THE EFFECT OF KRAFT MILL BLEACH PLANT EFFLUENT COMPOSITION ON THE EFFLUENT COLOR ADSORPTION RATE ONTO A MACROPOROUS ADSORBENT RESIN

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By

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ABSTRACT

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An experimental macroporous adsorbent/ion exchange resin was used to decolorize bleach plant effluents. The treated effluents were a combination of chlorination and alkali extract streams. A study of the rate mechanism was carried out in order to gain a better understanding of how process variables, namely effluent composition and flow rate, affect adsorption. Regeneration of the adsorbent was also investigated.

Both liquid and solid phase resistances were determined to be important, though a liquid-film control model was adequate to describe the system at low resin saturations. The effective diffusivity was determined to be about $3X10^{-7}$. This model suggests that the molecular weights of the treated effluents, namely the amount of high molecular weight (MW>10,000) color bodies greatly affect the mass transfer coefficient.

Using NaOH to regenerate the resin, the effluent streams could be concentrated to 10 times the initial color level.

This work is dedicated to my Lord and Savior, Jesus Christ, to my parents, and seven sisters, whose guidance, love and support has made the difference!

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LIST OF NOMENCLATURE

BPE - bleach plant effluent

BV - bed volume of resin particles plus void volume

E,E1 - effluent from the first alkaline extraction stage of the pulp bleaching process

C_D - effluent from the chlorination stage, which contains small amounts of chlorine dioxin, in the pulp bleaching process

C.U. - Color Units

LIST OF SYMBOLS

a - saturated resin capacity
C - concentration of unadsorbed color
Co - initial amount of color in effluent
d - diameter of pellet
D - diffusion coefficient
D_a - effective diffusivity
K - equilibrium constant
K_D - distribution coefficient
K_f - overall mass transfer coefficient
k_L - liquid-film mass transfer coefficient
K_os - overall mass transfer coefficient
k_x - solid mass transfer coefficient
n - exponential constant of Freundlich isotherm
q - amount of adsorbed color on adsorbent resin
R - radius of resin beads
s - external surface area of ion exchange resin per mass of resin
t - contact time
U - velocity
V - volumetric flow rate
x - weight of used resin bed
y - amount of color remaining in solution
y_L - liquid volume treated
Z - length of resin bed
ε - packed bed void fraction
ρ - density of resin beads
ν - kinematic viscosity

INTRODUCTION

To comply with present and forthcoming governmental regulations and public concerns, the pulp and paper industry is looking for ways to insure that the effluents it releases into the environment are safe. Of particular concern are the effluents from the pulp bleaching process, which are known to cause toxicity and color problems for the receiving waters into which they are released. Both the toxicity and color problems are a result of the extraction/bleaching portion of the Kraft pulping process.

There are a number of methods to handle these problems. Either bleaching process changes can be made to reduce the amount of toxic material and color being formed, or the effluent streams can be treated directly to remove or degrade them. However, since some bleaching process modifications alter the product quality and others do not completely eliminate the effluent color problem, an effluent treatment method to eliminate color from bleach plant effluent might be useful and is the focus of this investigation.

Ultrafiltration, ozonation, adsorption, and fungal degradation are among the effluent treatment methods presently available or being developed. However, high cost is usually the main obstacle to using these methods industry-wide. Part of the cost can be attributed to technical difficulties arising from poor understanding of the composition of bleach plant effluents (BPE). Thus, the objectives of this study were to investigate the ability of an experimental ion exchange/adsorbent resin to decolorize combined effluents from the chlorination and alkali extraction stages of the pulp bleaching process, and to get a better understanding of the effect the effluents' constituents have on the success of this decolorization method. This includes the determination of the rate mechanism and rate constants. Regeneration of the resin was also studied.

CHAPTER I

BACKGROUND

The search for an effective way to decolorize bleach plant effluents from pulp mills has been ongoing for decades. In the past, some of the difficulty in resolving this problem was caused by the lack of understanding as to the origin of the problem, the nature and makeup of the effluents involved, and the debate concerning whether effluent treatment was really necessary. Some of these issues still exist. This section presents some of the available information concerning the bleaching process which produces the color problems, the characterization of the effluent streams involved, and a discussion of why it is becoming increasing important to successfully solve the bleach plant effluent color problems.

