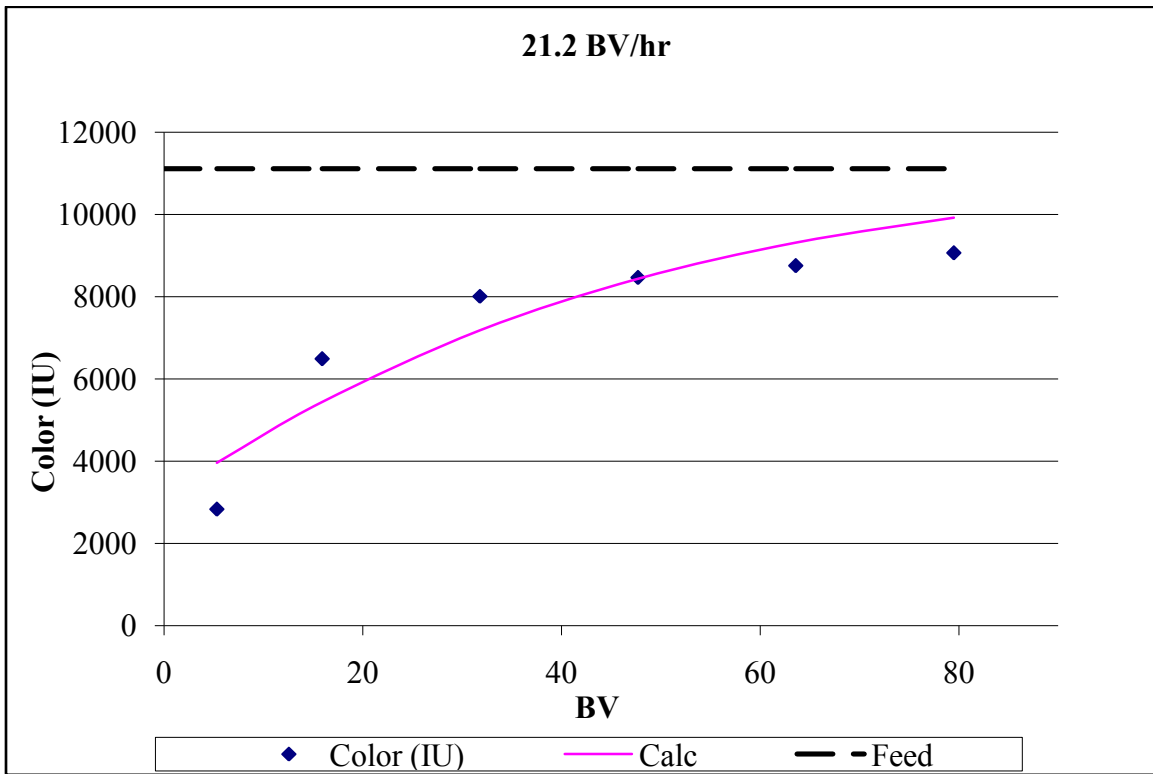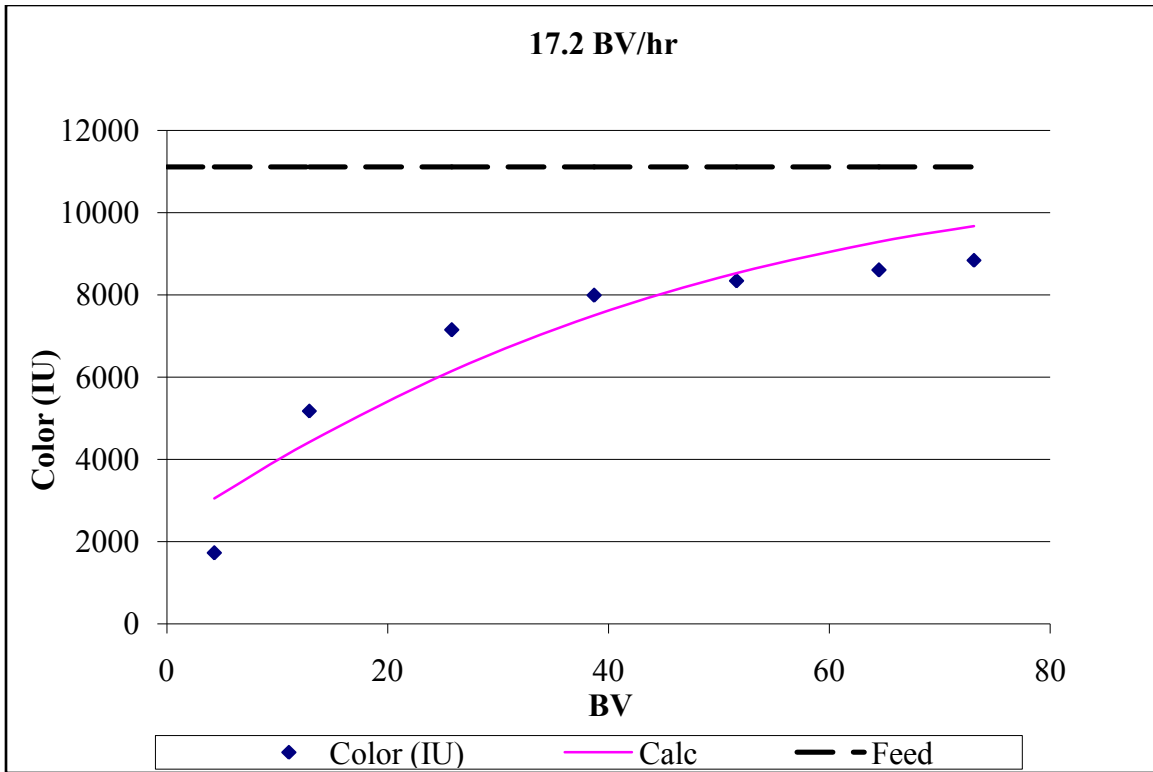
Appendix D. Ion Exchange Test Results
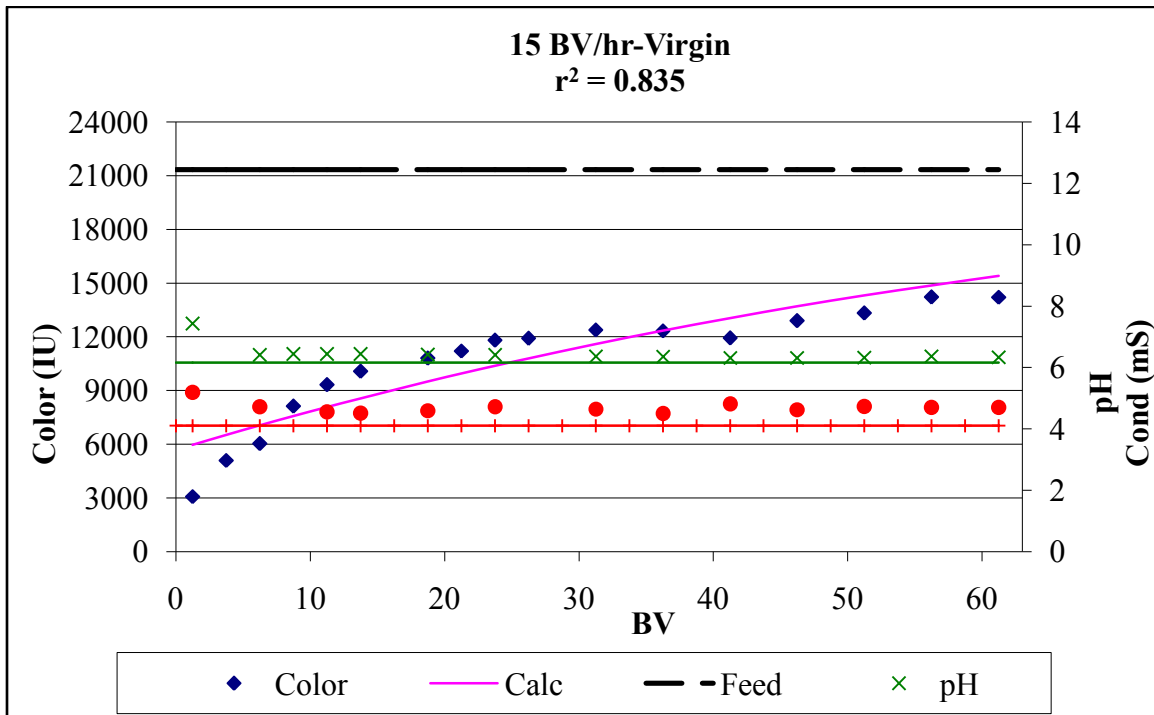
Figure D.1.1. IX test 1 - carbon product
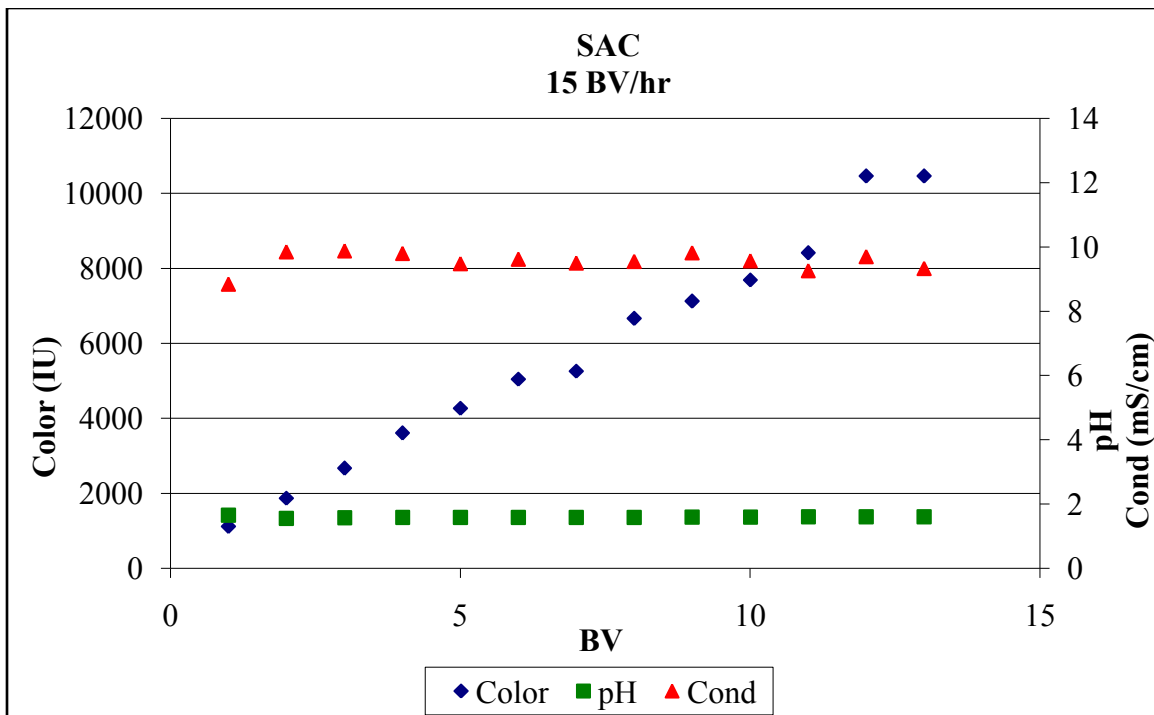
Figure D.1.2. SAC product
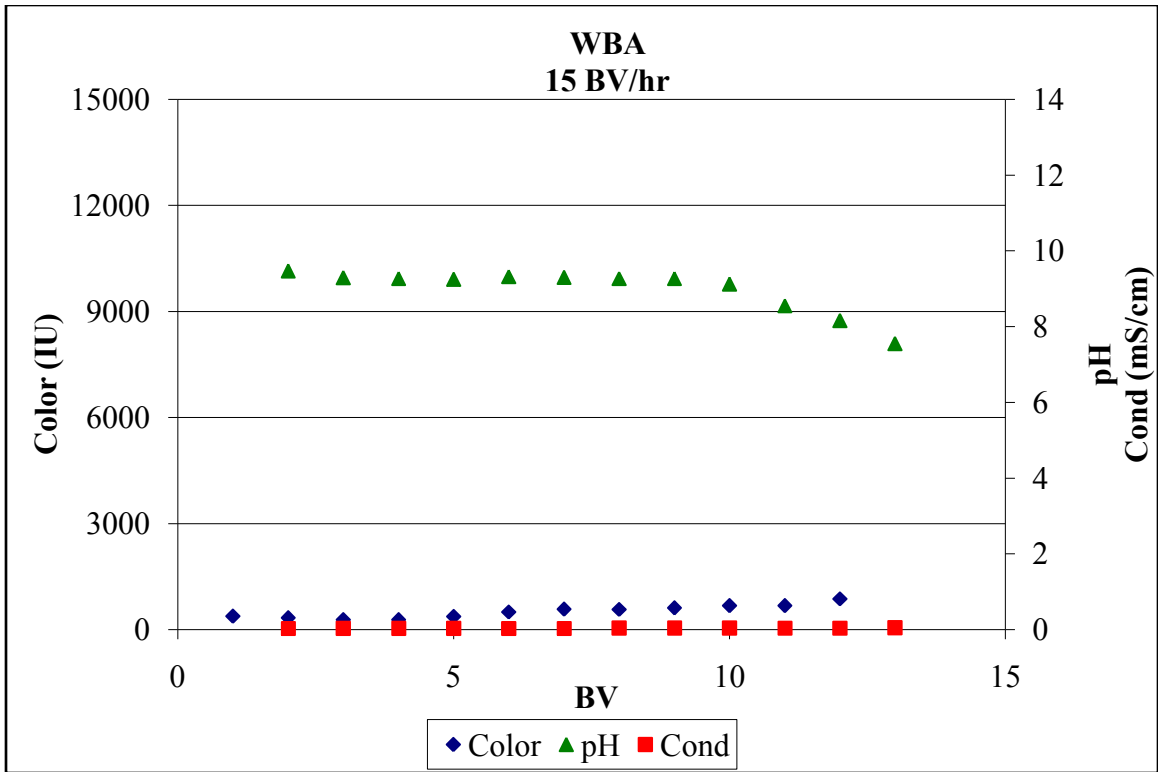
Figure D.1.3. WBA product
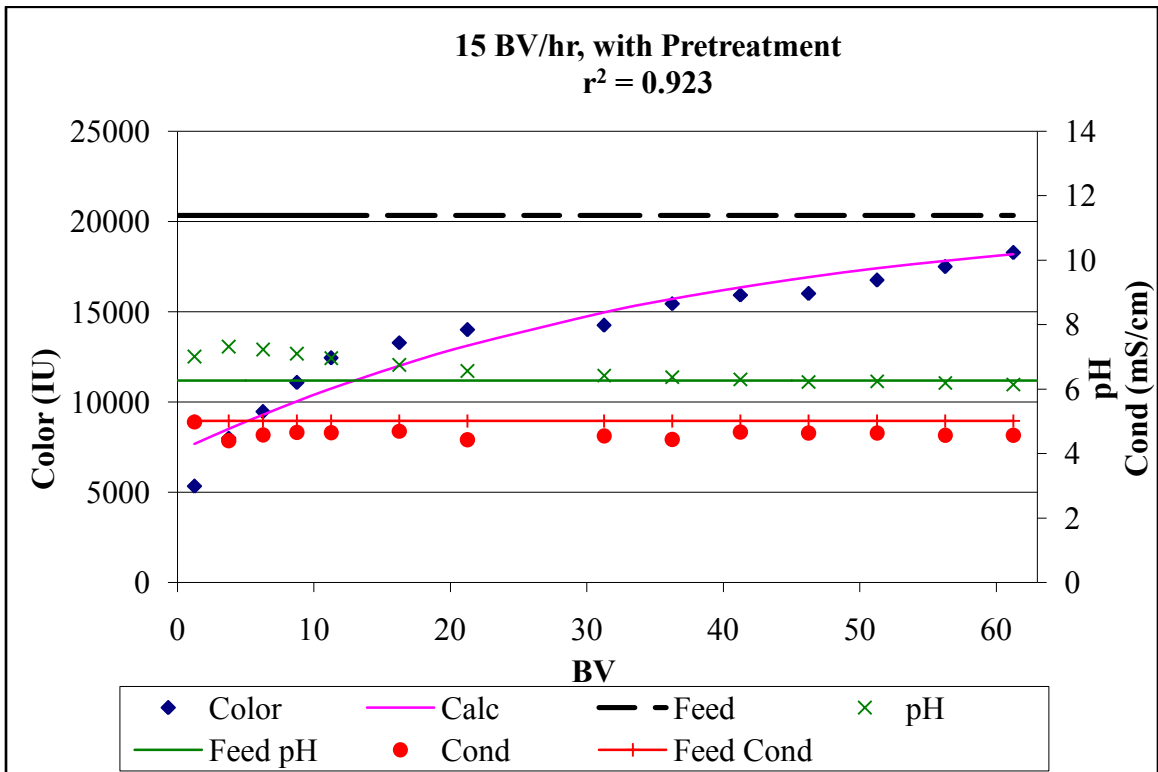
Figure D.2.1. IX test 2 carbon product, 1 regeneration
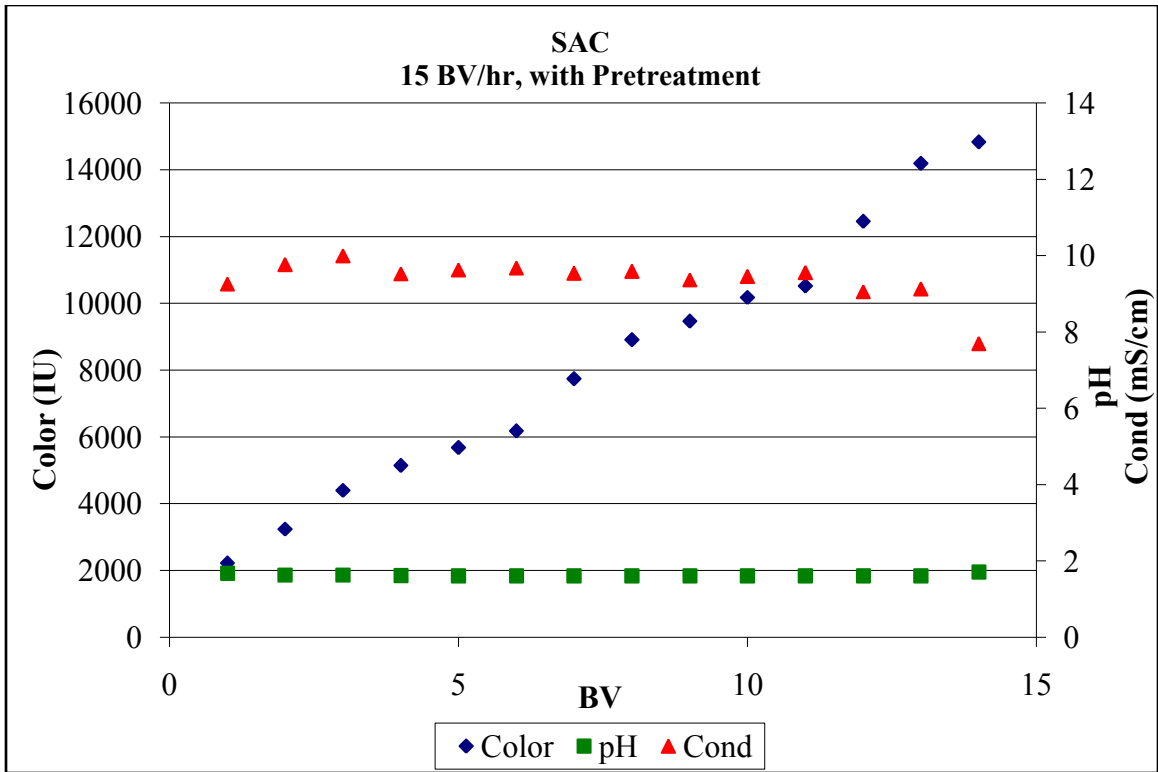
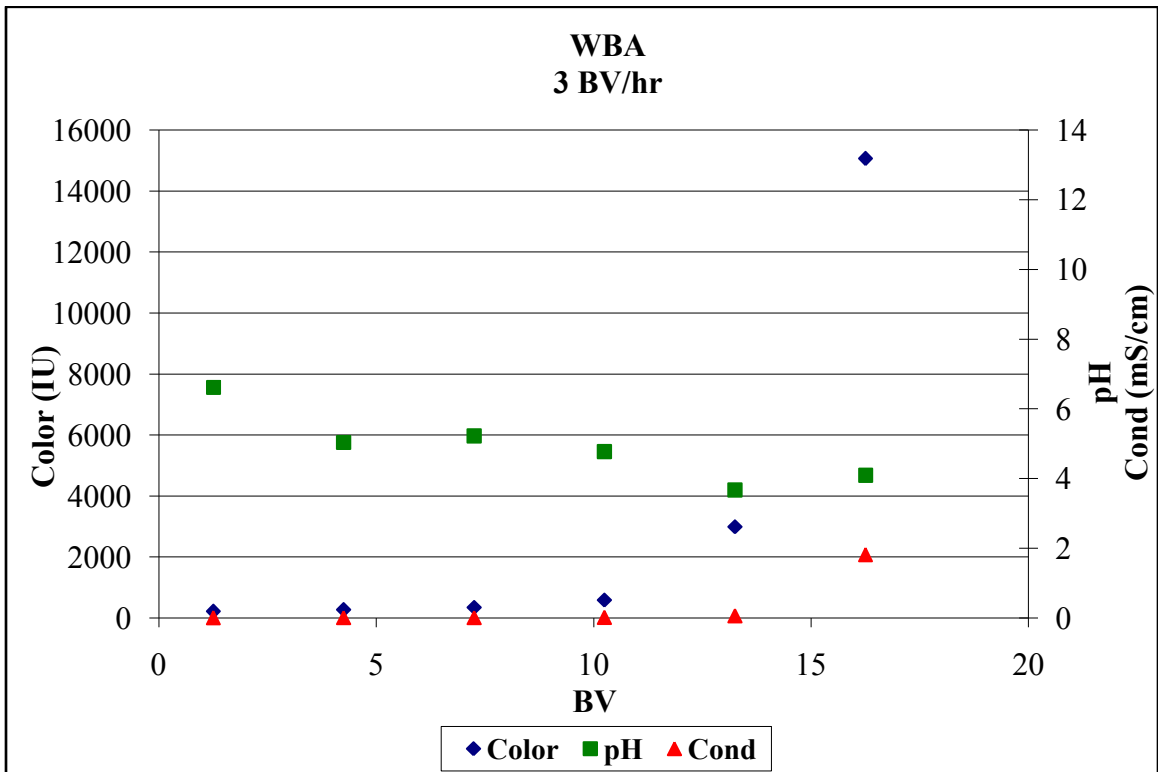**Figure D.2.2. SAC product, 1 regeneration**
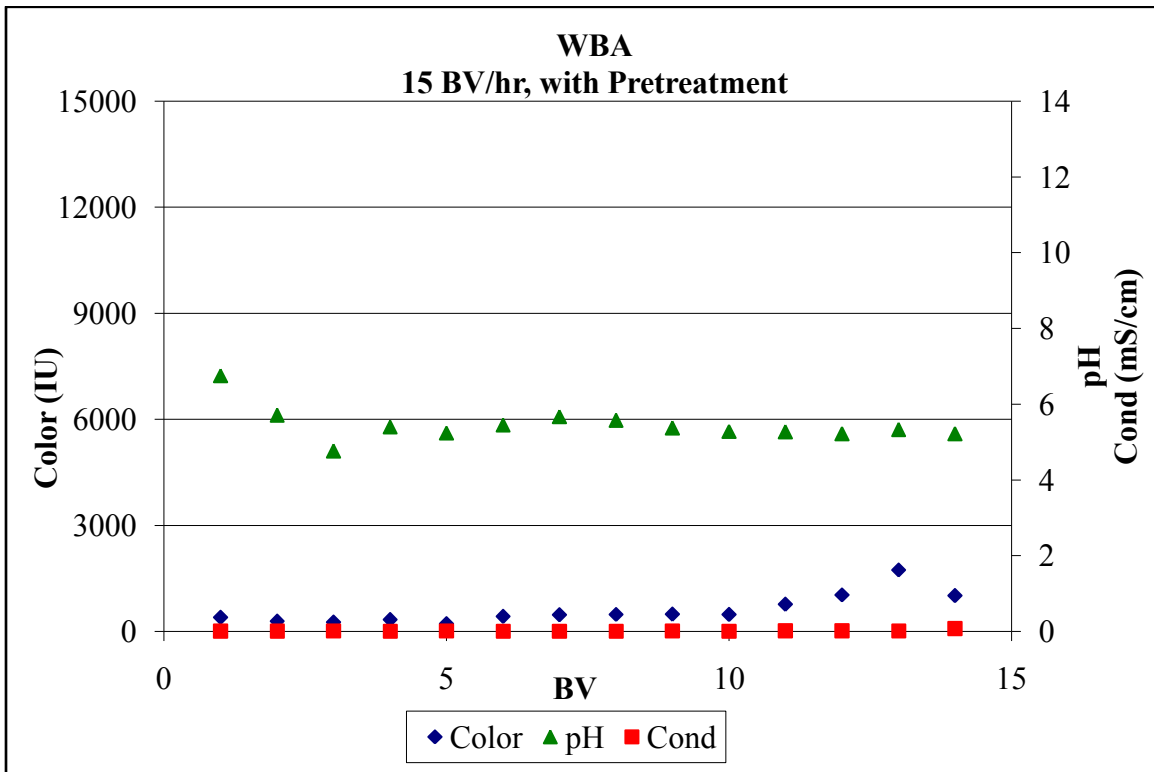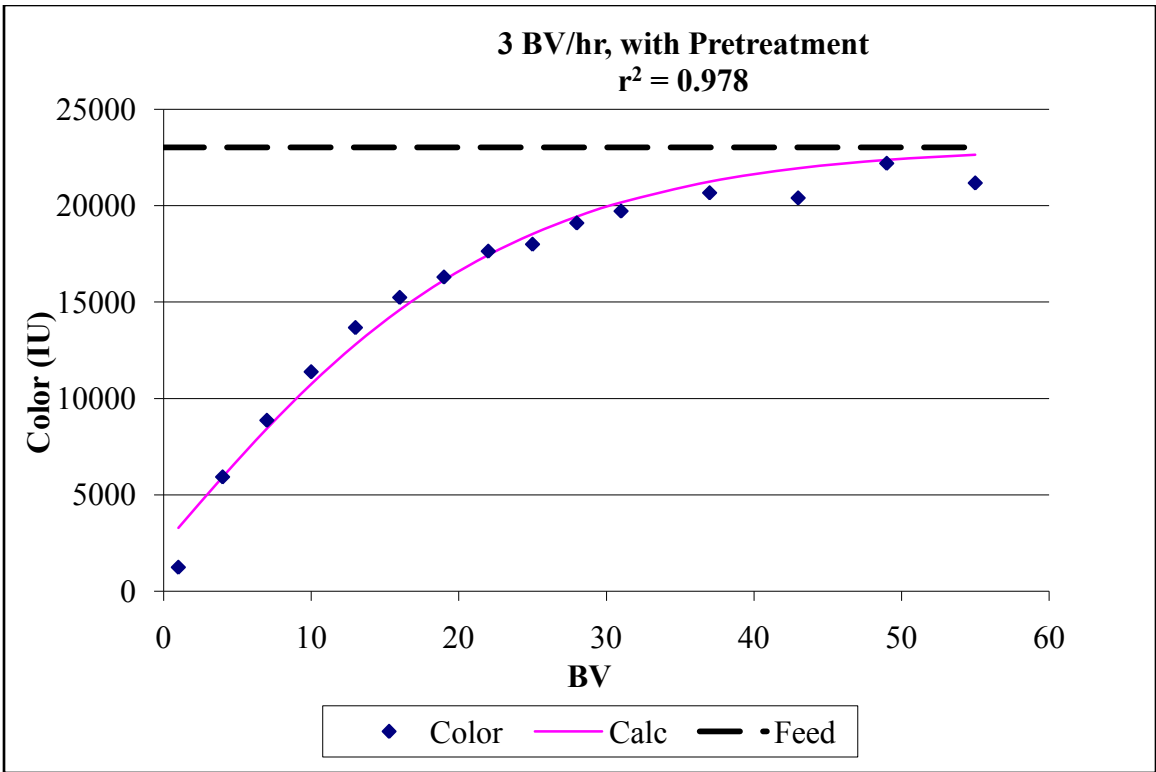