A. Kraft Pulping Process

The Kraft pulping process is the most commonly used pulping process in the pulp and paper industry. Over 70% of the pulp produced is manufactured by this process. It is known for producing high strength pulp and, conversely, for producing very dark colored bleach plant effluent. The aim of this pulping process is to remove fibers from wood by dissolving a highly reactive polymer called lignin so paper products can be made.

Lignin is responsible for holding tree fibers together and is also the source of 90% of the effluent color problems.[1] The molecular weight of lignin can range from 2,000 to 1 million, depending on its source. Thus, it must be degraded and modified by the pulping process before it can be dissolved. Figure 1 is an illustration of a Kraft process.[1]

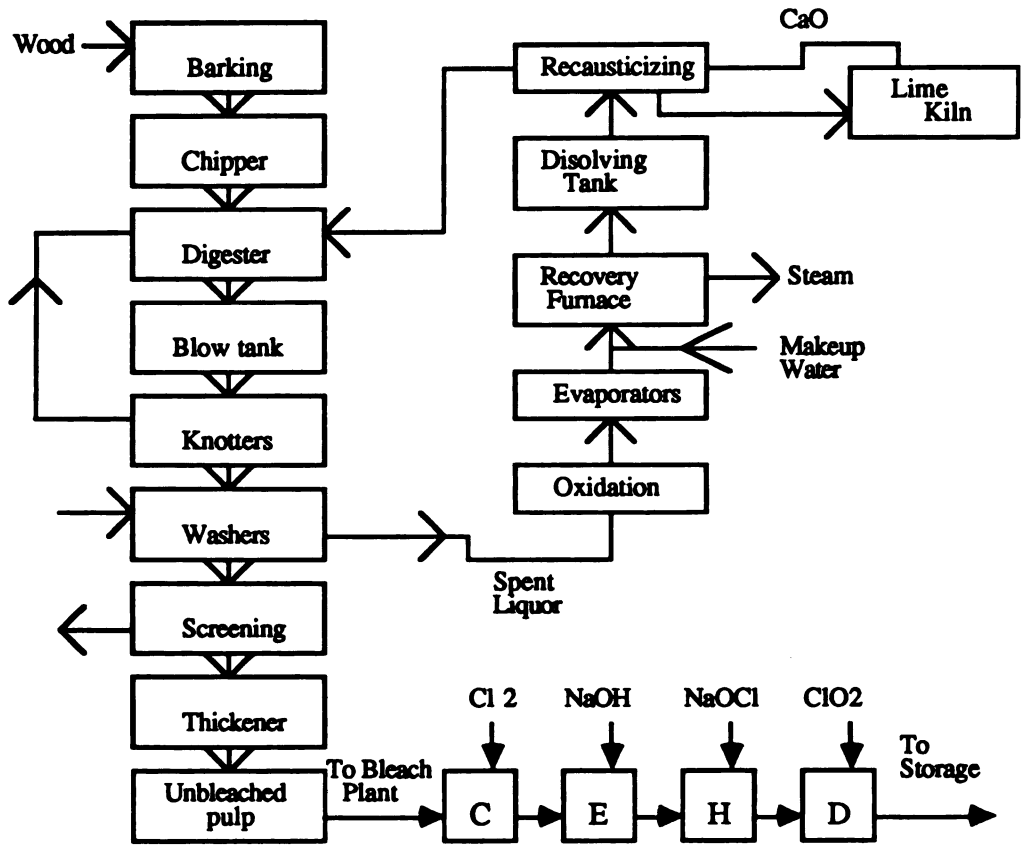


Figure 1 Kraft Pulping Process

The Kraft pulping process entails debarking the wood before it is sent to the chipper where the wood is reduced to small uniform pieces. The chips are then sent to the digester where they are cooked in order to degrade the lignin. The chips go to the blow tank where the temperature of the chips is reduced before they go to the knotter for the removal of uncooked chips. After the pulp is washed and screened for undesirable wood fibers, it is thickened to its final unbleached form.

In order to produce white paper products, after pulping, the pulp fibers are bleached with a sequence of chemicals to remove the lignin. There can be as many as eight stages in sequence. The stages are usually identified in the following way:[1]

C = Chlorination

E = Alkaline Extraction

H = Hypochlorite Bleaching

D = Chlorine Dioxide Bleaching

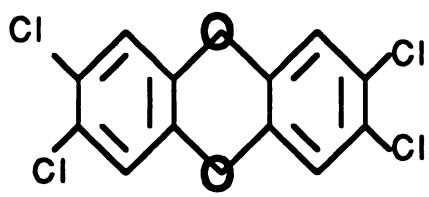
P = Peroxide Bleaching

O = Oxygen Bleaching

C_D = Chlorination, with small amount of chlorine dioxide

There are a number of different variations to the bleaching sequence and bleaching agents used. Figure 1 includes only one type of bleaching sequence Traditionally, the main bleaching sequences include chlorination, and alkali extraction stages. The effluents from these stages are of the most concern because they contain most of the color and toxic material that is produced in the bleach plant.