Figure D.2.3. WBA product, 1regeneration
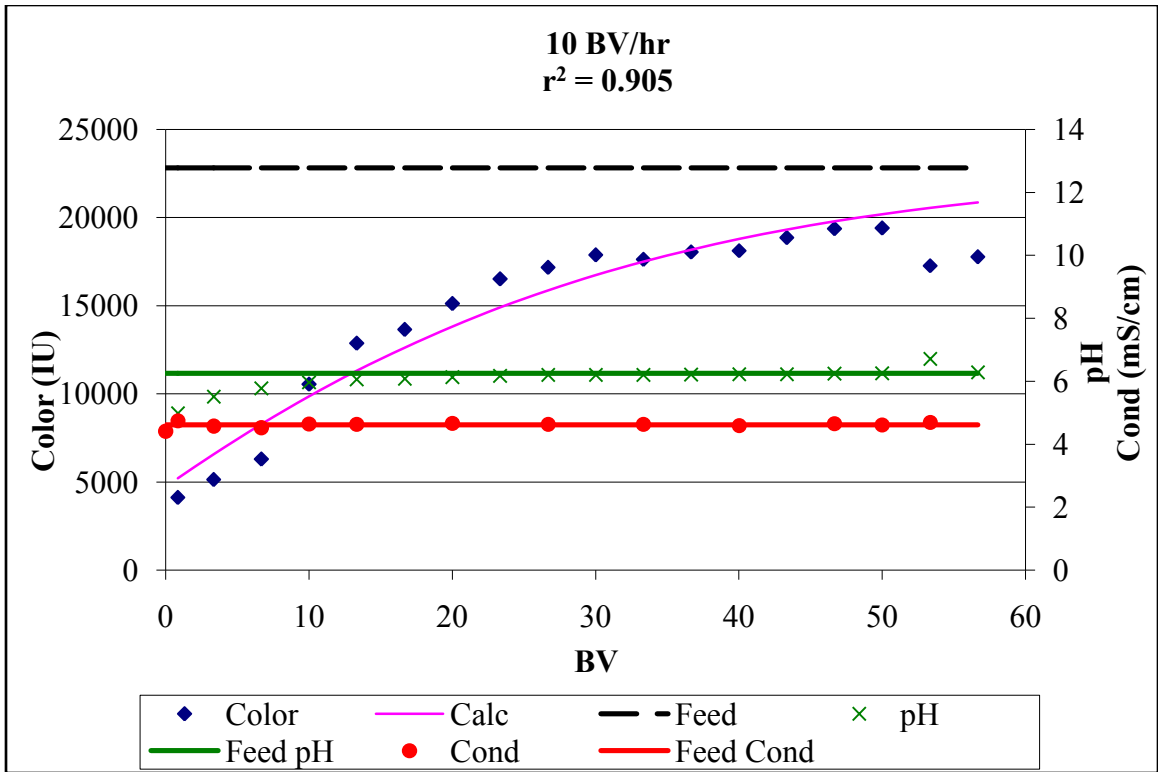
Figure D.3.1. IX test 3 carbon product, 2 regenerations
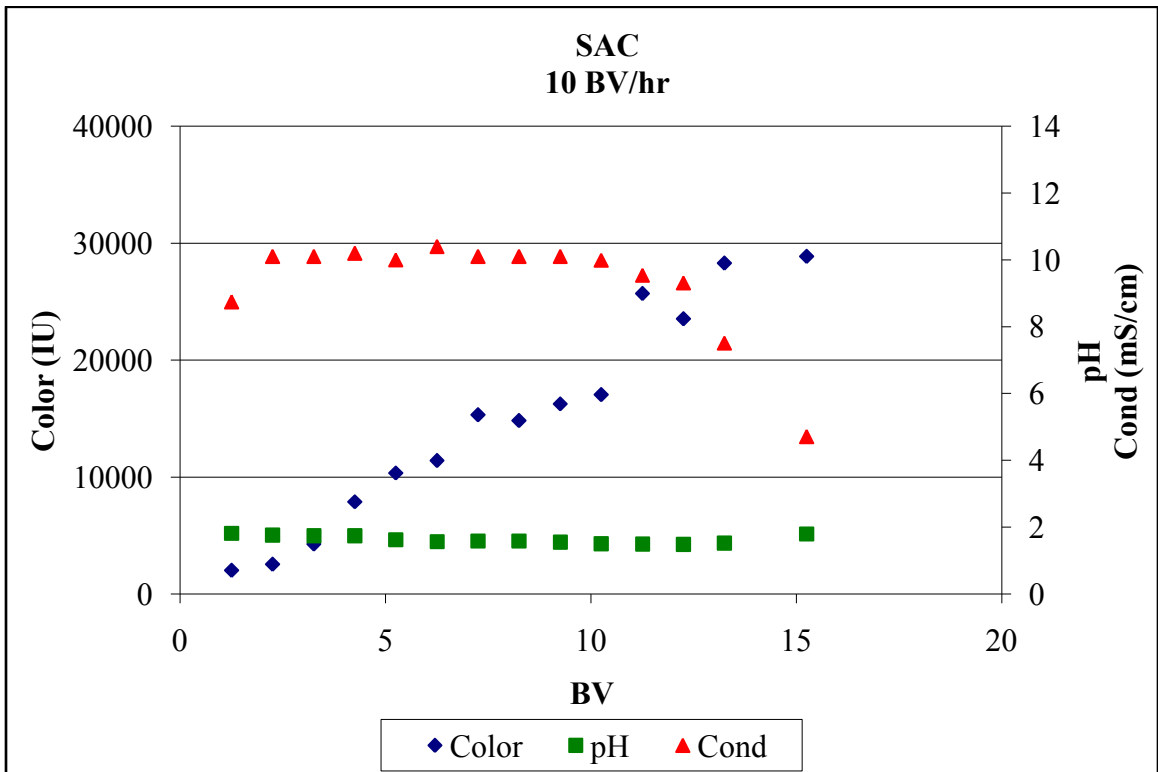
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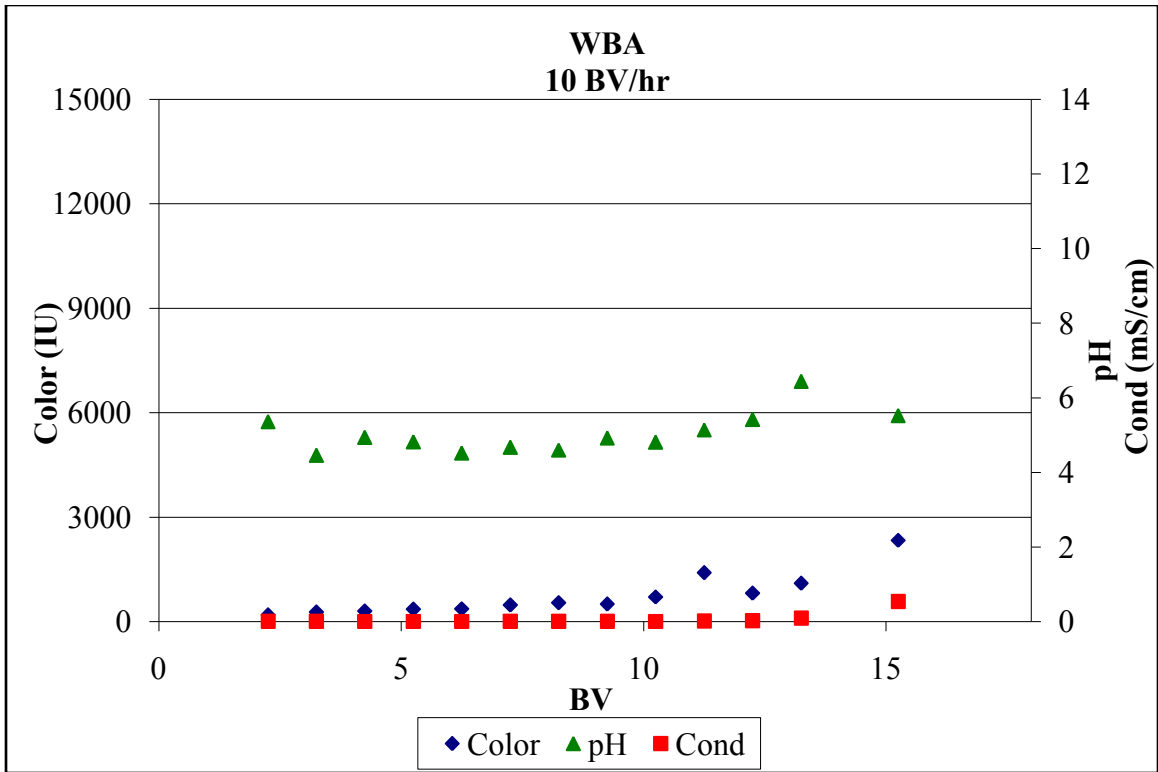
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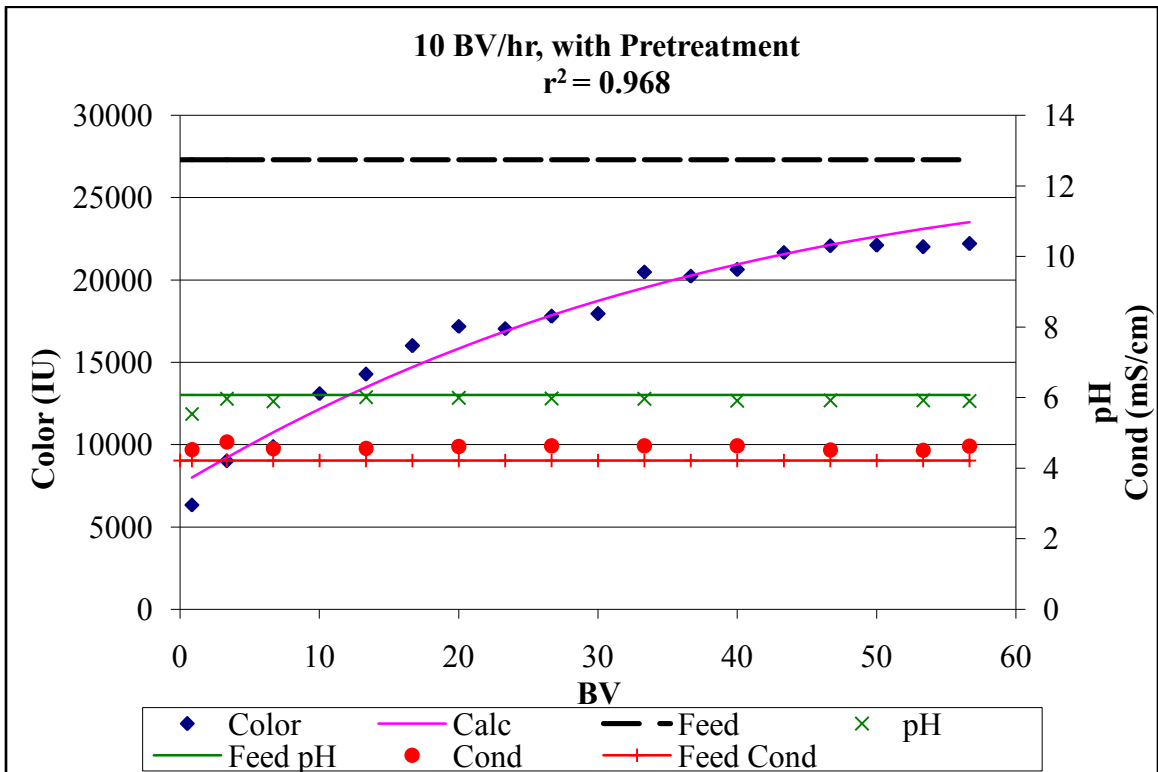

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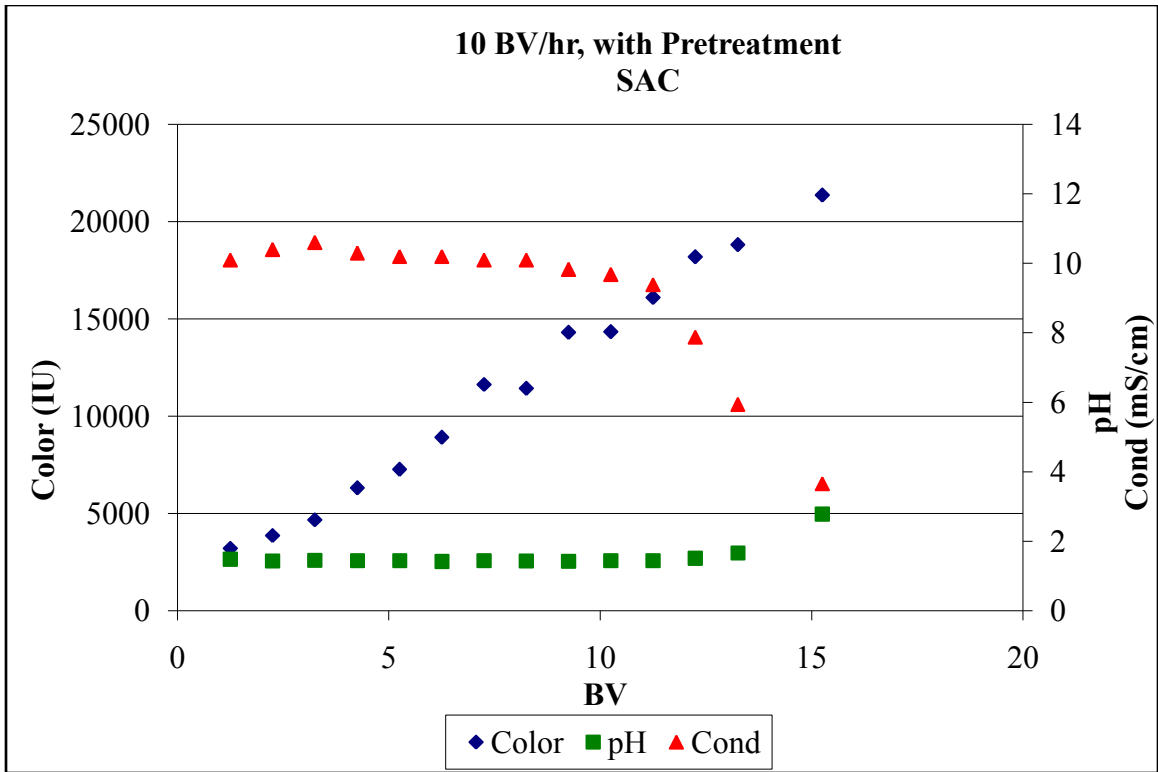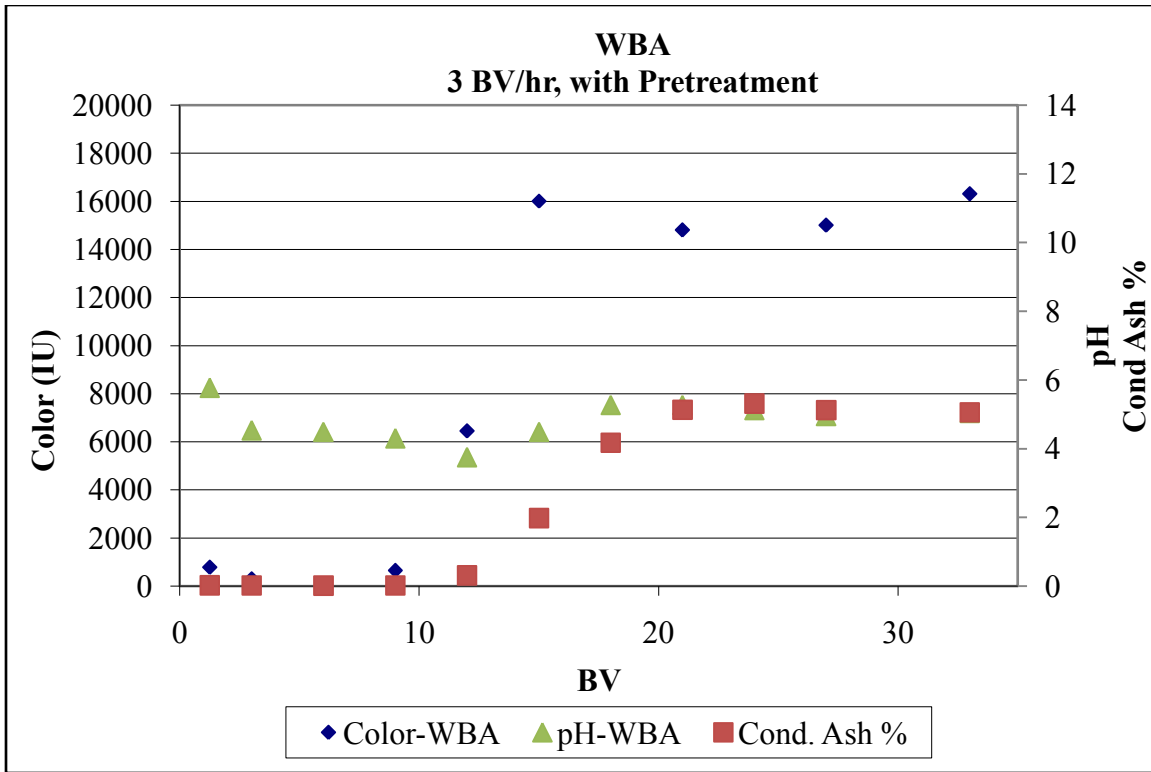
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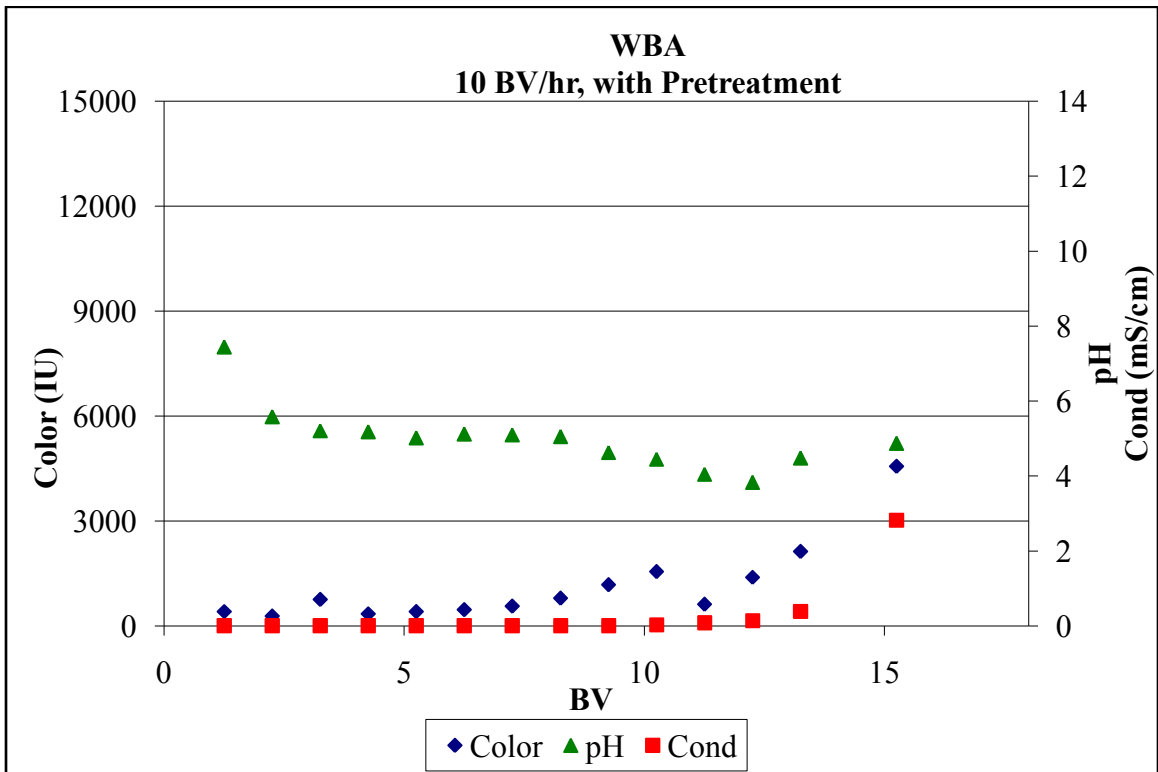
Figure D.4.3. WBA product, 3 regenerations

72
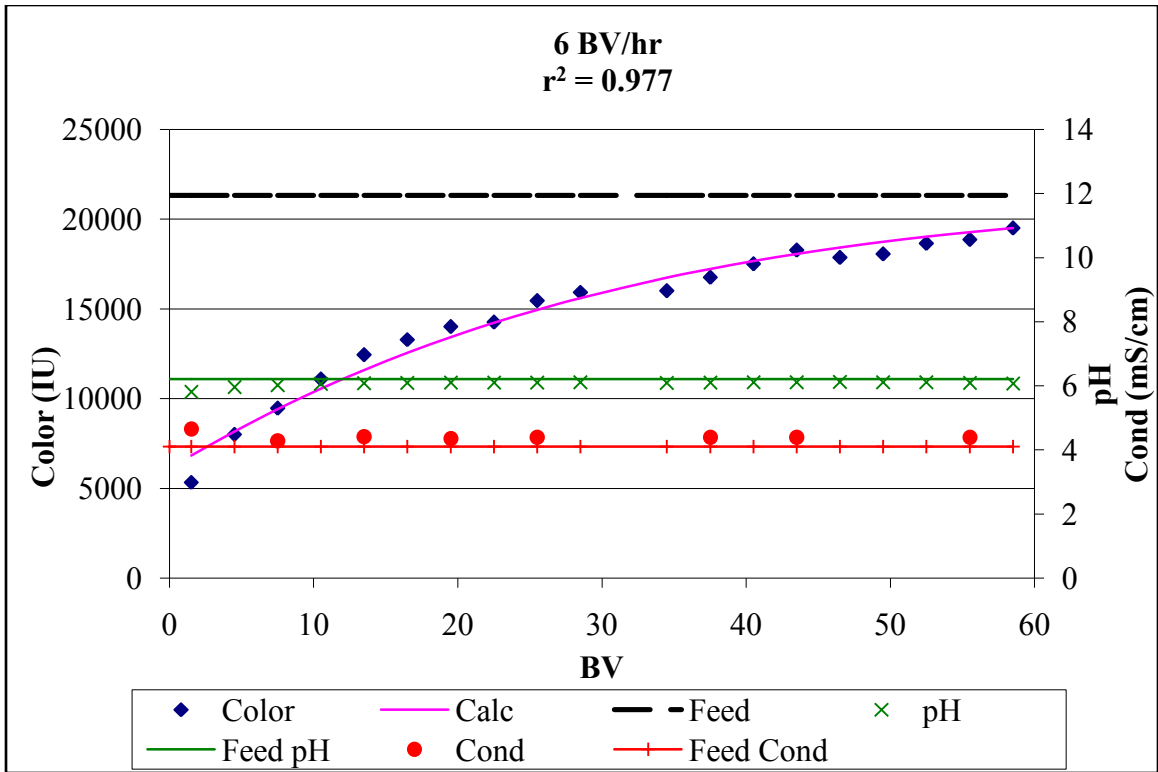
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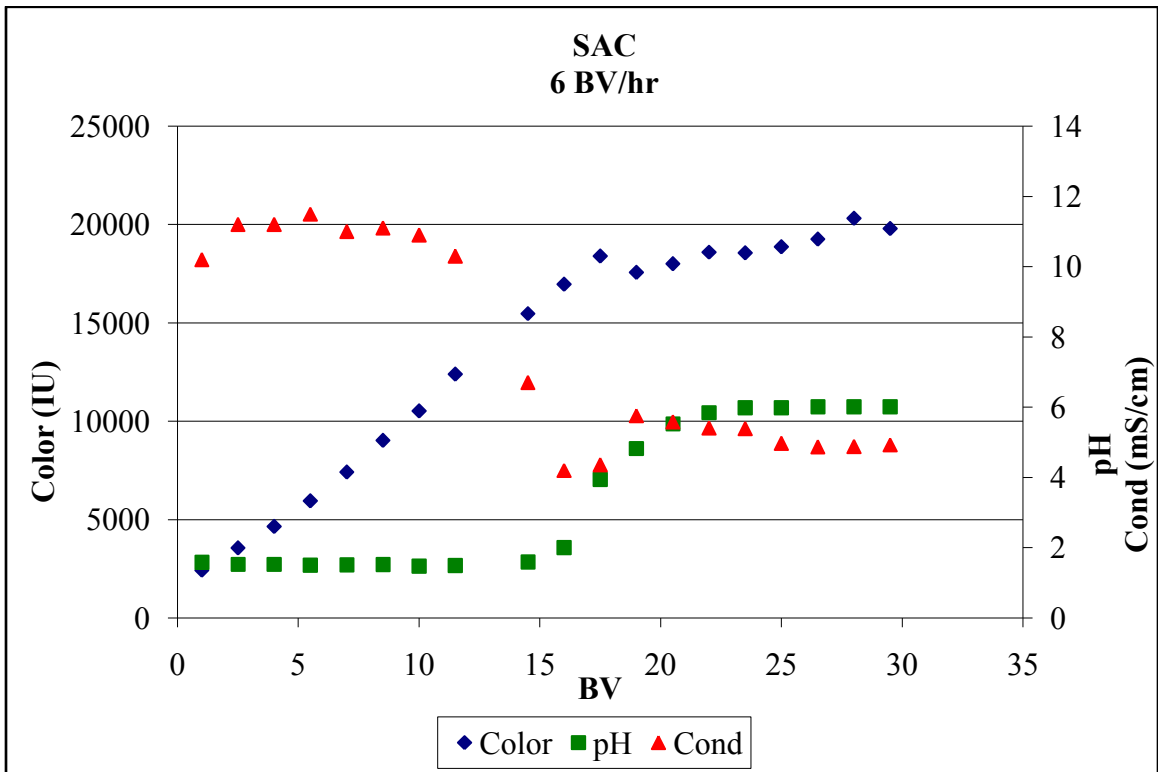
Figure D.5.2. SAC product, 4 regenerations

73
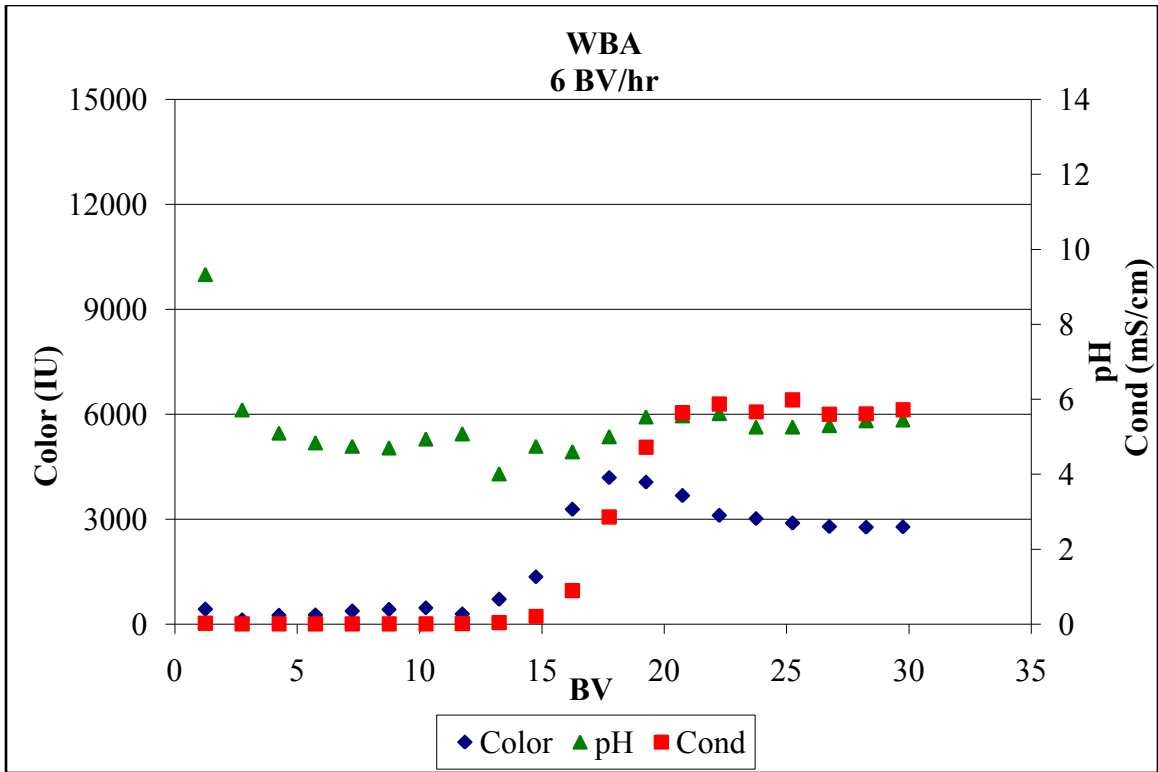
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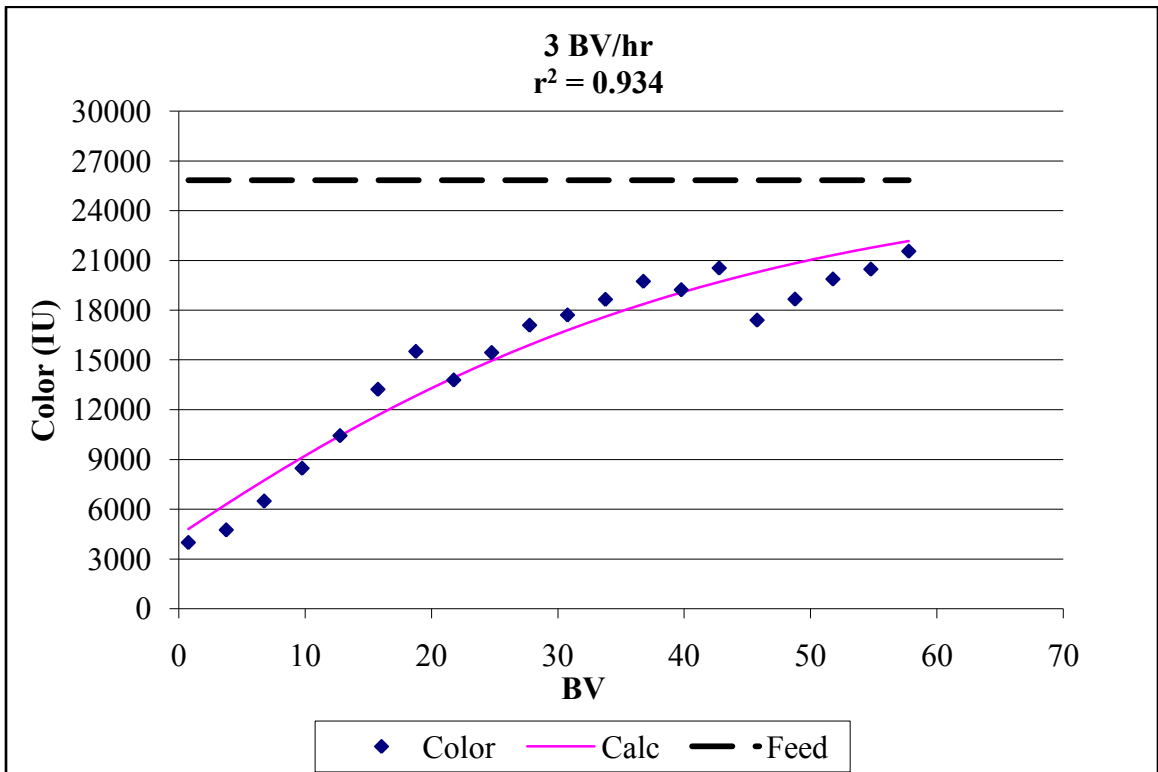
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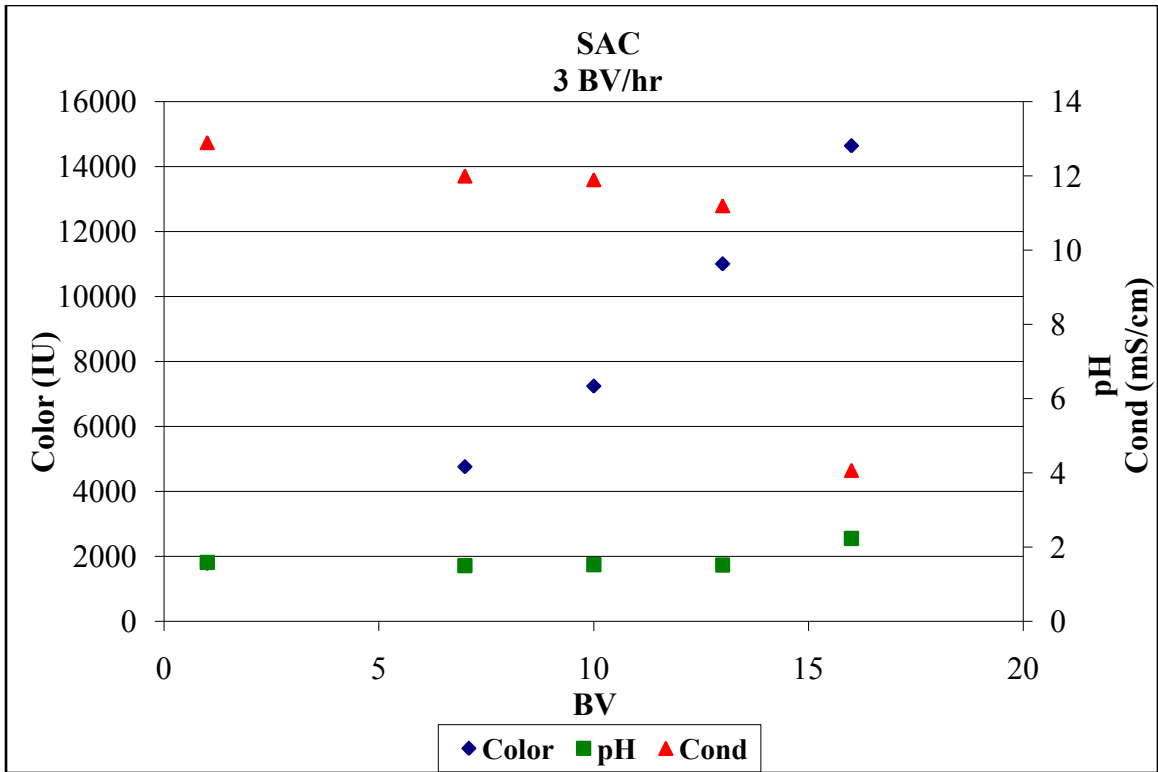
Figure D.6.2. WBA product, 5 regenerations

Figure D.6.3. WBA product, 5 regenerations

Figure D.7.1. IX test 7 carbon product, 6 regenerations
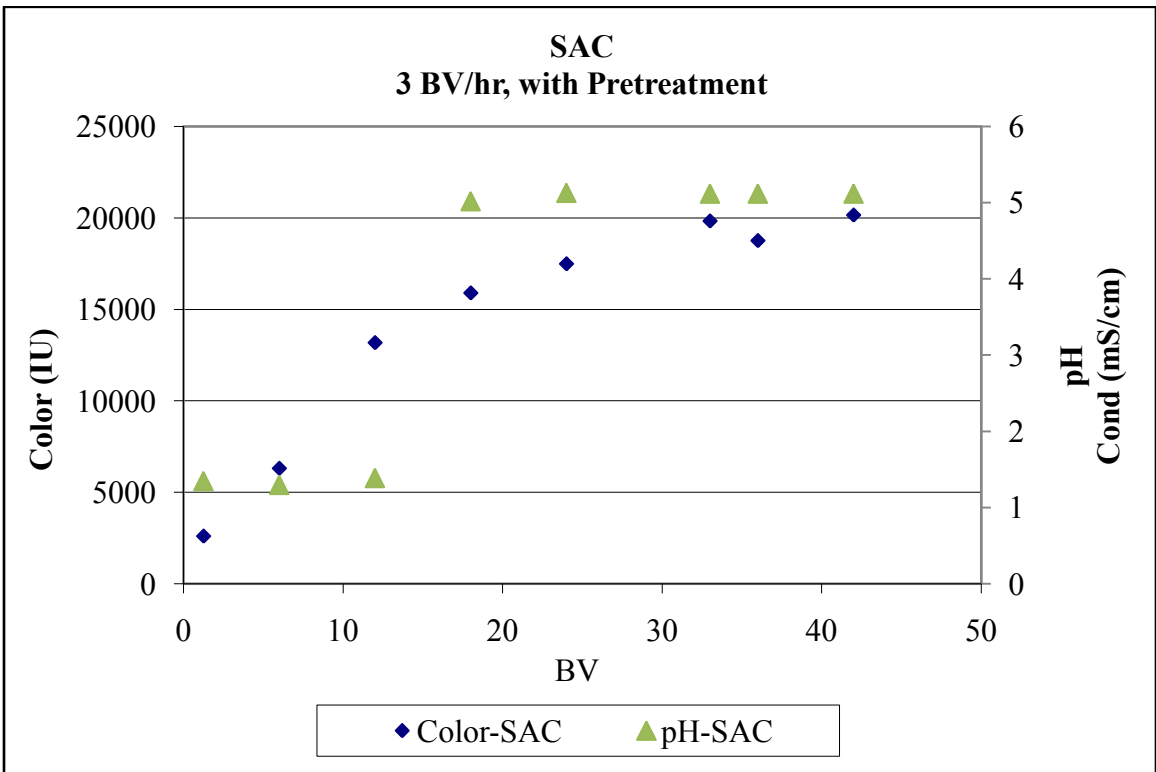
Figure D.7.2. SAC Product, 6 regenerations

Figure D.7.3. WBA product, 6 regenerations

Appendix E. Pilot Study Report

The following is the report submitted to the management of Raceland Raw Sugar Corporation in conjunction with the pilot study conducted during the 2006 milling season. The project was designed at the Audubon Sugar Institute under the direction of Dr. Peter Rein. Operating instructions were developed by Dr. Luis Bento and are included for clarity. The author was assign as a technical advisor to the factory personnel designated to monitor the pilot plant.

OBJECTIVES

- Investigate the use of packed bed adsorbent columns in the production of white sugar in a raw sugar factory.

- Study the effectiveness of chemical regeneration of granular activated carbon.

- Investigate the de-ashing of cane juice by ion exchange resins

- Produce white syrup for crystallization studies and to determine color formation in an evaporator.

- Convey the results of the pilot study to interested parties and offer recommendations for future projects.

CONCLUSIONS

- Several problems occurred during the pilot plant study which contributed to unsatisfactory results.

- Certain issues must be resolved in order for any additional studies to result in sound findings.

- Cost effectiveness of the system cannot be determined due to unsound results. However, cost for additional testing is decreased by the fact that the plant is already constructed.

E.1. Introduction

This report discusses the results of the pilot plant study that was conducted at the Raceland Raw Sugar Factory during the 2006 grinding season. The study was part of an ongoing investigation into the Direct White Sugar Production (DWiSP) system, designed to produce white sugar in raw sugar factories. Diagrams and operating instructions were distributed to all interested and involved parties prior to the grinding seasons and are included below in appendices F and G. The reader may refer to them for details concerning design and operation of the pilot plant.

The plant was operated at a flow rate of 100-120 liters of juice per hour. Each of two carbon columns, operated in parallel, contained 50 liters of carbon. Each ion exchange column, operated in series, contained 100 liters of resin. Therefore, all columns were operated at approximately 1 bed volume per hour.

Regeneration of the carbon columns was scheduled for every sixth day, alternating between each column every third day. For instance, on day three the first carbon column is regenerated and the second is regenerated on day six. Ion exchange column regeneration was scheduled for every third day with both columns being done on the same day. Pre-filter guard column was not regenerated.

E.2. Data

Figure E.2.1 shows feed color of the pilot plant for the entire season. Figures E.5.1-E.5.27 illustrate the percent color removed by each carbon column, as well as percent color removed in the final product. All percentages are relative to the color of the incoming juice (feed). Tables E1-E.3 contain information on the regeneration schedule, significant events and washdowns.
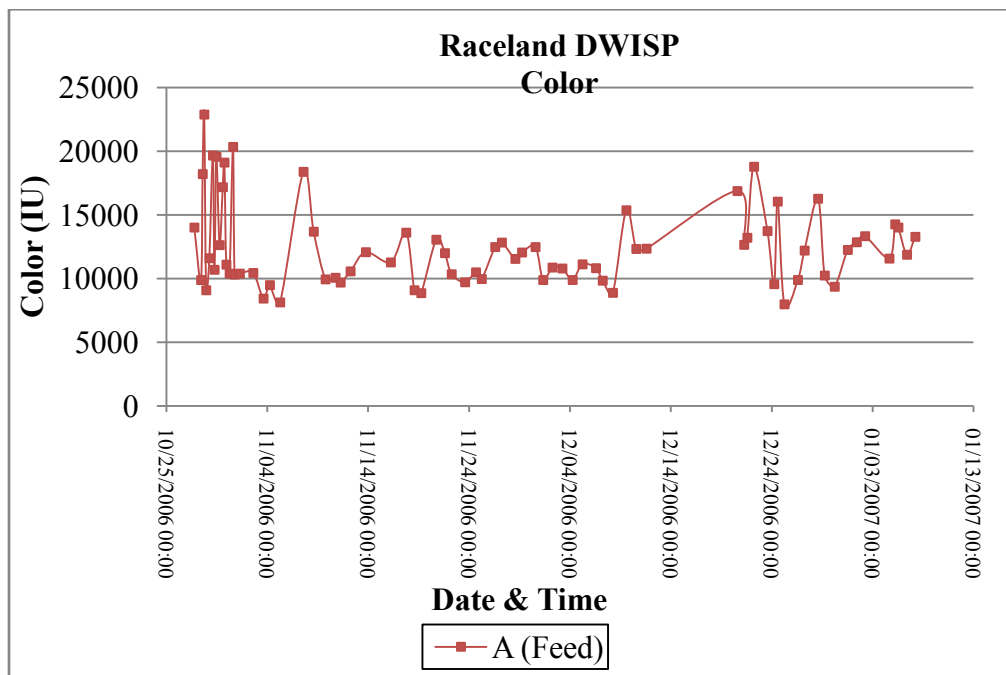

Figure E.2.1. Raceland feed color for entire season

E.3. Results and Discussion

E.3.1. Carbon Columns

Two granular activated carbon columns were used to remove the bulk of the juice colorants. They were preceded by a smaller guard pre-column containing carbon which acted as a filter. To remove sediment, the guard column was backwashed daily until the rinse ran clear,

which took approximately 1 hour. It was not regenerated during the study. The rest of the system was either drained or rinsed if necessary.

Significant fouling of the carbon columns occurred due to carryover of mud and fines. This was apparent as far downstream as the first ion exchange column. This may be attributed to the operation of the factory clarifier(s), but it is something that was also noted during the previous season's experiment conducted at St. James Factory (SLSC). A more effective means of filtration may be required to control this occurrence.

Column 1 operated during the entire season. Decolorization performance is illustrated in figures A1-A9. The column operated as expected for the first two cycle. Performance decreased significantly afterward. A decrease in performance is expected due to the fact that chemical regeneration is not 100% efficient. But laboratory experiments, as well as data from the St. James project indicate that the decrease was greater than expected. This is most likely due to the fouling and problems with regeneration (regeneration problems are detailed below).

Column 2 was in operation until December 27th, when an apparent screen failure caused the loss of most of the carbon. Performance was similar to that of column 1 (figures B1-B9). After the screen failure, column 2 was taken out of service and flow through column 1 was doubled.

E.3.2. Regeneration Problems

Regeneration of the columns was attempted as per the instructions. However, several problems were encountered. The centrifugal pumps used to regenerate the columns lacked the capacity to pump through the columns at the prescribed flow rates. This caused regeneration times to be more than doubled. Some regenerations had to be completed on the day following

commencement. As the study proceeded, fouling of the resin columns made flow extremely difficult, and backwashing or siphoning had to be used to allow for flow.

The pumps also suffered from repeated impeller damage due to exposure to the regenerants, and ultimate failure. They were eventually replaced with peristaltic pumps on loan from the LSU Biological and Agricultural Engineering Department.

E.3.3. Pressure, Temperature and Flow

Pressure and temperature were monitored at various points along the carbon columns by means of instrumentation and recorded on a datalogger. Data was recorded on a datalogger and is represented in figures E.3.1-E.3.10. A 4-channel datalooger was used until Dec. 20th and replaced with a 6-channel recorder. Press1 was measured at the inlet to the guard column. Press2 indicates carbon column 1 inlet pressure. Temp1 was measured at the inlet to column 1. Temp2 measured carbon column mixed product temperature (the plant diagram shows this temperature probe in the wrong position).