The Chlorination (C) stage converts the lignin in the pulp to water- or alkali-soluble compounds. Unfortunately, some of the chlorinated lignin compounds that are formed are not only color causing, they are also known to be hazardous. For an example, 2,3,7,8 - tetrachlorodibenzo-p-dioxin (also known as dioxin), which has the structure,



has been known to have a toxic effect on fish in the receiving streams in which it is released and is considered a carcinogen.[2]

During the alkali extract (E) stage, the color causing and toxic lignin compounds are dissolved and removed. The spent liquor is then discarded into aerated lagoons where some of the color bodies settle out in the lagoon. However, other color bodies remain in the lagoon effluent which is released out into nearby rivers. Thus, this method of handling the waste water effluents is no longer being viewed as effective or acceptable due to the poor degradation of the chlorinated organics.

B. Characterization of Effluent Streams

The spent liquor from the chlorination stage contains mostly low-molecular weight compounds such as methanol, glucolic, fumaric, succinic, and chlorofumaric acids. It contributes about 19% of color to the total pulp mill effluent, and in a typical mill, can be produced at 5 million gallons per day. The C-stage effluent typically has a pH of 1-2. The alkali extraction stage produces high molecular weight material and contributes about 66% of the color to the total mill effluent, at an average rate of 1.7 million gallons per day per mill.[3] The pH of the E-stage effluent is usually around 9 or 10.

Both streams contain chlorophenols, chloroguaiacols, chlorovanillins, and chlorosyringols. Chlorocatechols are the dominant species in C-stage effluents, while chloroguaiacols are the dominant species in E-stage effluents. About 70% of the material in C-stage effluents have molecular weights under 10,000, and approximately 40% under 1,000. About 75% of the material in E-stage effluents have molecular weights over 10,000, with 50% over 25,000. Color is largely associated with the high molecular weight compounds, as demonstrated by the high color load in E-stage effluents.[4]

It should be noted that the characterization of bleach plant effluents is not likely the same from mill to mill because of the different types of wood used (softwood, hardwood, etc.), and the different pulp bleaching sequences employed. Table 1 gives typical color ranges for C and E-stage effluent streams.

Table 1 Typical Bleach Plant Effluent Characteristics

Stream	Color (C.U)	pH
Chlorination	600-2,000	1-2
Alkaline Extraction	4,000-20,000	9-10

BPE color is normally measured by comparing the effluent color with the amount of color in a platinum-cobalt solution. A unit of color is the amount of color produced by 1 mg/l of platinum, in the form of chloroplatinate ions.

C. Environmental Concerns

The total amount of color in the bleach plant effluents often warrants a need for more effective treatment of the effluents for the following reasons:

1. The Clean Water Act of 1987 is requiring Kraft pulp mills to greatly reduce the amount of harmful chlorinated lignin by-products in their effluents by 1992. (Color is an indirect measure of lignin and lignin derivatives).
2. Governmental regulations specifically for color are expected soon.
3. Some states currently have effluent color limits.
4. Some operating permits for mills have effluent color restrictions.
5. There has been public concern over color changes in rivers and possible toxicity effects.
6. Color bodies interfere with aquatic life, cause foam build-up, and may cause bacterial problems.

It is reported that the total annual capital expenditures of mills in the 1990's is expected to exceed $5 billion. From 1989-1992, $1.2 billion is expected to be spent on environmental issues. Of this amount, $66 million (55%) is estimated to be spent on waste water issues.[6] The industry realizes that color removal systems are expensive and could cost up to 10% of the value of the final pulp product, but in some cases, there are no alternatives.

It has been projected that the next few years will bring new regulations on the toxicity of effluents from bleach plant mills. EPA regulations on color are also expected. Since color and the toxic chlorinated lignin are closely related, the treatment of one problem will often alleviate the other problem. Therefore, even though color pollution is becoming more of an issue, the actions the pulp industry are taking to handle the toxicity problems are solving some of the color problems. Some process changes can reduce color by 80%.