Pressure was monitored to determine if fouling of the carbon columns by mud/fines would present any problems. As shown in figures E.3.1-E.3.5 and figures E.3.8 and E.3.9, pressure remained below 15 psig, which was the setpoint of relief valves installed on the columns.

The desired temperature for the carbon columns is 80°C, which provides improved color removal and resistance to microbial activity, while not causing too great an increase in color. The temperature drop across carbon column 1 can be determined by examining the difference between Temp1 and Temp2. The average operational temperature drop was approximately 10°C during the season. This indicates that temperature control of the carbon columns, in the form of

heater bands and insulating jackets, is necessary. Heater bands were installed on the columns, but were not powered until the third week of December.

An electronic Omega[®] Flow Transmitter FLM- series flowmeter was also installed at the discharge of the first feed pump (P2, figure F1). However, it failed to function as desired. Initial indications were inaccurate and had to be hand-calibrated. Eventually, the float in the meter began to stick, which restricted flow. Repair attempts rendered it temporarily inoperable, and it was left in the full deflection (maximum indication) position until Dec. 20th. Figure E.3.7 gives the indicated flow values. Mechanical flowmeters were installed on the inlets of the carbon columns in order to monitor flow manually.
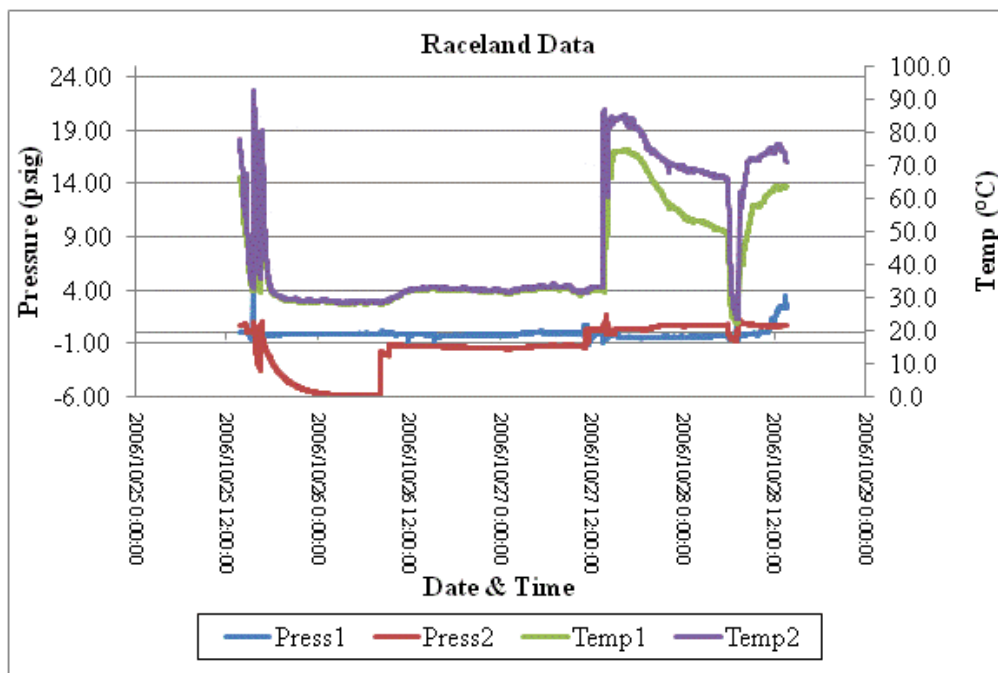
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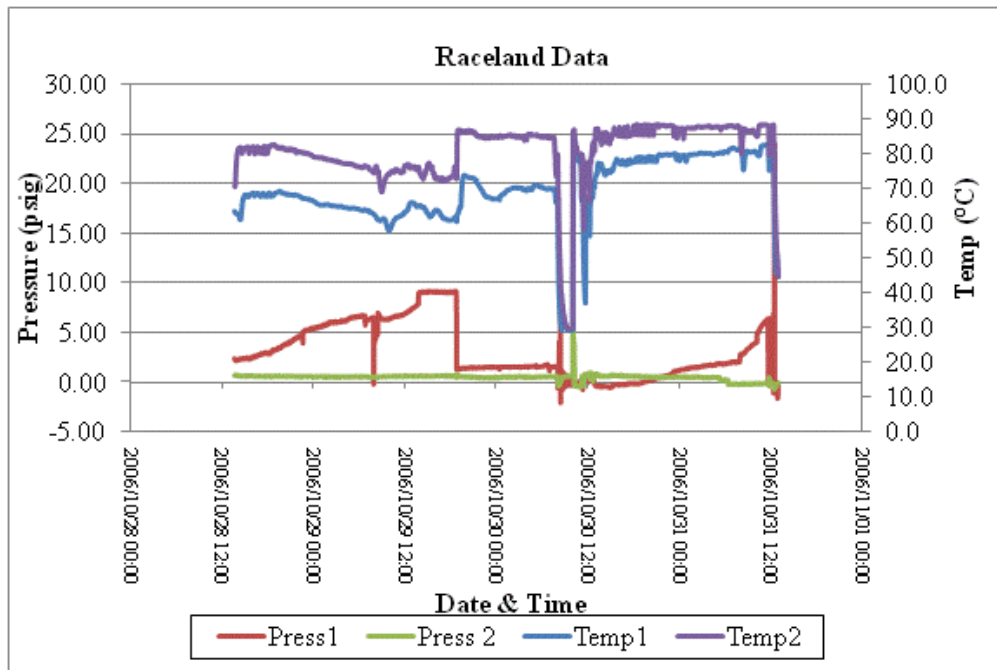
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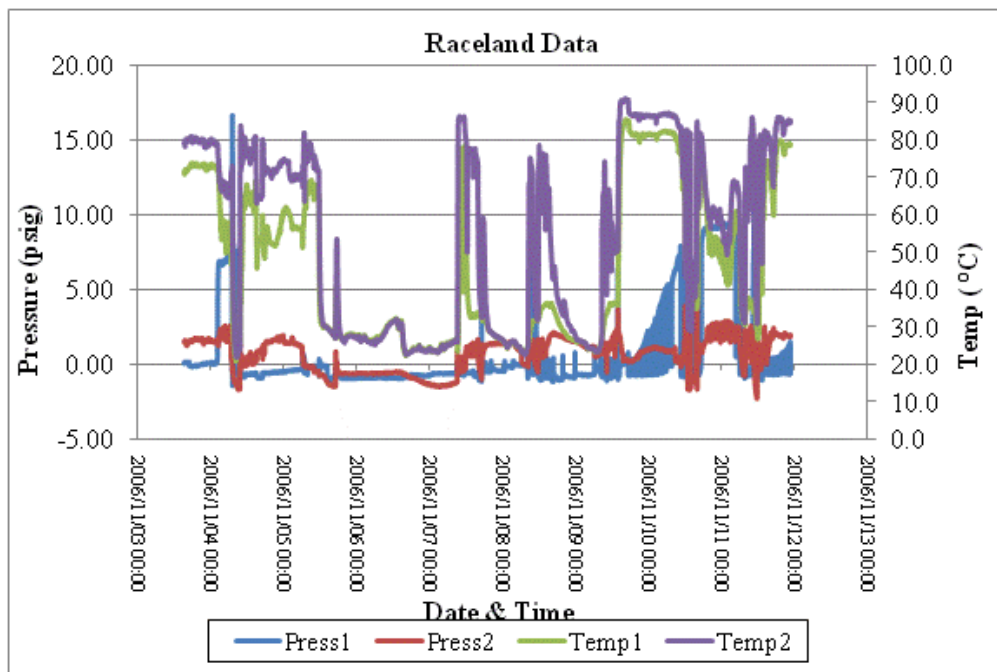
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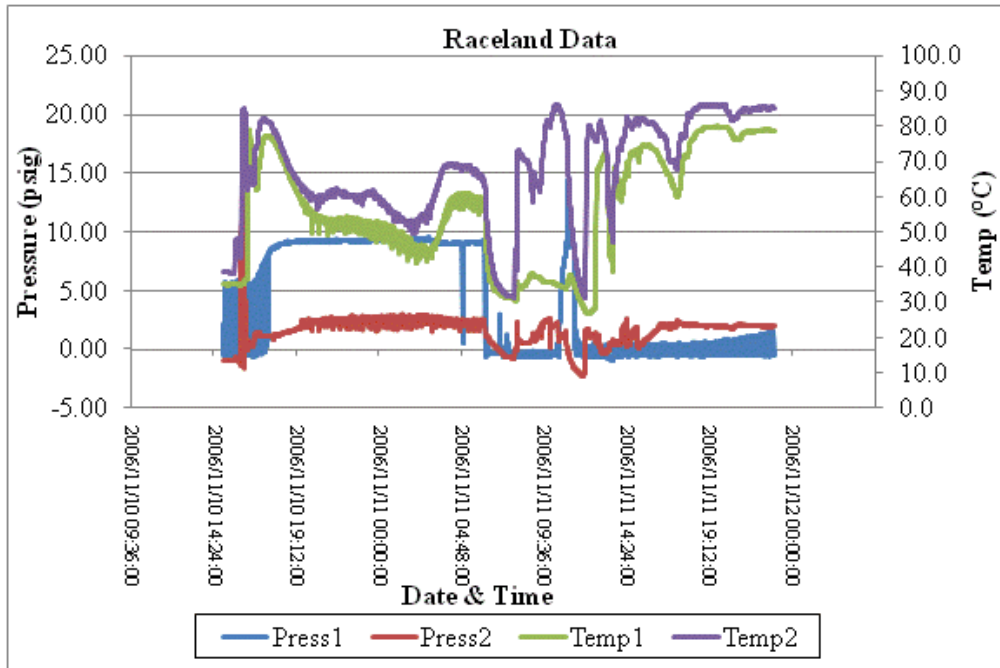
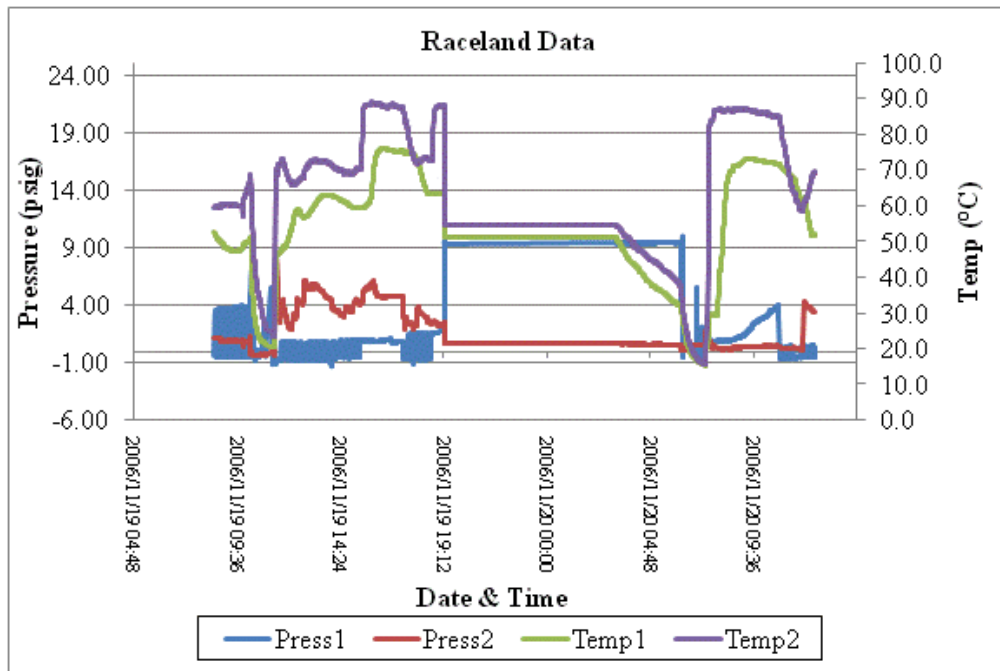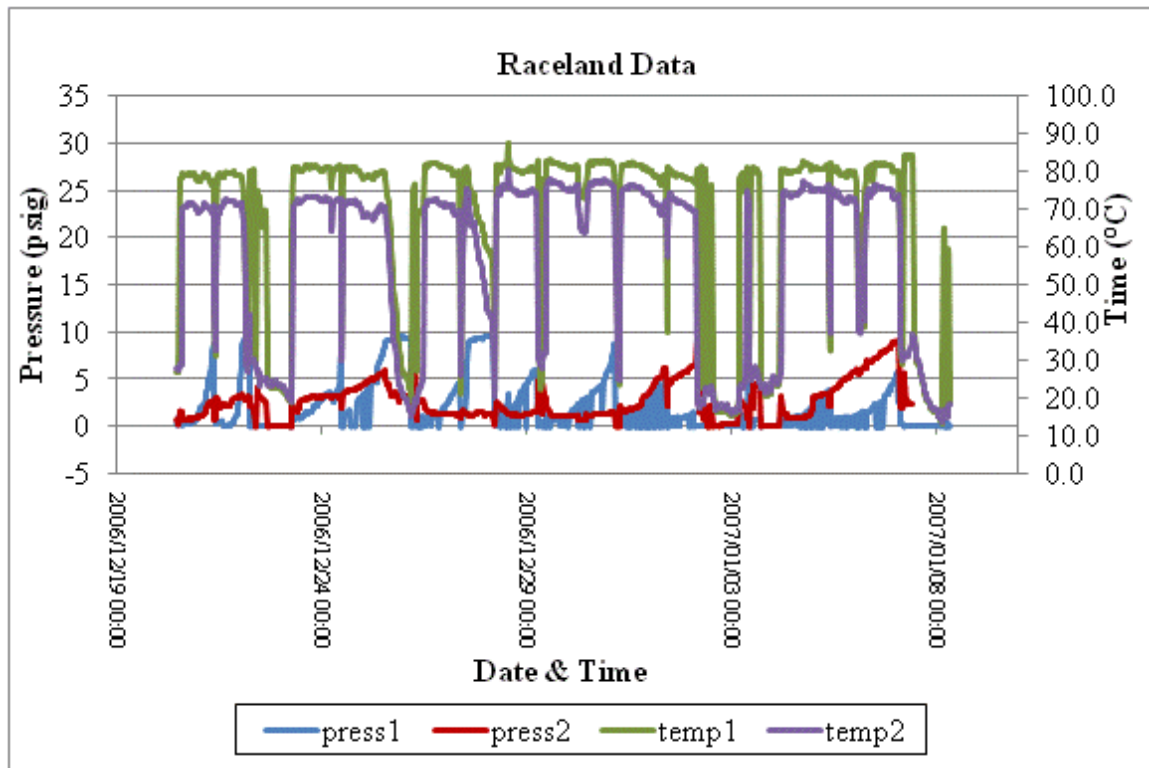**Figure E.3.4.**

Figure E.3.5.
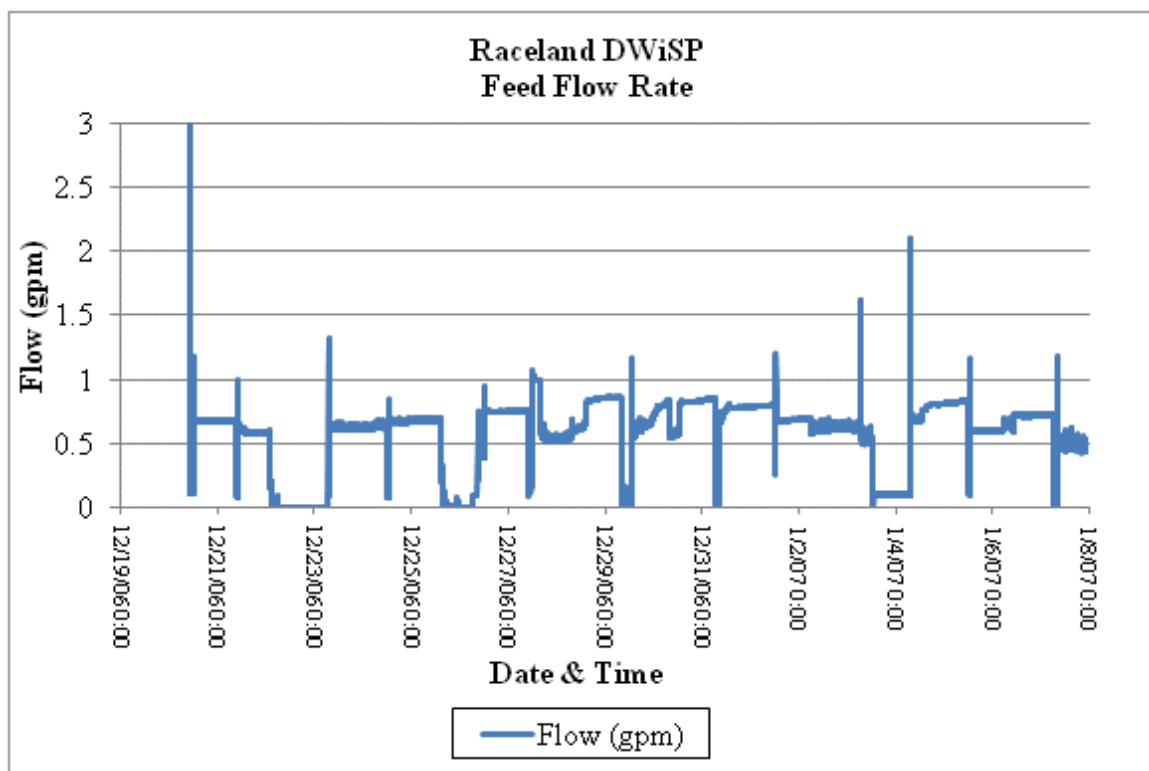
85

Figure E.3.6.

Figure E.3.7.

E.3.4. Ion Exchange Columns

Two ion exchange columns were used downstream of the carbon columns to de-ash the juice, as well as remove a majority of the remaining color. The first column was loaded with strong acid cationic (SAC) resin. The second contained weak base anionic (WBA) resin.

The pH of the juice is lowered significantly by the SAC resin (<2.0 until exhaustion). Cooling of the juice stream to 10°C is required prior to introduction to the SAC column in order to minimize inversion. A recirculating refrigerated bath and plate heat exchanger were used to achieve this purpose. However, the bath was unable to maintain temperature control due to early termination of the cooling cycle. Instead of cycling off when the temperature setpoint was reached, the bath would turn off after a fixed amount of time, as if on a timer circuit. Eventually, there was no cooling evident at all. This caused the feed to the SAC column to be at much higher temperature than desired.

Microbial activity was also apparent, since inspection of the columns revealed a gel-like substance on the bed surface. It is presumed that this was dextran. At times during operation, flow through the WBA column became impeded. Drainage of the column produced a large volume of clear viscous fluid, presumed as well to be dextran. When this occurred, the column was drained and rinsed vigorously before resuming operation.

Performance of the ion exchange columns is shown in figures E.5.18-E.5.27. Percent color removed is relative to the guard column feed color. This gives an overall color removal indication. It is apparent that performance improved significantly after the new regeneration pumps were employed (cycle 7 and thereafter).

E.3.5. Conductivity Ash

One of the objectives of the DWiSP system is the removal of ash from the product stream. This benefits the plant by reducing/eliminating scale formation on heating surfaces. Another benefit may involve higher sugar yield (yet to be verified). Analysis was performed to determine conductivity ash of the product at various points in the system.

Ash is removed by the ion exchange resins. The carbon used in the plant has been shown to have no effect on ash content. This is evident in figure E.3.8, which shows ash data for samples gathered before the ion exchange columns were placed into service. Figure E.3.9 shows the action of the ion exchange columns after initial startup. De-ashing occurs as expected at the beginning, but becomes less effective as the study progressed. There is no discernable de-ashing between the 20th of November and the 14th of December (figure E.3.10). It is during the latter part of the month, after the new regeneration pumps were employed, that de-ashing becomes apparent again. The columns behaved as is expected. The ion exchange columns were taken offline for a period of 12 days in order to inspect and address issues that were causing poor performance. Gaps in the curves on figure E.3.10 are the result of this.

E.3.6. Crystallization

One of the objectives of the study was to produce crystals from the pilot plant final product. Thirty five gallons of syrup were produced from final product juice in two batches on consecutive days in November using a small evaporator. The color of the juice used was 9500 ICUMSA units (IU) on average, and the syrup produced was 10500 IU, for a 10% increase. This is expected as heat will cause an increase in the color of sugar solutions. The longer the solution contacts heat surfaces, the higher the color increase. Faster evaporation can be achieved by using higher vacuum (plant vacuum used was approx. 10-15 in Hg).
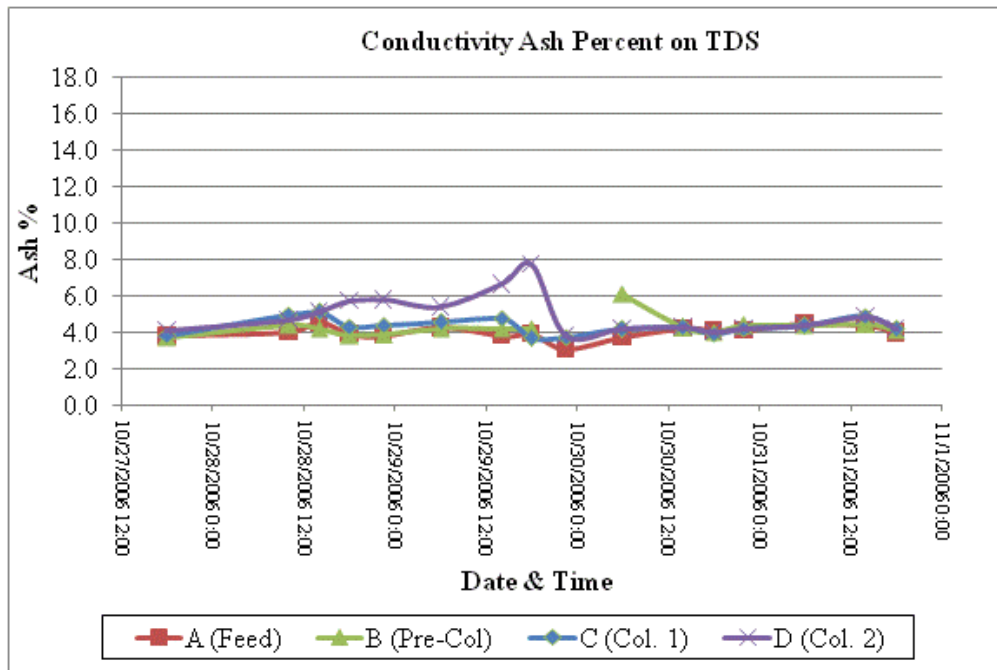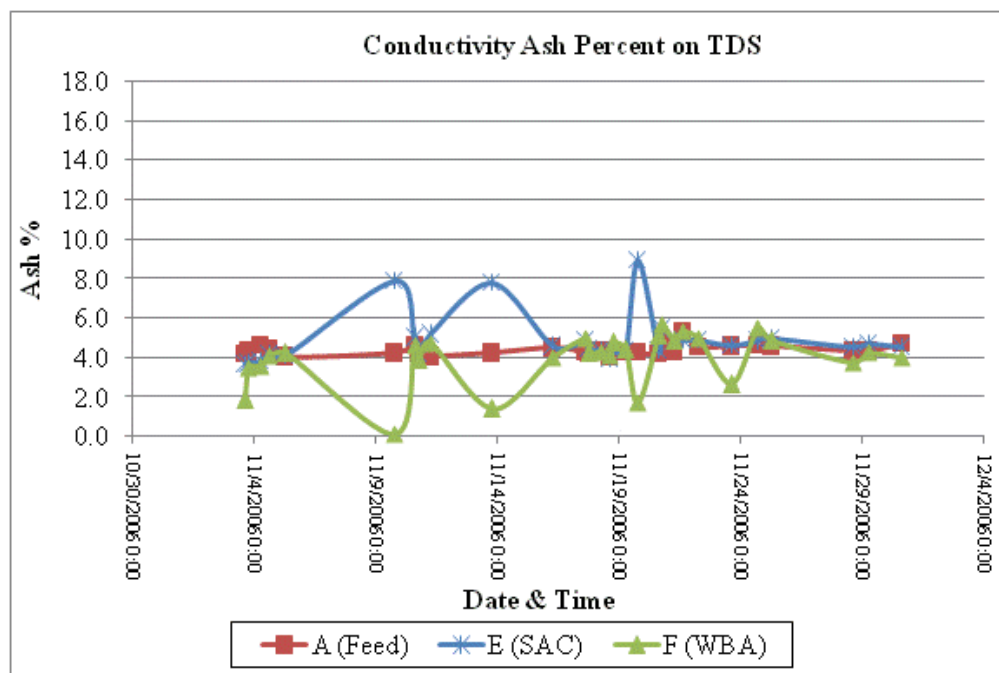
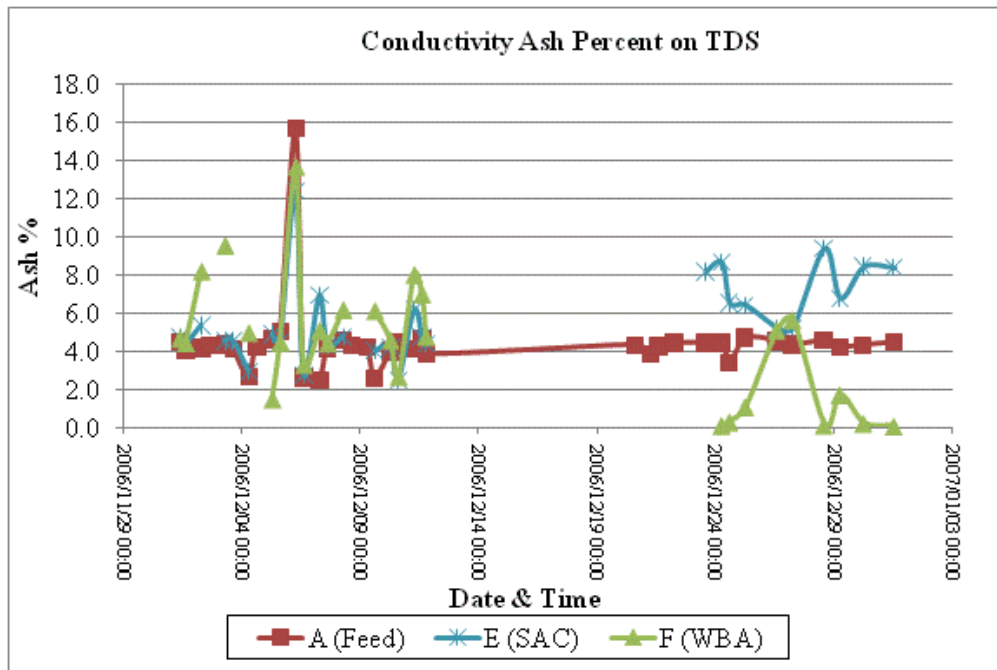**Figure E.3.8.**

Figure E.3.9.

Figure E.3.10.

Table E.3.1 compares the syrup produced by the pilot plant with a typical sample of mill syrup from the 2007 season. As can be seen, a large amount of inversion occurred. This was most likely caused by the low pH/high temperature conditions in the SAC column, as well as from microbial activity. Insufficient sucrose remained in the syrup for crystallization to occur.

Table E.1. Comparsion of syrup from pilot plant to normal factory syrup

	Brix	App. Purity	True Sucrose %	Ratio Pol/Sucrose	True Purity %	Fructose % T.S.	Glucose % T.S.
DWiSP Syrup	68.9	25.2	26.1	0.665	37.9	23.9	27.3
Raceland Syrup	63.5	88.4	58.1	0.97	91.5	1.7	1.7

E.4. Conclusions and Recommendations

Initial results indicated that the system works if properly assembled, operated and maintained. However, equipment failure led to several problems, thereby preventing the achievement of several of the objectives set forth in the experimental plan.

Since startup costs have already been incurred, any additional funding can be directed towards improvements and modifications. The cost of the modifications should be nominal compared to the money already spent. In order to avoid incurring similar difficulties in future studies, the following recommendations are suggested:

1. New regeneration pumps capable of handling the load are essential to the success of any future studies. The pumps must be resistant to the corrosive effects of the regenerants.

2. Better temperature control of the carbon columns is needed. In addition to heater bands, the carbon columns should also be insulated.

3. Either a reliable refrigerated bath is utilized, or a new ion exchange system must be used. A system involving a different combination of ion exchange resins should be tested at Audubon (e.g. strong base anion resin followed by a cation resin). Without proper cooling, the current ion exchange regime is not recommended.

4. Better filtration of the feed is necessary. There are several options available for consideration.

5. Better flow monitoring is necessary. Flow rate is an essential parameter in the study. The flowmeter used during the season was unreliable, failing several times and displaying inconsistent information. A reliable replacement will provide useable data and better control of plant operation.

6. Some reconstruction of the piping system is required. Several threaded joints leaked or failed completely during the season. Liquid thread sealant was used throughout, which contributed to the problem. All threads should be sealed with Teflon tape.

The following suggestions may improve the operation of the plant and provide more valuable data.

1. A higher flow rate should be used, not less than 3 bed volumes per hour on carbon.

2. Peroxide use as a pretreatment should be tested, if not discontinued. Recent laboratory work calls into question the efficacy of peroxide as a pretreatment for carbon. If the carbon columns are operated in parallel, then one should be pretreated and compared to the untreated column.

3. Evaporation of juice for the production of syrup should commence as early as possible. A better vacuum source would improve evaporator performance.

4. Dedicated supervision of the pilot plant should lead to better operation. The more dedicated the better.

E.5. Column Results
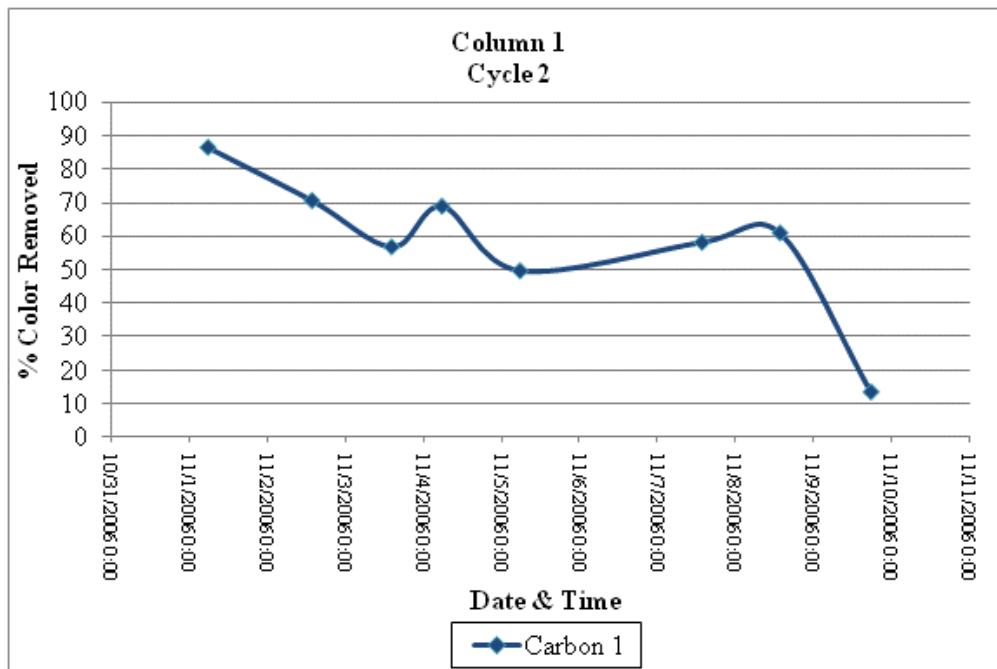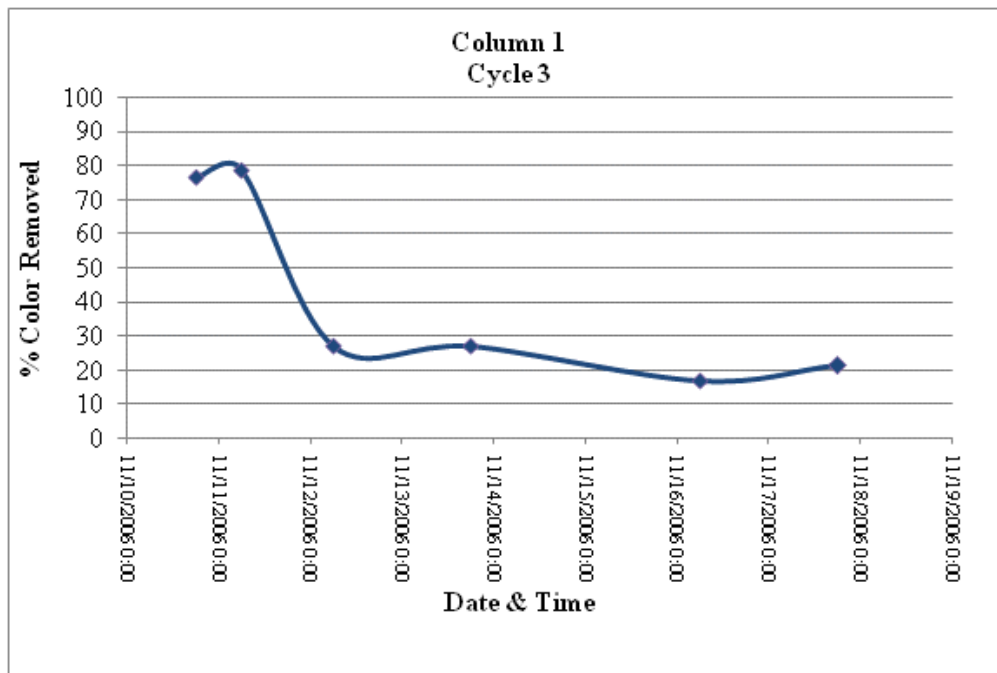
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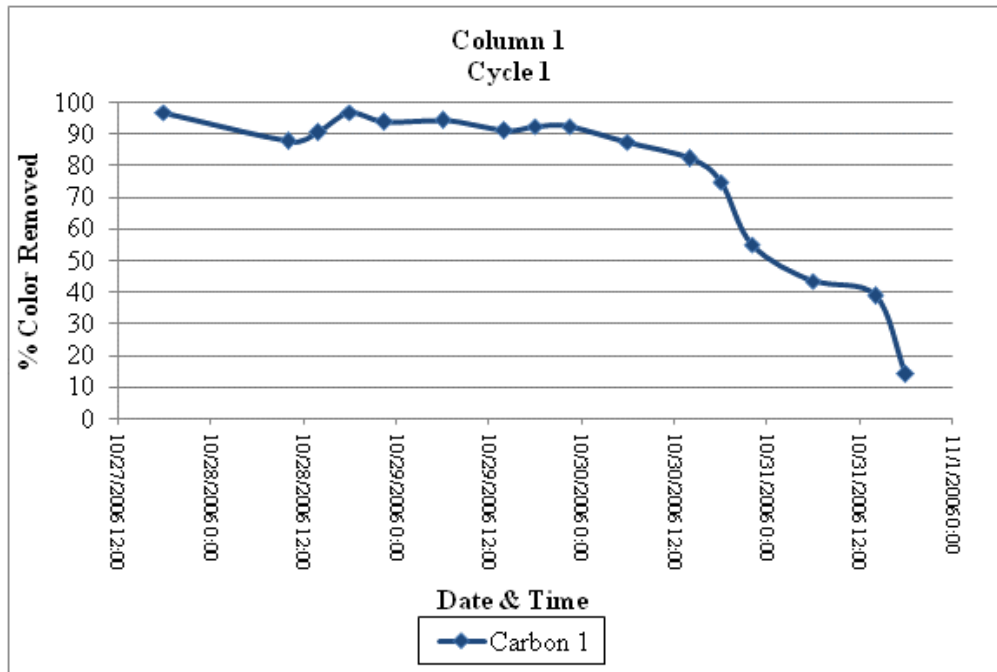
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Figure E.5.2

Figure E.5.3
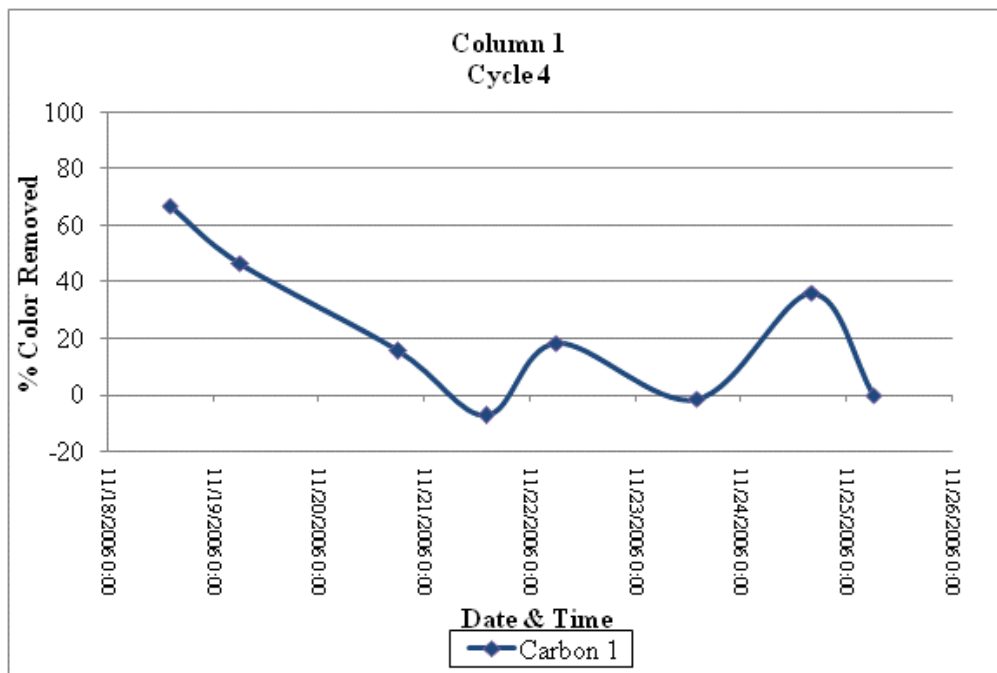
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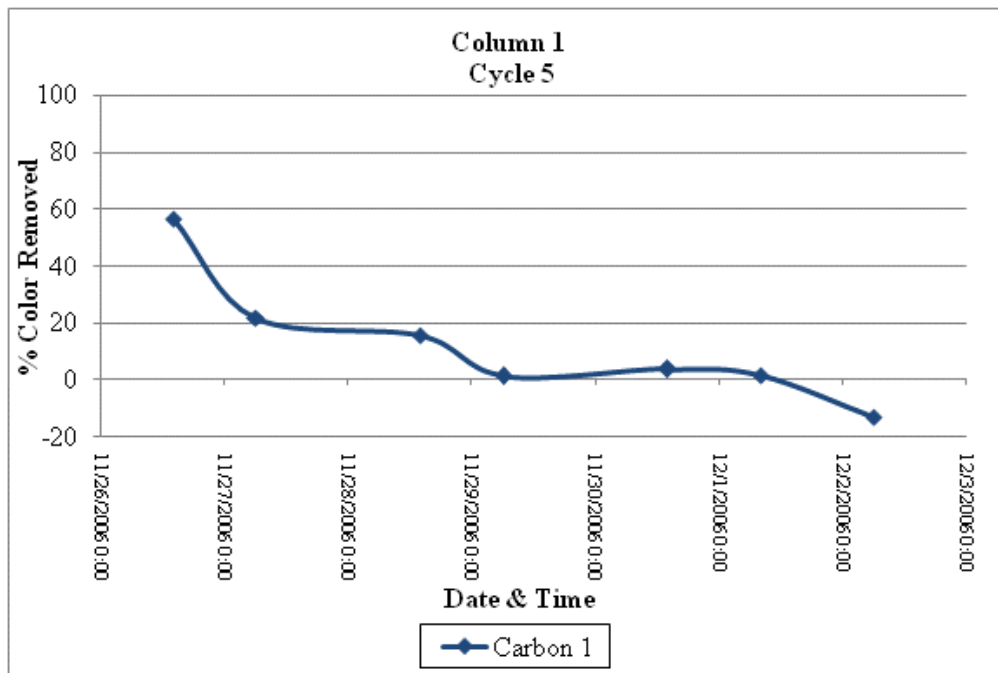
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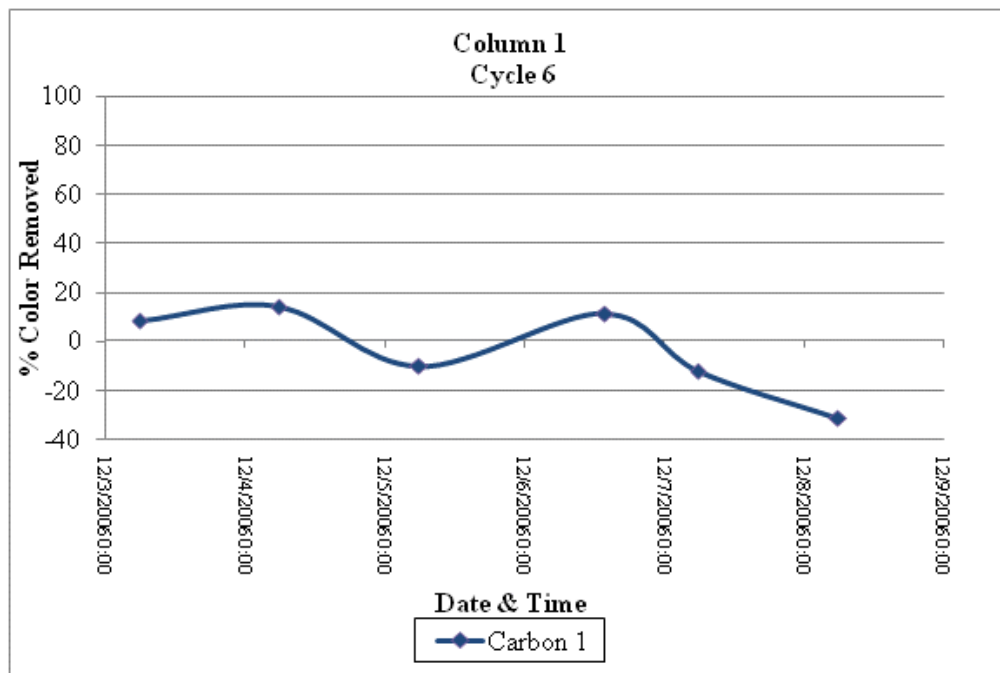
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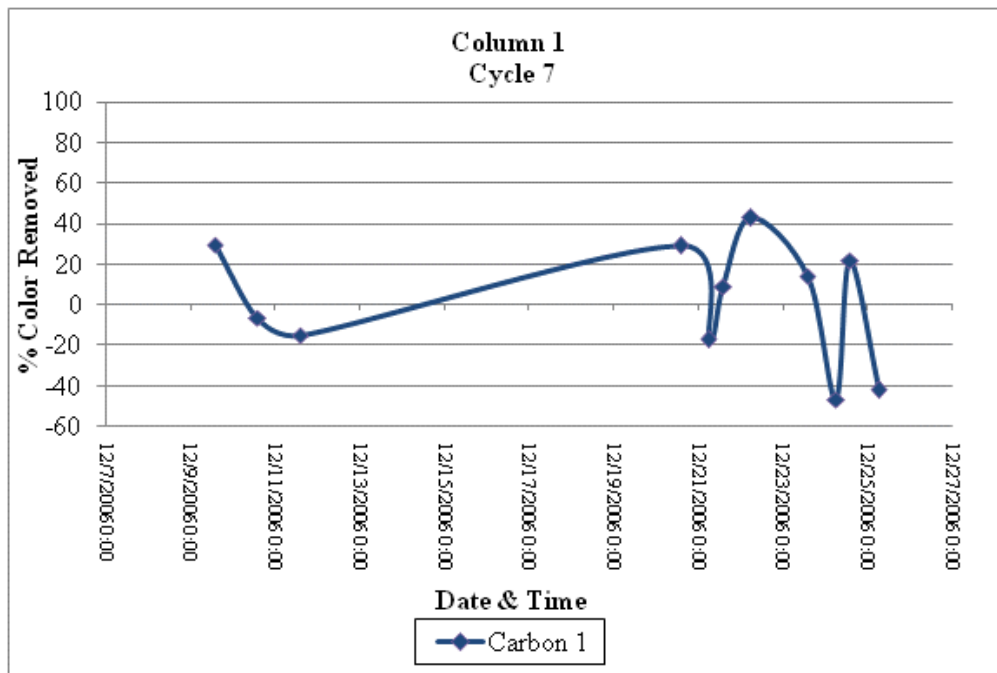
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Figure E.5.8

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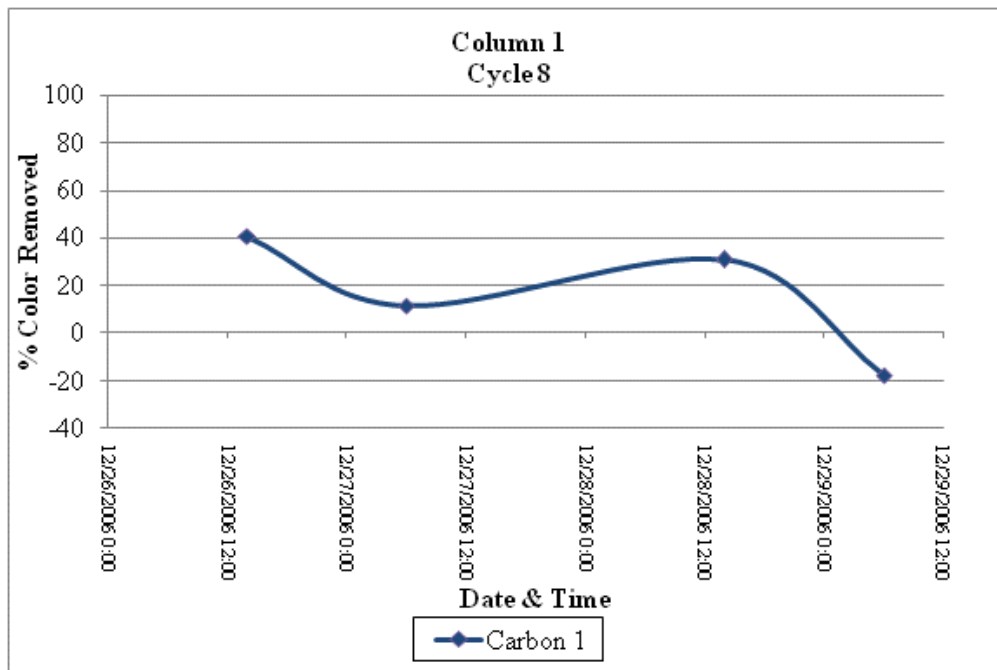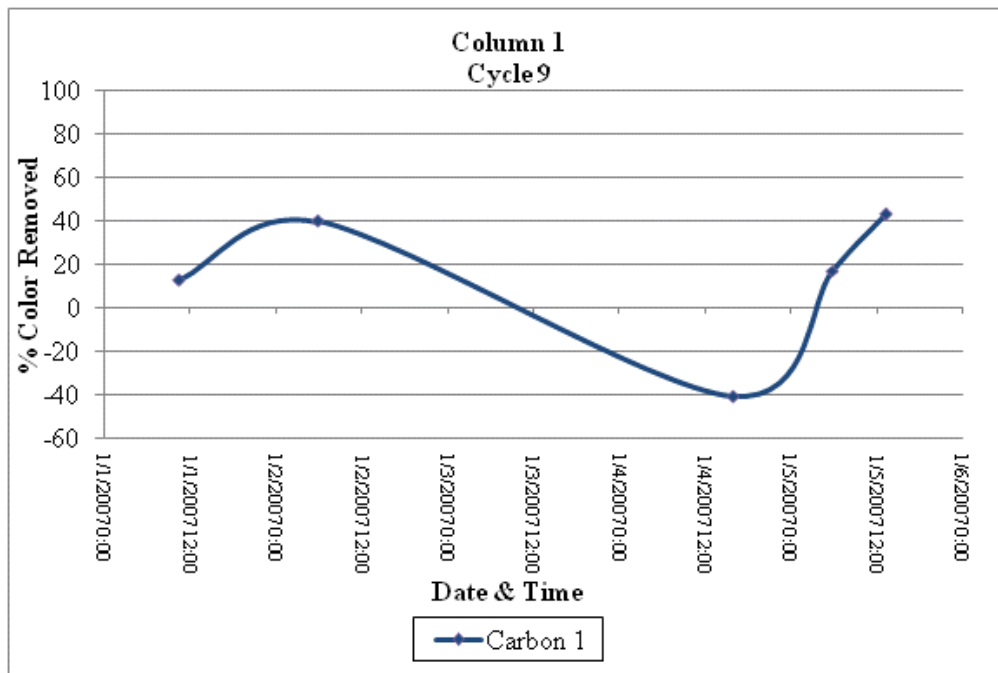
Figure E.5.9

Carbon Column 2
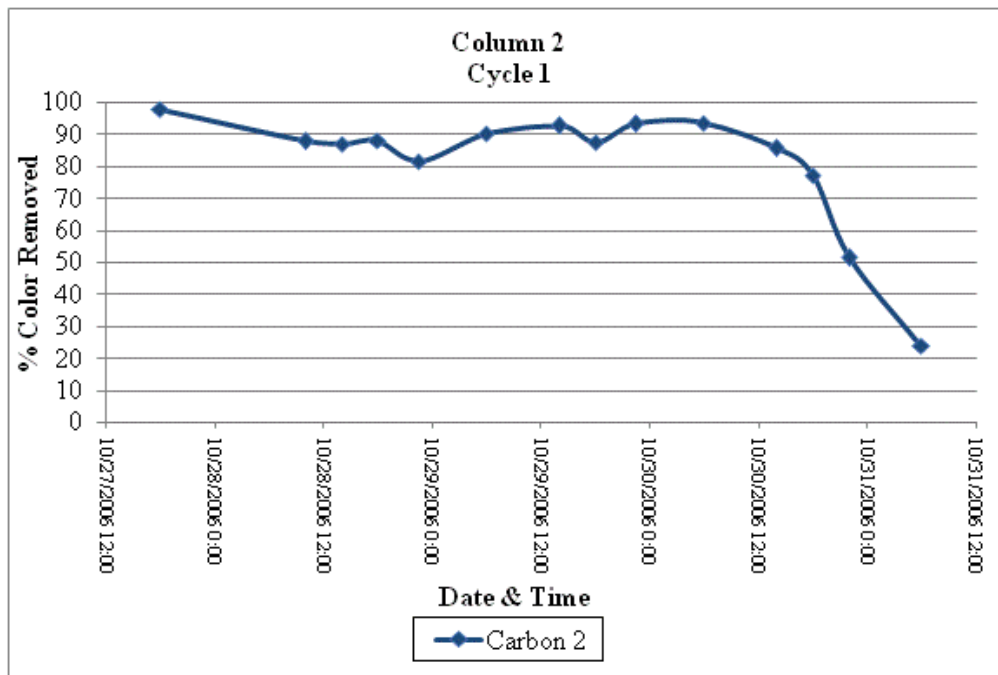
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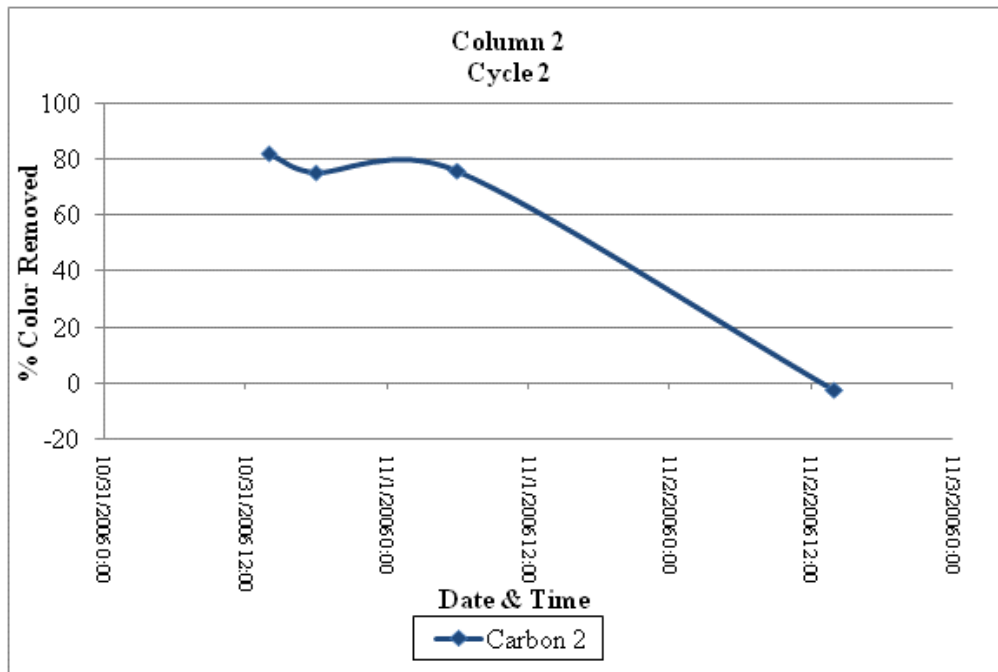
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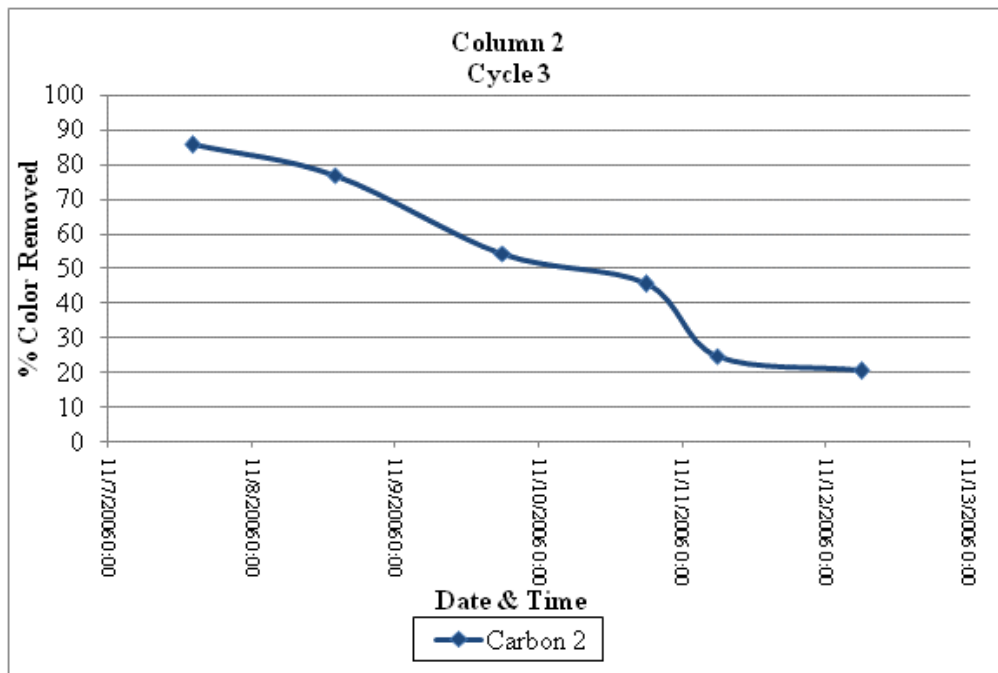
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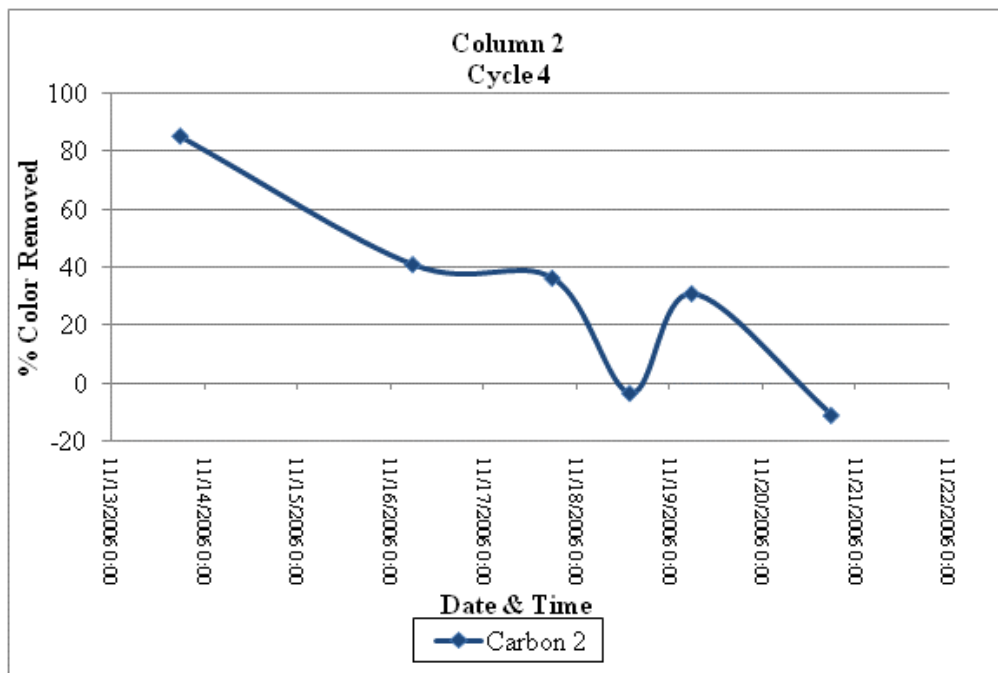
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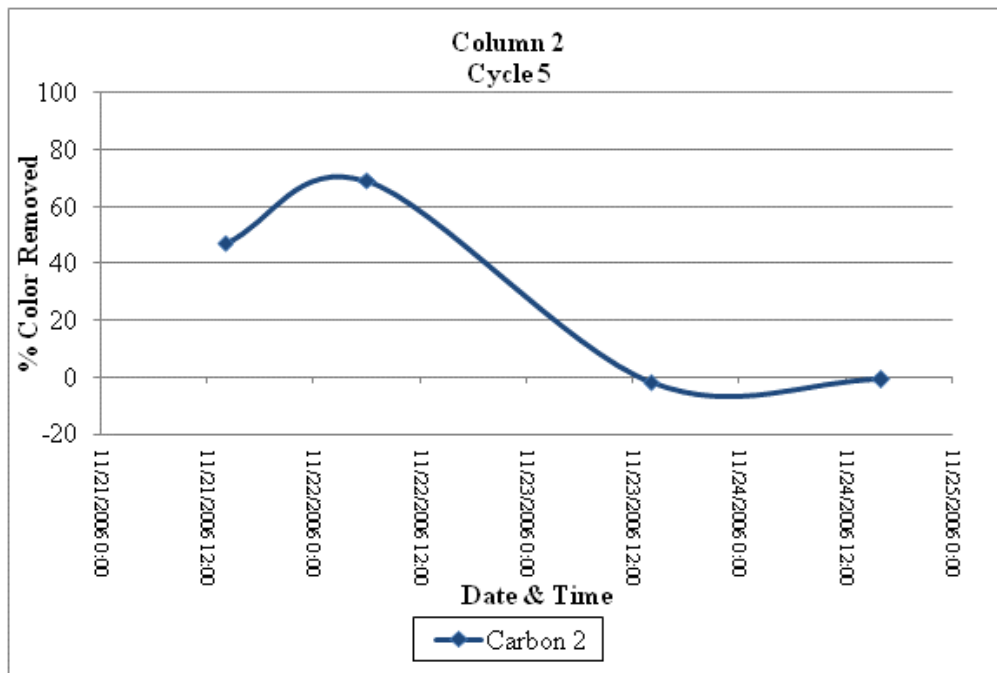
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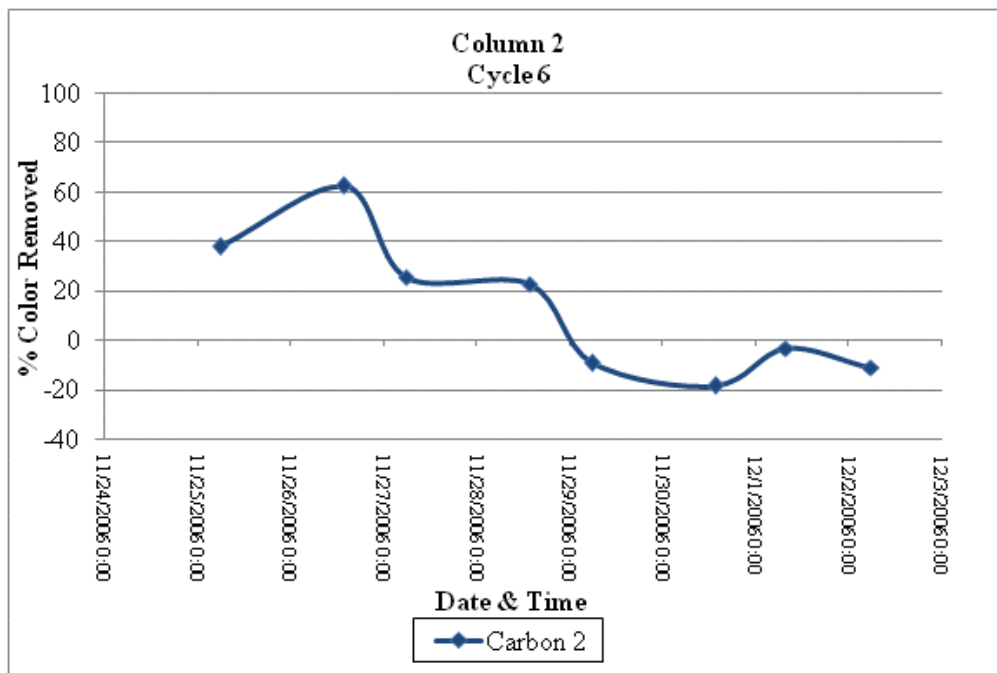
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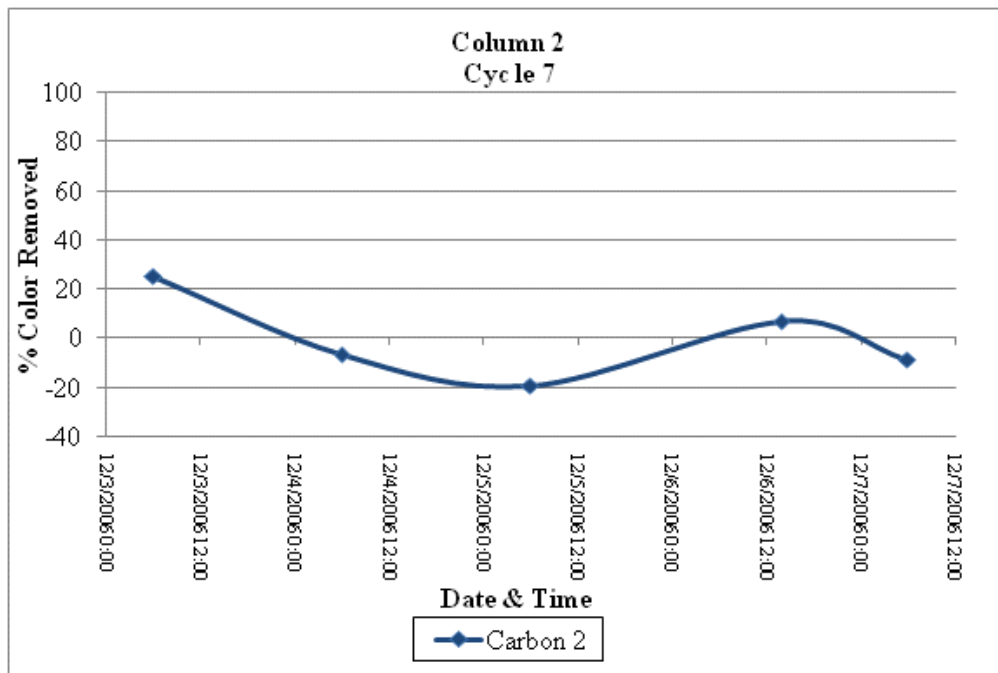
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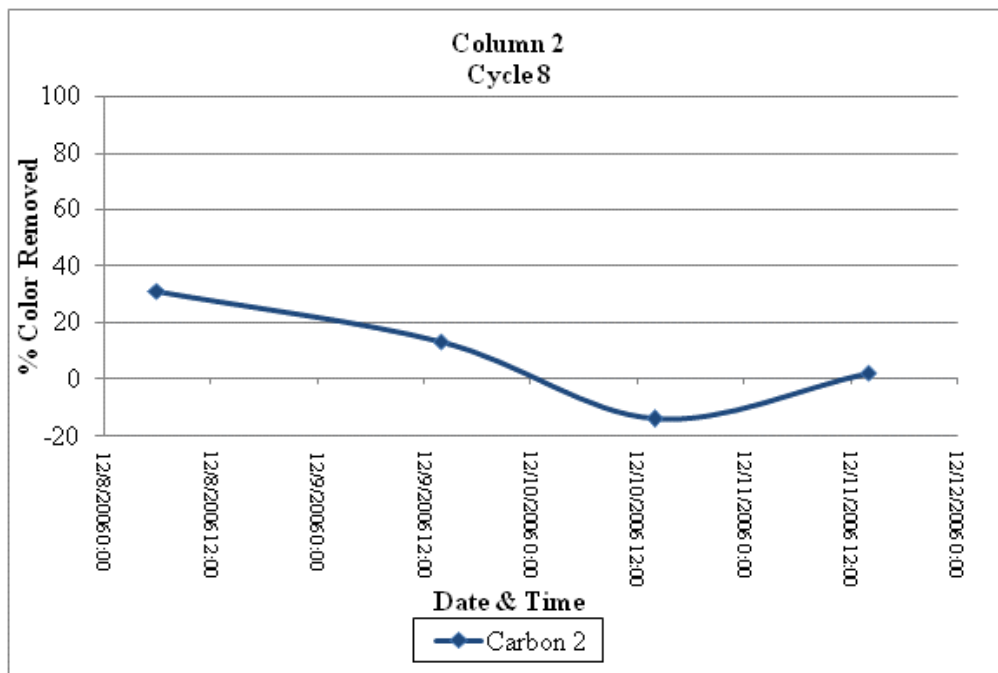
Figure E.5.17

Final Product (WBA column output)
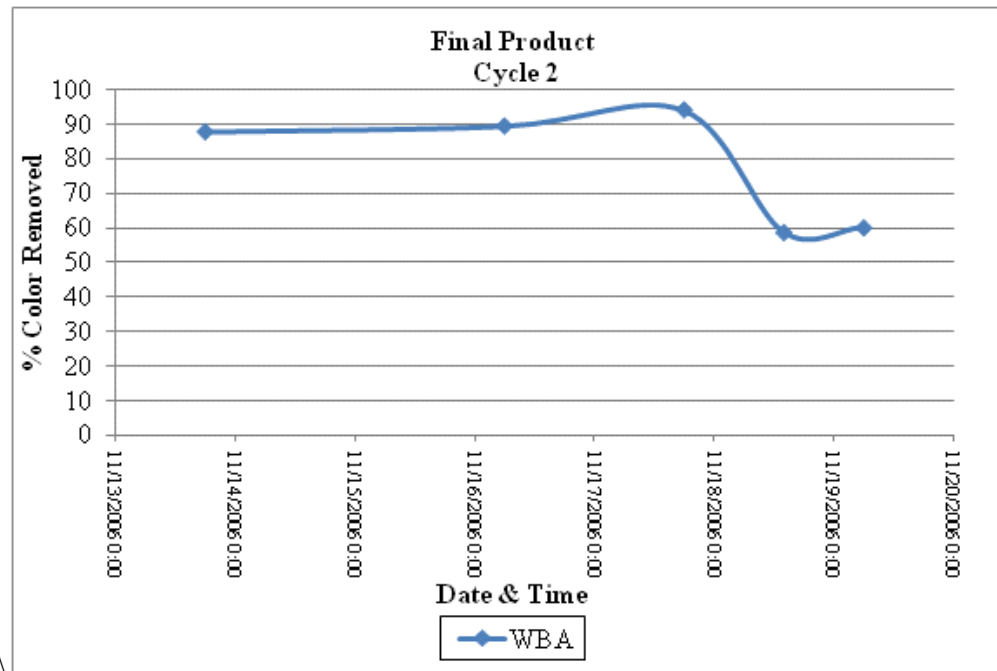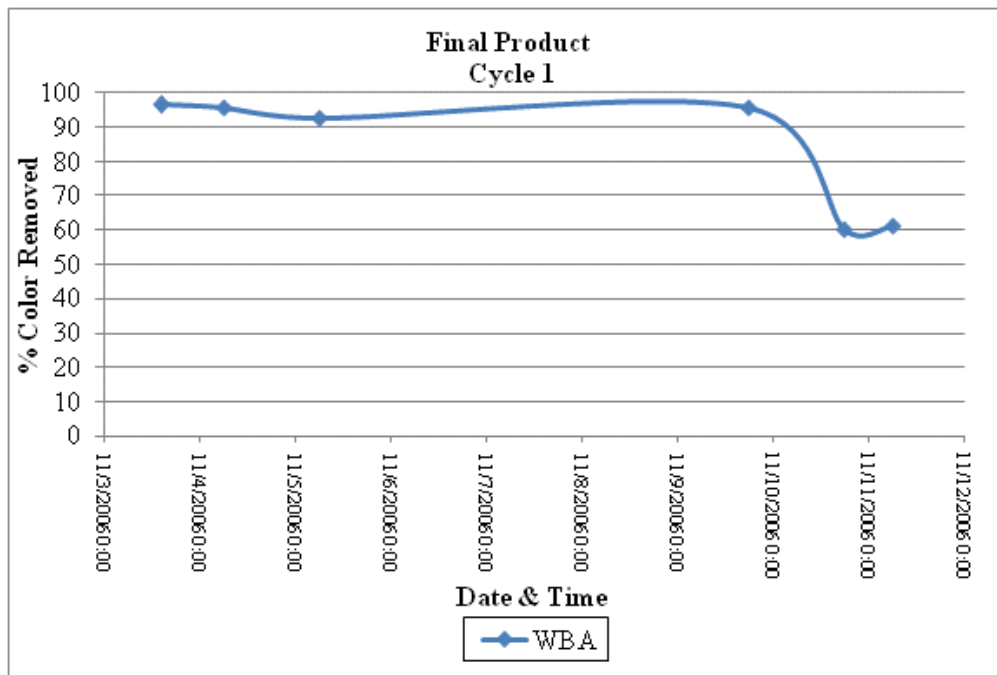
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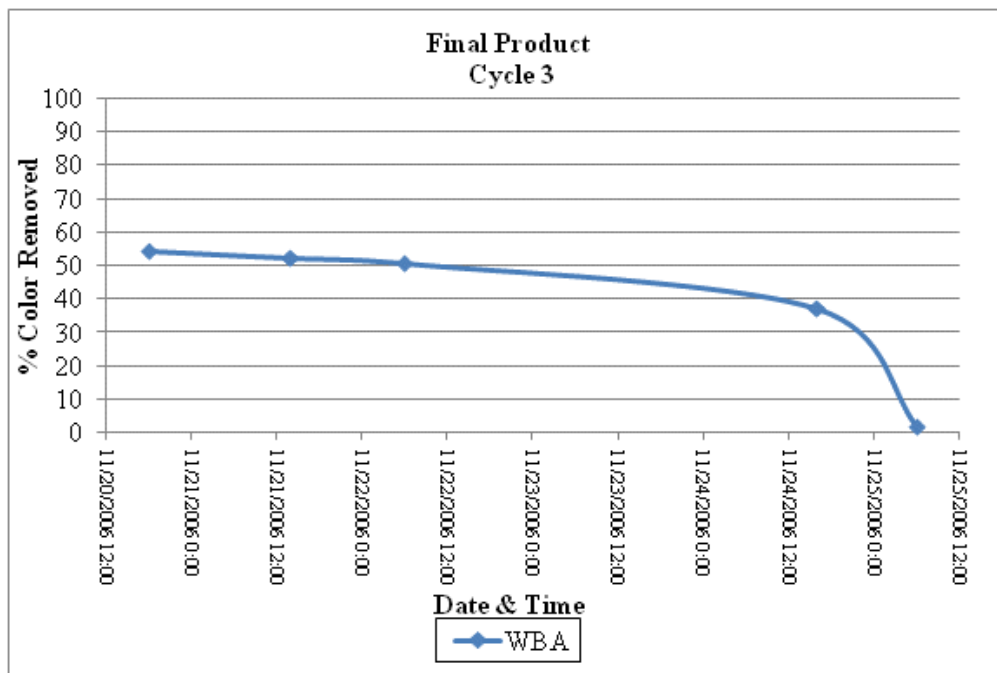
Figure E.5.20.

Figure E.5.21.

103
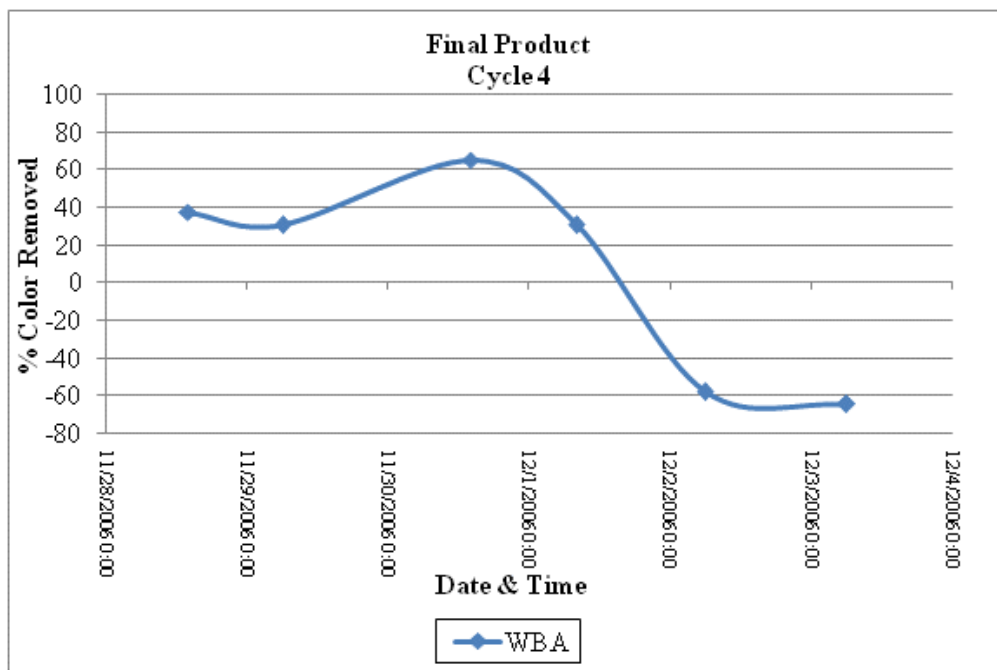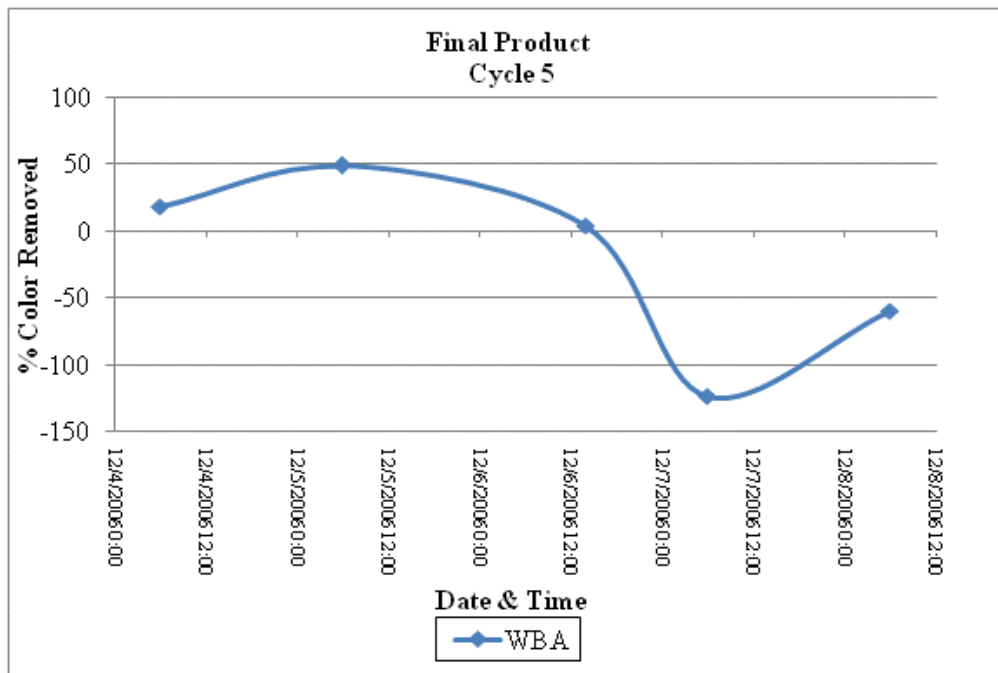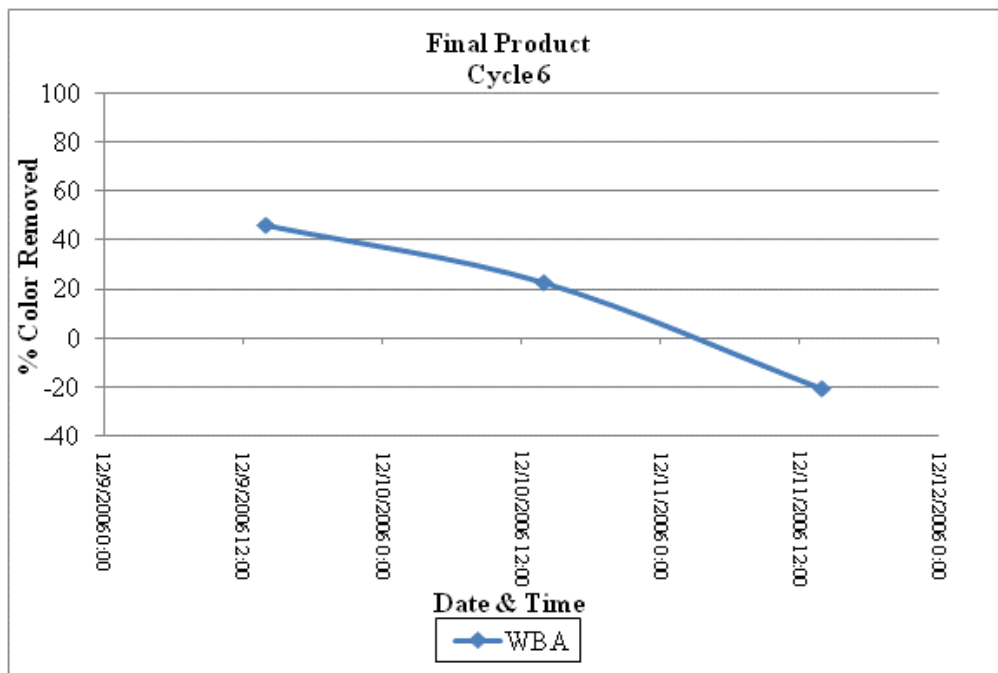
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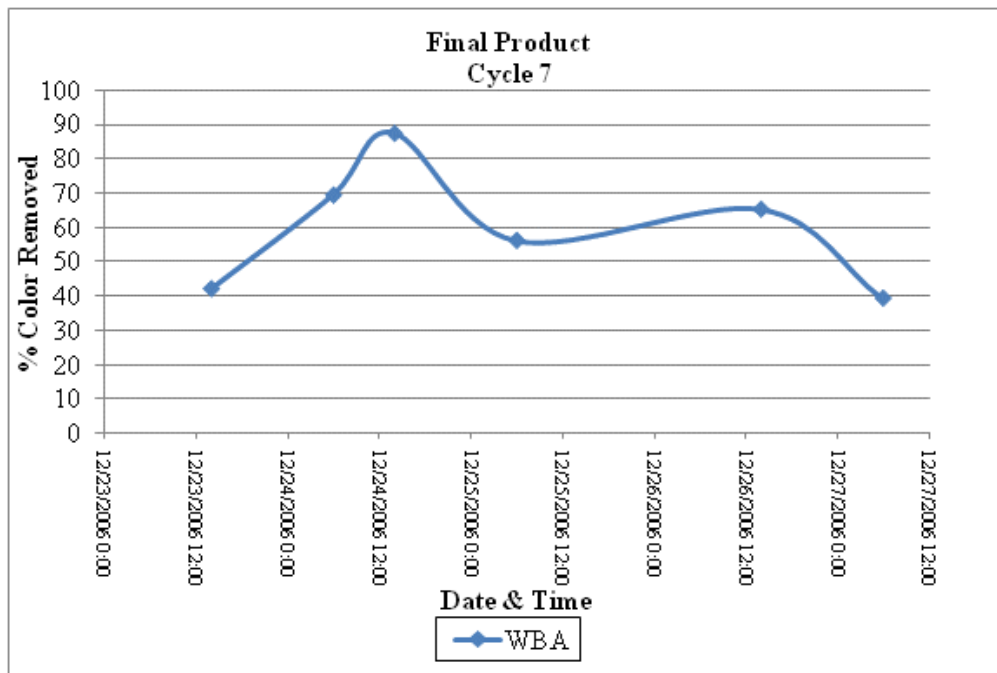
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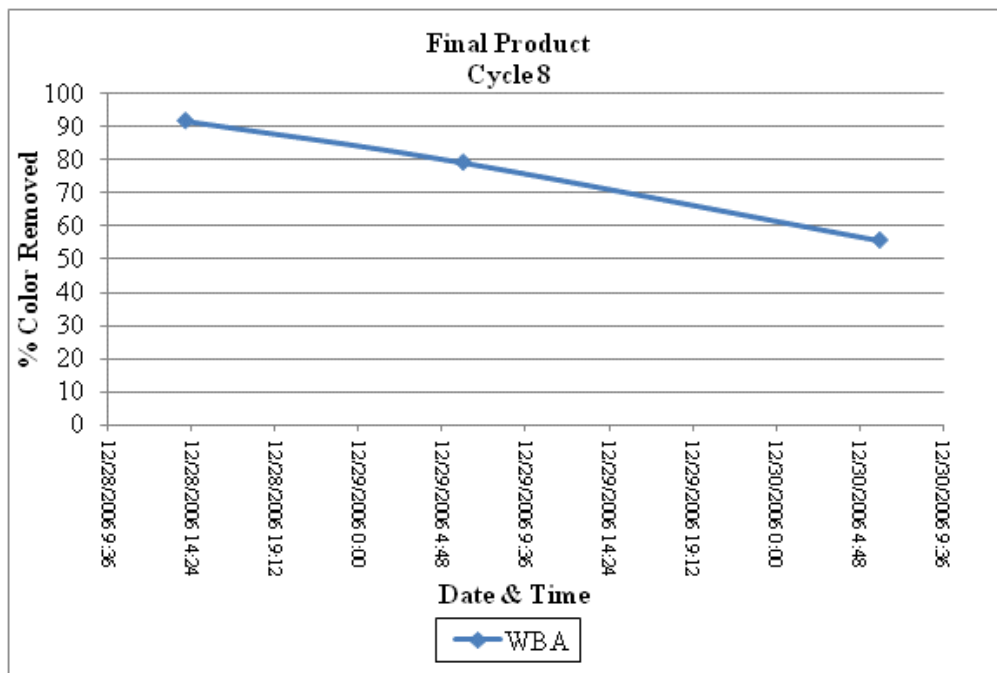
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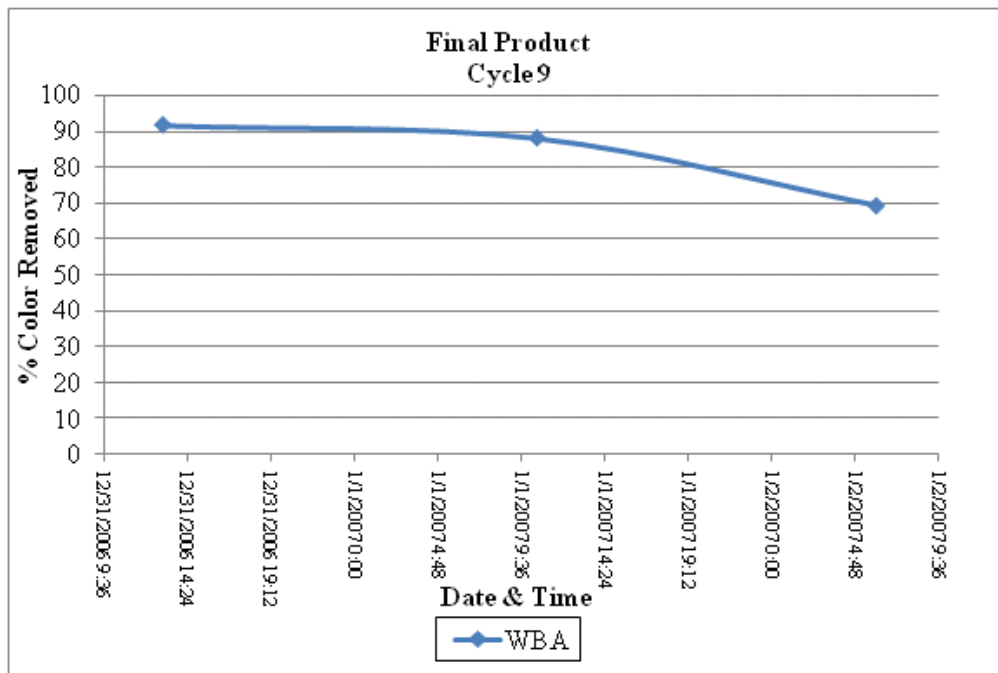
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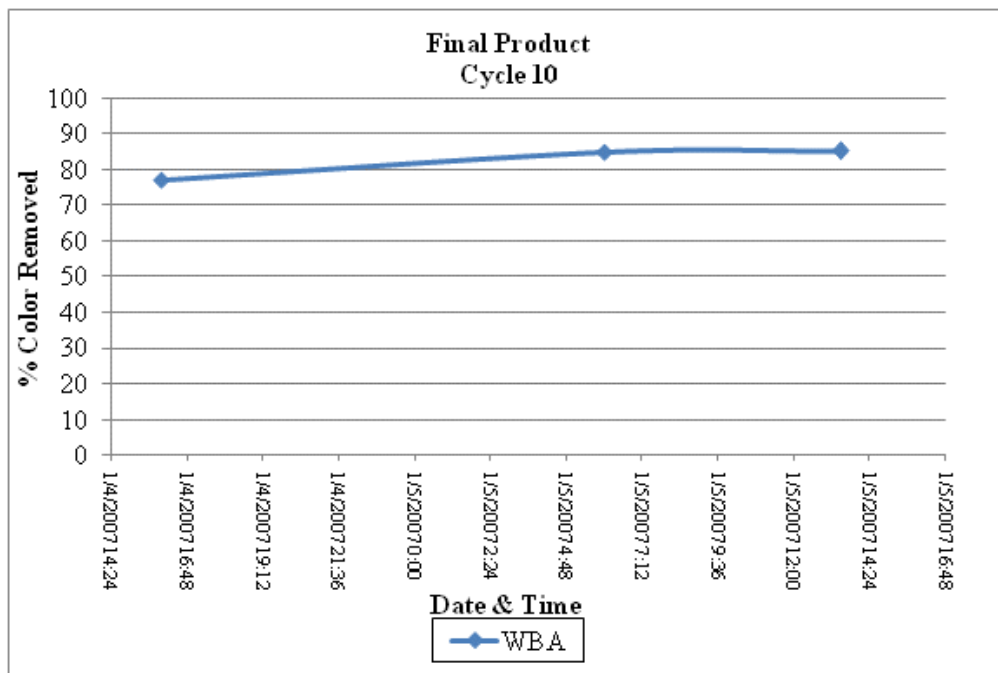
Figure E.5.27.

E.6. Events

Table E.1. Pilot plant regeneration dates

Regeneration Regime		
GAC1	GAC2	Ion Exchange
11/1/2006	11/6/2006	11/11/2006
11/10/2006	11/13/2006	11/19/2006
11/18/2006	11/21/2006	11/22/2006
11/25/2006	12/2/2006	11/27/2006
12/3/2006	12/7/2006	12/4/2006
12/16/2006	12/19/2006	12/8/2006
12/26/2006		12/27/2006
12/29/2006		12/30/2006
1/2/2007		1/3/2006
1/8/2007		

Table E.2. Log of significant events

Significant Events	
31-Oct	Peroxide dosing commenced
1-Nov	Automatic feed control valve installed
3-Nov	Ion Exchange columns online, feed reduced from 1.5 to 0.8 gpm on flowmeter
7-Nov	Auto feed valve online
9-Nov	Flow meter failed closed,then fully open after rinsing
10-Nov	Flow adjusted manually
13-Nov	Flow meters installed on GAC columns
14-Nov	Pump P3 replaced
19-Nov	Peroxide dosing adjusted, was 10X too high
21-Nov	Dextran formation noted in SAC column
23-Nov	WBA column blockage due to dextran
30-Nov	Reaction tank heater online; peroxide dosing corrected
6-Dec	Ethanol supply depleted. Replacement ordered
12-Dec	Full washdown off all columns in preparation for total regeneration (fouling, poor performance)
20-Dec	New regeneration pumps brought to pilot plant; regen time cut in half
21-Dec	Plant back online
27-Dec	Screen failure suspected in GAC 2; heavy loss of carbon; taken offline GAC 1 flow increased to .6 gpm and regen interval set at three day
5-Jan	Insufficient vacuum for evaporator
8-Jan	Shutdown

Table E.3. Washdown schedule for Raceland factory

Factory Washdowns
10/24/2006
11/5/2006
11/16/2006
11/26/2006
12/12/2006
12/22/2006
1/2/2007

Appendix F. Operating Instructions

RACELAND 2006 PILOT STUDY - OPERATING INSTRUCTIONS

1. **Water test**

- Before charging the columns with carbon or resin the installation must be tested with water. Pumps must run with water and flows must be checked.

- Water inside the columns must be pressurized with the pumps and existence of leakage must be checked and corrected.

- Close all the valves to the columns.

- Fill the Pre-column with water opening valves V4, V8 and V15.

- When the column is full, close valve V15.

- Check for water leakage in the column, pipe or valves.

- Repeat this procedure with the other columns using the pump to pressurize the water inside the columns. The pressure inside the columns must be raised to 15 psig.

- Heaters and cooling system must be checked with water flowing through the columns.

- The evaporator must be checked boiling water. Evaporation rate must be measured to see that the anticipated evaporation of 30 gal water per hour can be achieved at a vacuum of about 24 "mercury.

2. **Charging the carbon columns**

- Carbon columns must be in place and with the tops removed.

- All valves to the columns must be shut.

- Carbon columns must be charged to the specified height (bed height):
  - Pre-column: 48 cm (19")
  - GAC column 1 and 2:   127 cm (50")

- Carbon can be charged in dry form. If used carbon is to be charged, a slurry charge is preferable. After charging the columns with carbon columns tops must be replaced.

- Then an up-flow wash with water must be done to remove the fine particles. For this operation:
  - close all the valves in the columns;
  - open valves:
    - V9, V10, V14 on Pre-column;
    - V26, V28, V31 on GAC 1;
    - V41, V 43, V46 on GAC2.
    - slowly open valve V4 on Pre-column; V23 on GAC 1 and V38 on GAC 2;
    - control the water flow to maintain the carbon free flowing but avoiding carbon carry over to the drain;
    - Maintain the wash until the outlet water is free of carbon fines.

3. Charging the resin columns

- Resin columns must be in place and with the tops removed. All the valves to the columns must be shut.

- Before charging, sand must be screened through a 0.2 mm aperture screen, in order to remove fine particles (particle size 0.45 to 0.55 mm). Charge the resin columns with 30 liters of silica sand #20 in each column (for columns with a diameter of 20"). Be sure that the sand is horizontally leveled in the column bottoms.

- Water must then be feed to the columns, in up flow to half column height. For this operation open valves V60 in the cationic column and V77 on the anionic column.
- Open slowly valves V58 and V75 until water reaches the desired level. As the water level inside the column increases when resin is added, remove the excess water through the bottom drain.

- Resin columns must be charged to the specified height (bed height) (for columns with a diameter of 20"):
  - Cationic column: 48.3 cm (19") (wet resin in H form) (Resin Purolite 150 C)
  - Anionic column: 48.3 cm. (19") (wet resin in OH form) (Resin FPA51)

Do not charge the resin columns with dry resin!

- The resins must be placed in an acid solution (cationic resin) or alkali solution (anionic resin) before being placed in the columns.

- For cationic resin prepare a solution of 5 % HCl with condensate water. Place the resin in this acid solution and leave overnight. Then displace the acid with condensate water and use the resin to fill the cationic column.

- For the anionic resin use the same procedure using a solution of 4% NaOH.

- When small quantities of resin are added to correct the resin volume, this addition can be made through the resin feeding pipe.

- After charging the resin, column tops must be replaced and the resin must be washed with water (condensate, temperature less than 35 °C (95 °F) for anionic resin) in an up-flow way to remove fine particles and color. For this operation open valves V60, V62 and V66 on the cationic column and V77, V79 and V83 on the anionic column. Then open carefully water valves V58 and V75 on each column. Control the water flow in a way to maintain the resin in suspension but avoiding sand suspension and resin carry over.

- Maintain the wash until the outlet water is clear.

When anionic resin is in the OH form (during and after regeneration and the working cycle) the temperature must not be higher than 35 °C (95 °F)!

4. **Regeneration of the cationic resin**

- Close V51 and open V52 to send the juice from the GAC columns back to process.

- Close all the valves on the cationic column

- Pass condensate water in down flow at a flow rate of 300 l/h (1.3 gpm)
    - Open valves V59, V66 and V63
    - Open hot water valve V58
    - Check the flow in the drain discharge

- Maintain the wash for 30 minutes or, if after a working cycle, when the outlet concentration is less than 2° brix. Then close valves V58 and V59.

- Open the air valve to the resin column (valve V71).

- Let air mix the resin for 5 minutes (if the resin is not free flowing, pass more air until the resin flows freely).

- Close the air, valve V71.

- Pass condensate water through the resin in up-flow.

- For this operation open valves V60, V62, V66 and the water valve V58

- Control the water flow carefully in order to avoid resin losses.

- When the effluent water is free of suspended solids close the water valve V58 and all other valves on the cationic resin column.

- Pass a solution of HCl at 5% (w/w) at a flow rate of 300 l/h (1.3 gpm) for one hour.

- For this operation open valves V55, V59, V63 and V66.

- Start the cationic pump P7.

- Turn off pump after 1 hour. Close valve V55 and open V58.

- Pass condensate water at a flow rate of 300 l/h (1.3 gpm) for two hours.

- For this operation open valves V59, V63 and V66 and water valve V58.

5. **Regeneration of Anionic Resin**

CAUTION: all regeneration of anionic resin must be done at a temperature less than 35 °C (95 °F)

- Close all valves on the anionic column

- Pass condensate water (cooled) in down flow at a flow rate of 300 l/h (1.3 gpm)
    - Open valves V76, V83 and V80
    - Open water valve V75
    - Check the flow in the drain discharge

- Maintain the wash for 30 minutes or, if after a working cycle, when outlet concentration is lower than 2° brix.

- Then close valves V75 and V76

- Open the air valve to the resin column (valve V88).

- Let air mix the resin for 5 minutes (if the resin is not free flowing, pass more air until the resin flows freely). Then close valve V88.

- Pass condensate water (cooled) through the resin in up-flow.

- For this operation open valves V77, V79, V83 and water valve V75

- Control the water flow carefully in order to avoid resin losses.

- When the effluent water is free of suspended solids close water valve V75 and all other valves in Anionic resin column.

- Pass a solution of NaOH at 4% (w/w) at a flow rate of 300 l/h (1.3 gpm) for one hour.

- For this operation close valve V74 and open valves V73, V76, V80 and V83.

- Start pump P4.

- Pass a solution of condensate water at a flow rate of 300 l/h (1.3 gpm) for two hours.

- For this operation open valves V76, V80 and V83 and water valve V75.

6. Washing the Pre-column

- Pre-column must be washed with water at a frequency depending on the suspended solids in clarified juice. If there is no great quantity of suspended solids in juice this wash can be made every time a GAC column is regenerated, that is every three working days (with 6 days cycles of the GAC columns). If these washes are not enough, that is, if the juice flow in the Pre-column decreases below 120 l/h (0.5 gpm), this wash must be done more frequently, every two days or at every working day.

- Wash the Pre-column as follows:
- Close valve V3.
- Stop pumps P1, P2, P3, P4, and P5 (if working).
- Water wash 1:
  - o Open valve V4 and control the water flow at 150 l/h (0.7 gpm) (approximately).
  - o Maintain the water flow to the Pre-column until the outlet juice brix is lower than 2 ^{o} brix (if the Pre-column was working with juice; if not, that is if Pre-column is with water, the Water wash1 is not necessary)
  - o Close valves V8, V11 and V13 (if Pre-column was operating with juice).
- Water wash 2:
  - o Open valves V9, V10 and V14.
  - o Slowly open water valve V4.
  - o Control the water flow to maintain the carbon free flowing but avoiding carbon carry over to the drain;
  - o Maintain the water flow until the outlet water is clear.
- Close all valves on the Pre-column.
- Open valves V8, V11 and V14.
- Open valve V3.
- When the outlet brix is higher than 5 ^{o} brix, open valve V13 and start pumps P1, P2, P3, P4, and P5 (when necessary).

7. **Regeneration of GAC**

- For the first cycle, GAC does not need any regeneration, only the water wash described in section 2. (Charging the carbon columns).

- Regeneration of GAC columns is done normally one at a time. The other column will continue to work treating the juice.

- <u>For the regeneration of GAC 1 column</u> (at the end of the working cycle):
- Close valve V22.
- Open valve V23; (if the column was stopped and all valves are closed, open valves V25, V29 and V31).
- Regulate the water flow at 240 l/h (1 gpm) Check the flow in the drain discharge.
- Maintain the water flow to the GAC 1 column until the outlet juice brix is lower than 2 $^{\circ}$ brix;
- Then close valves V23; V25 and V31.
- Open the air valve to the GAC 1 column (valve V35).
- Let the air mix the GAC for 5 minutes (if the GAC is not free flowing, pass more air until the carbon flow freely). Then close V35.
- Pass condensate water through the carbon in up-flow.
- For this operation open valves V26, V28, V31 and water valve V23
- Control the water flow carefully in order to avoid carbon losses.
- When the effluent water is free of suspended solids, close the water valve V23 and all other valves on the GAC 1 column.
- a) <u>Acid wash</u>: Pass a solution of 5 % HCl at a flow rate of 160 l/h (0.7 gpm) for 30 minutes.
- For this operation:
    - o Open valves V25, V29 and V31.
    - o Open valve from the HCl tank to the chemical pump P6.
    - o Open valve V21 and start pump P6.
- After 30 minutes, stop pump P6 and close the HCl valve to pump P6 and valve V21.
- b) <u>Water wash 1</u>: Wash the carbon with water:
    - o Open water valve V23;
    - o Maintain a high flow (800 l/h; 3.5 gpm) for 30 minutes.
- Close valve V23.
- c) <u>Alkaline wash 1</u>: Pass a solution of NaOH at 2% (w/w) at a flow rate of 160 l/h (0.7 gpm) for 30 minutes.
- For this operation:
    - o Prepare NaOH solution (see section 8. <u>Chemicals Preparation</u>);
    - o Open valves V5 (check) and V21;
    - o Start pump P6.
- d) <u>Regeneration</u>: Pass a solution of NaOH/Ethanol/peroxide solution at a flow rate of 160 l/h (0.7 gpm) for 60 minutes.
- For this operation:
    - o Prepare NaOH/Ethanol/peroxide solution (see 8. <u>Chemicals Preparation</u>);
    - o Open valve from preparation tank to pump P6;

- o   After 60 minutes close tank valve.
- e) <u>Alkaline wash 2</u>: Pass a solution of NaOH at 2% (w/w) at a flow rate of 160 l/h (0.7 gpm) for 30 minutes.
- For this operation:
  - o   Prepare NaOH solution (see 8. <u>Chemicals Preparation</u>);
  - o   Open valve from preparation tank to pump P6;
  - o   After 30 minutes stop pump P6 and close valve V5 (check) and V21.
- f) <u>Water wash 2</u>: Pass condensate water at a flow rate of 300 l/h (1.9 gpm) for two hours.
- For this operation open valve V23.
- If there is color formation when juice is fed to the GAC 1 column, make an acid wash to the carbon followed by a water wash (as in (a) and (b)).
- • All the flows must be controlled by measurements on the drain line.

- • <u>For the regeneration of the GAC 2 column</u> (at the end of the working cycle):
- Close valve V37.
- Open valve V38; (if the column was stopped and all valves are closed, open valves V40, V44 and V46).
- Regulate the water flow at 240 l/h (1 gpm) Check the flow in the drain discharge.
- Maintain the water flow to the GAC 2 column until the outlet juice brix is lower than 2 ^{o} brix;
- Then close valves V38; V40 and V46.
- Open the air valve to the GAC 2 column (valve V50).
- Let air mix the resin for 5 minutes (if the GAC is not free flowing, pass more air until the carbon flow freely). Then close V50.
- Pass condensate water through the carbon in up-flow.
- For this operation open valves V41, V43, V46 and water valve V38
- Control the water flow carefully in order to avoid carbon losses.
- When the effluent water is free of suspended solids close water valve V38 and all other valves on the GAC 2 column.
- a) <u>Acid Wash</u>: Pass a solution of HCl at 5 % at a flow rate of 160 l/h (0.7 gpm) for 30 minutes.
- For this operation:
  - o   Open valves V40, V44 and V46.
  - o   Open the valve from HCl tank to the chemical pump P6.
  - o   Open valve V36 and start pump P6.
- After 30 minutes, stop pump P6 and close the HCl valve to pump P6 and valve V36.
- b) <u>Water Wash 1</u>: Wash the carbon with water:
  - o   Open water valve V38;
  - o   Maintain a high flow (800 l/h; 3.5 gpm) for 30 minutes.
- Close valve V38.
- c) <u>Alkaline Wash 1</u>: Pass a solution of NaOH at 2% (w/w) at a flow rate of 160 l/h (0.7 gpm) for 30 minutes.
- For this operation:
  - o   Prepare NaOH solution (see 8. <u>Chemicals Preparation</u>);
  - o   Open valve V5 and V36;

- o Starts pump P6.
- d) <u>Special Regeneration:</u> Pass a solution of NaOH/Ethanol/peroxide solution at a flow rate of 160 l/h (0.7 gpm) for 60 minutes.
- For this operation:
  - o Prepare NaOH/Ethanol/peroxide solution (see 8. <u>Chemicals Preparation</u>);
  - o Open valve from preparation tank to pump P6;
  - o After 60 minutes close valve tank.
- e) <u>Alkaline Wash 2</u>: Pass a solution of NaOH at 2% (w/w) at a flow rate of 160 l/h (0.7 gpm) for 30 minutes.
- For this operation:
  - o Prepare NaOH solution (see 8. <u>Chemicals Preparation</u>);
  - o Open valve from preparation tank to pump P6;
  - o After 30 minutes stop pump P6 and close valve V5 and V36.
- f) <u>Water Wash 2</u>: Pass a solution of condensate water at a flow rate of 300 l/h (1.9 gpm) for two hours.
- For this operation open valve V38.
- If there is color formation when juice is fed to the GAC 2 column, in the start up of a new cycle, make an acid wash to the carbon followed by an water wash (as in (a) and (b)), before feed the juice to GAC 2 column.
- All the flows must be controlled by measurements on the drain line.

8. **Chemicals Preparation**

- The chemicals used in this process must be handled according to safety rules.

- The main chemicals will be stored in the following tanks:
  - o Tank for NaOH @ 4% (m:m)   T8
  - o Tank for HCl @ 5% (m:m)   T7
  - o (Tank for H_2SO_4 @ 2% (m:m)   CT3 (only if necessary)

- Two other tanks T6 and T9 will exist to prepare the GAC regeneration mixtures.

- The solutions prepared previously are stocked in the tanks T7, T8 and CT3.

- For GAC regeneration, HCl from tank T7 is fed to the GAC column through pump P6 at a flow and time specified in Section 7. (Regeneration of GAC).

- To the preparation tank T6, 20 l of NaOH from tank T8 is mixed with 20 l of water.

- This solution flows to the GAC carbon through pump P6 for Alkaline Wash 1.

- In the second preparation tank, T9, the mixture of NaOH, Ethanol and peroxide must be prepared, using 30 l of NaOH from tank T8, 20 l of Ethanol 200 proof, from the ethanol container, and 250 ml of Hydrogen Peroxide at 30 % (m:m).

- This solution flows to the GAC carbon through pump P6 for Special Regeneration.

- In tank T6, when empty, prepare a second portion of diluted NaOH, as previously, for Alkaline Wash 2.

- Chemicals for resins regeneration will flow directly from tanks T7 and T8 to pumps P7 and P4 to cationic and anionic columns, respectively.

9. <u>Working cycle</u>

- The first working cycle, treating clarified juice in the GAC and resin columns, must only be made after the water test, loading the GAC and resins in the columns, and the regeneration of cationic and anionic resins.

- To start the working cycle:
  - Close all the valves on the installation.
  - Start the heating on Pre-column and GAC1 and GAC2 (it is assumed that all columns are filled with water).
  - Open valve V1 to the screen tank T1.
  - Open valves V3, V8, V11 and V14 in the pre-column.
  - Control the flow in the column outlet to a value of 120l/h (0.5 gpm).
  - When the brix in the flow coming out from the column reaches 5 $^\circ$ brix, open valve V13 and close valve V14.
  - When the juice starts overflowing in reaction tank T2, start the heating, regulating the temperature to 85 °C (185 °F), the agitation and the peroxide pump P1. (The peroxide bottle must be full and the chilled water in circulation).
  - Open valves V20, V25, V29, V31, V40, V44 and V46.
  - Start pump P2.
  - Slowly open valves V22 and V37.
  - Control the flow in the column outlet to values of 60 l/h (0.26 gpm.) in each column.
  - When the brix in the flow coming out from the column reaches 5 $^\circ$ brix, open valve V30 and close valve V31 in GAC 1 and open valve V45 and close valve V46 in GAC 2, and open valve V51.
  - Start juice flow through the cooling system, opening valves V53 and V56 and start pump P3.
- When juice temperature reaches 10 °C (50 °F), open valves V59, V63 and V66, and close valve V56.
- Slowly open valve V57.
- Control the flow in the cationic column outlet to values of 120 l/h (0.5 gpm.).

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- When the brix in the flow coming out from the cationic column reaches 5 $^\circ$ brix, open valve V65 and close valve V66.
- When Tank 4 is overflowing, open valves V74, V76, V80 and V83.
- Slowly open valve V93.
- Control the flow in the anionic column outlet to values of 120 l/h (0.5 gpm.).
- When the brix in the flow coming out from the anionic column reaches 5 $^\circ$ brix, open valve V82 and close valve V83.

- If the evaporator is not in operation, open valve V89 which returns the treated juice to process. If the evaporator is running, close valve V89 and open valve V90. Pump P5 is used to pump the juice to the evaporator.

10. **Shutdown and start-up on maintenance days**

- When the mill shuts down for evaporator cleaning and maintenance, the columns should be left full of water, not juice. The pre-column should be back-flushed at the same time.

- The shutdown procedure is as follows:

Pre-column:

- Close valve V3.

- Stop pumps P1, P2, P3, P4, and P5 (if working).

- Water wash 1:
    o Open valve V4 and control the water flow at 150 l/h (0.7 gpm) (approximately).
    o Maintain the water flow to the Pre-column until the outlet juice brix is lower than 2 $^\circ$ brix
    o Close valves V8, V11 and V13.

- Water wash 2:
    o Open valves V9, V10 and V14.
    o Slowly open water valve V4.
    o Control the water flow to maintain the carbon free flowing but avoiding carbon carry over to the drain;
    o Maintain the water flow until the outlet water is clear.

- Close all valves on the Pre-column.

- Close valve V1 (feed of clarified juice) and drain Tank T1 by opening drain valve V2.

GAC columns

- Close valve V22.

- Open valve V23, close valve V30 and open V31.

- Regulate the water flow at 240 l/h (1 gpm) Check the flow in the drain discharge.

- Maintain the water flow to the GAC 1 column until the outlet juice brix is lower than 1° brix;

- Then close valves V23; V25 and V31.

- Close valve V37.

- Open valve V38, close valve V45 and V46.

- Regulate the water flow at 240 l/h (1 gpm) Check the flow in the drain discharge.

- Maintain the water flow to the GAC 2 column until the outlet juice brix is lower than 1° brix;

- Then close valves V38; V40 and V46.

- Open valve V19 to drain the reaction tank T2

Cationic column

- Close V51 and open V52

- Close all the valves on the cationic column

- Pass condensate water in down flow at a flow rate of 300 l/h (1.3 gpm)
  - Open valves V59, V66 and V63
  - Open hot water valve V58
  - Check the flow in the drain discharge

- Maintain the wash for 30 minutes or, if after a working cycle, when the outlet concentration is less than 1° brix. Then close valves V58 and V59.

Anionic column

CAUTION: the water temperature must be less than <u>35 °C (95 °F)</u>

- Close all valves on the anionic column

- Pass condensate water (cooled) in down flow at a flow rate of 300 l/h (1.3 gpm)
  - Open valves V76, V83 and V80
  - Open water valve V75
  - Check the flow in the drain discharge

- Maintain the wash for 30 minutes or, if after a working cycle, when outlet concentration is lower than 1° brix.

- Then close valves V75 and V76

- Drain tanks T3, T4, and T5 by opening valves V54, V72, and V89

The startup procedure is as follows:

- Close all tank drains V2, V19, V54, and V72.

- Then follow the instructions in Section 9 (Working Cycle)

Regeneration on shutdown days:

- If advantage can be taken of shutdown days to regenerate any of the columns, then the procedures in Sections 4, 5, 6 and 7 can be followed. The first part of the regeneration, i.e. water wash is part of the shutdown procedure.
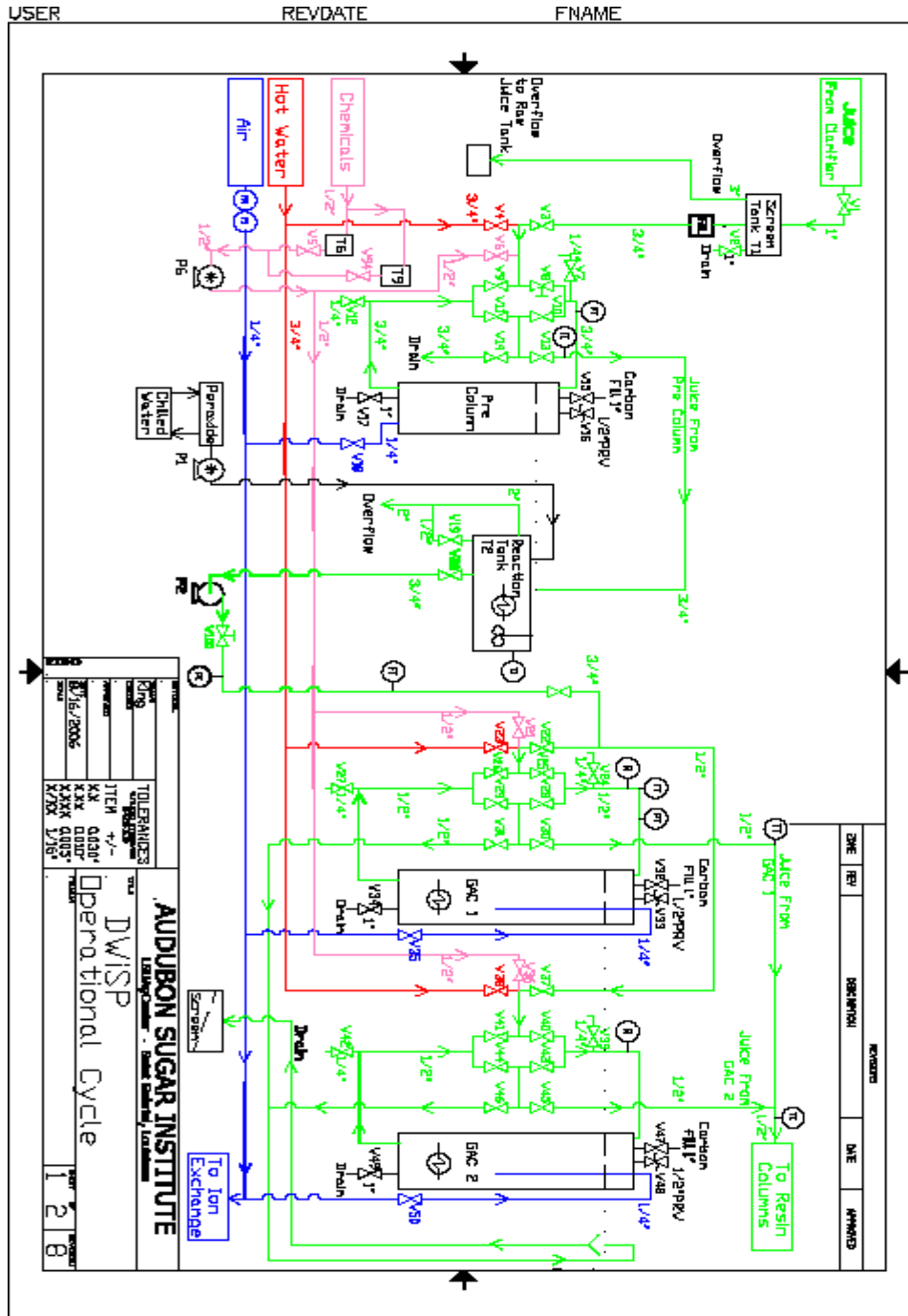
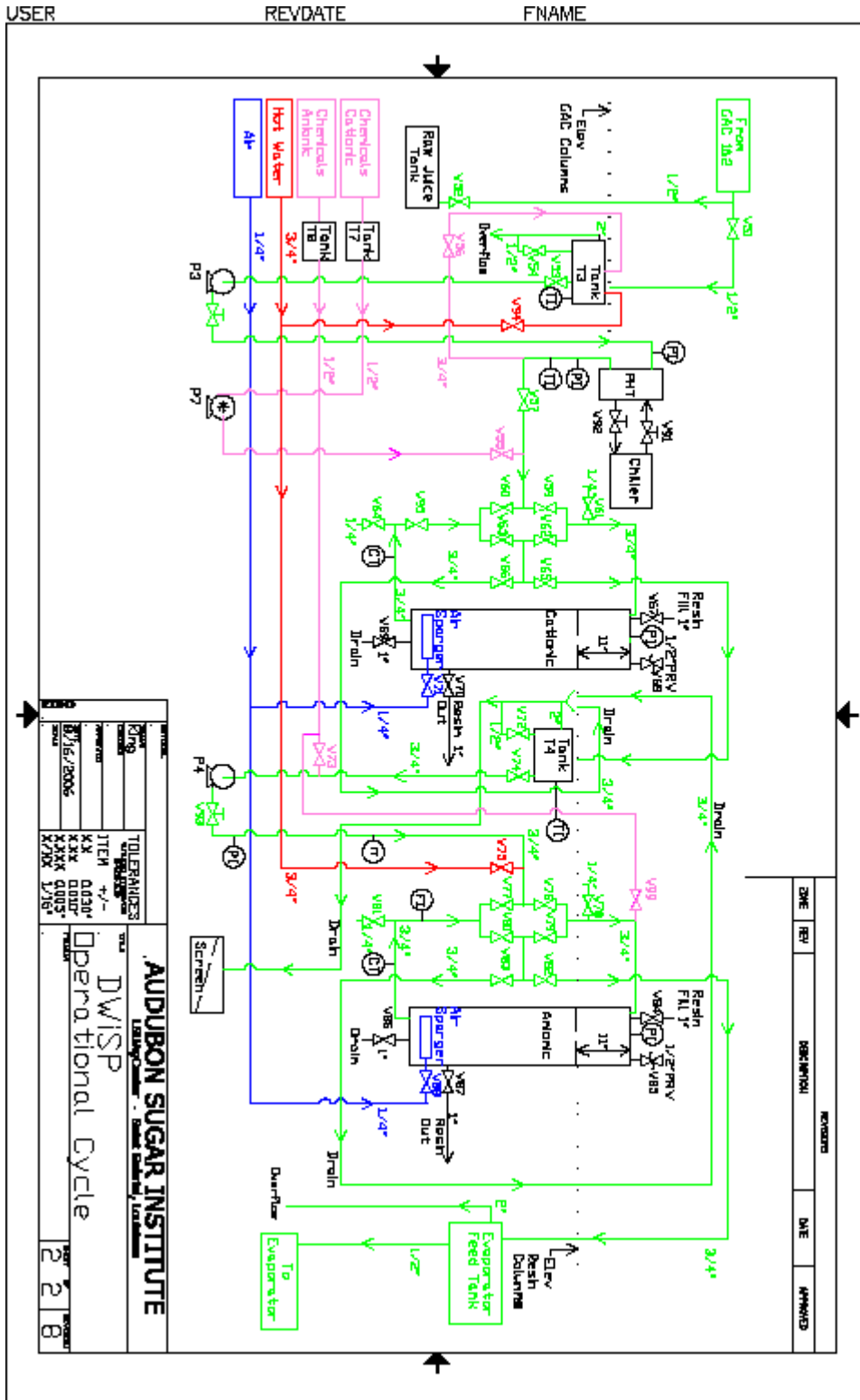# Appendix G. Diagrams

Figure G.1. Carbon columns diagram

Figure G.2. Ion exchange columns diagram

G.1. Ion Exchange Column Pictures

Figure G.3. SAC Column. Mud is visible on the surface of the resin.
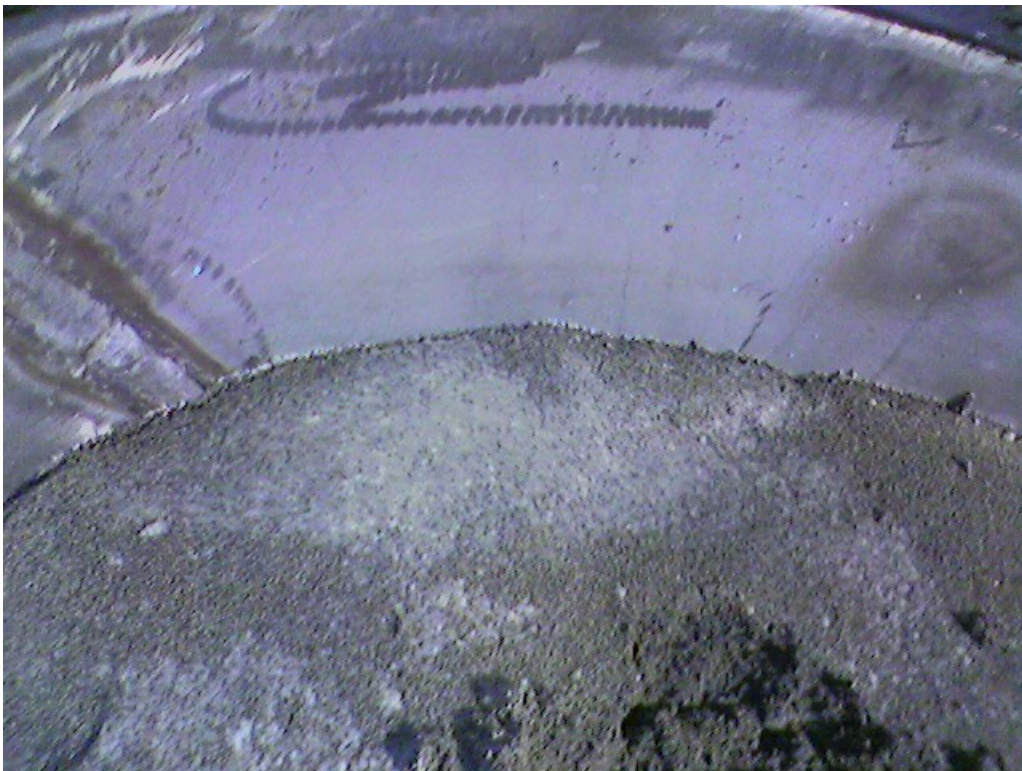
Figure G.4. SAC Column.

Figure G.5. WBA Column. White beads may be dextran or bacterial colonies.

Figure G.6. WBA Column.

Vita

Raúl Alejandro Cortés was born in Camden, New Jersey, where he lived until graduating from Woodrow Wilson High School. After serving five years as an Electrician's Mate in the United States Navy, he worked as a material handling equipment technician and home improvement sales associate. He received the degree of Bachelor of Science in Biological Engineering from Louisiana State University in 2003. He is the proud father of Ada Cortés.