The industry seems to be leaning toward having the long-term goal of preventing the formation of toxic material. Thus, a lot of research is being done on process modifications. By finding a bleaching process that eliminates the need for chlorine without compromising the final product, the effluent toxicity problem may largely be solved. The Food & Drug Administration is expected to mandate that only dioxin-free paper products can be in contact with food products, so it appears that the industry is on the right track. However, there still may be a need for effluent color removal systems until a process modification that can meet the needs of the majority of the pulp mill industry can be found. And depending on what that process modification is, a effluent treatment system may still be needed to use in conjunction with the process modification in order to meet some color regulations.

Using adsorbent resins to decolorize bleach plant effluents has been examined in the past, but has been plagued by inconsistent results and short resin lives. This has been partially blamed on resin variability from batch to batch. However, this may not be entirely the case. Some of the problems encountered could be caused by not taking into account how the variance in the effluent streams being treated may effect color adsorption.

CHAPTER II

COLOR TREATMENT SYSTEMS

A marketing study was done to see what type of methods are being used to treat bleach plant effluents, and to determine the advantages and disadvantages of trying to further develop an adsorption process for this application. This section present the different ways the pulp and paper industry is using or investigating for handling effluent color problems, and the type of attributes that may best fit their needs.

A. Description of Color Reduction/Treatment Methods

There are a number of ways that the pulp and paper mills can handle the effluent color problems. The different methods can basically fall under two categories: add-on systems and process modifications. Add-on systems treat the effluent directly by either separating out the color bodies from the waste water or by degrading them. Color reduction by process modification usually entails changing the delignification and/or bleaching process to eliminate the formation of some of the color in the effluent. Substituting for chlorine in the bleaching sequence is the most widely used method. Complete substitution can eliminate the formation of hazardous chlorinated organics entirely.[7]

Table 2 lists most of the currently available add-on systems and process modifications along with their specific advantages and disadvantages.

The use of ion exchange or adsorbent resins to decolorize bleach plant effluents has been around for a while. It is this type of technology, using an experimental resin, that is the basis of this thesis. This method usually entails packing a column with the resin beads.

Table 2 Color Removal/Reduction Systems for Bleach Plant Effluents

METHOD	DESCRIPTION	ADVANTAGES	DISADVANTAGES
Add-on Technology:			
		COLOR SEPARATION TECHNOLOGY	
Resin Processes	Ion Exchange or Adsorption	90 % color reduction Removal of toxic material	Short resin life Variable performance Concentrate disposal
Activated Carbon	Adsorption	Cleans water to reuse level Long standing process	Regeneration problems Biological growth in columns Concentrate disposal
Chemical Coagulation	Precipitation of color with lime, etc.	Cheap Simple process	Chemical recovery Waste disposal High precipitant usage
Organic Polymers	Precipitation of color with polyamines, etc.	Cheap Simple process	Sludge handling Waste disposal
Ultra filtration	Membrane filtering of color	90% color reduction	Membrane fouling Concentrate disposal Slow process
Reverse Osmosis	Membrane filtering of color	99 % color reduction Water reuse	Membrane fouling Concentrate disposal
		COLOR DEGRADATION TECHNOLOGY	
Fungi	Degrades toxic material	No waste disposal	Variable performance Difficult application
Ozonation	Breaks down color bodies	No waste disposal	High cost
Process Modifications:*			
		COLOR ELIMINATION TECHNOLOGY	
Extended Delignification	Modified pulp cooking	50 % color reduction	Slightly difficult process
Oxygen Delignification	Oxygen bleaching replaces chlorine	50% reduction of color Chlorine-free effluent	High capital cost Decreased pulp strength
Peroxide Bleaching	Peroxide bleaching replaces chlorine	90% reduction of color Easy to use	High cost of peroxide
Ozone	Ozone bleaching	Decrease in effluent color	Lower pulp strength High cost of ozone
Chlorine Dioxide	Used with/instead of chlorine	Decreases color Can use existing equipment	Expensive Must be made on site

* Some process modifications can be used in conjunction with one another.

Then the resin is sometimes activated by running an acidic stream through the column, after which the effluent is adjusted to some optimal operating pH, and run through the column for decolorization. Once the percentage of decolorization drops below a certain level, the resin is regenerated with a caustic stream. The different types of ion exchange/adsorbent resin systems will be discussed later.

The main problems encountered with these systems are high cost caused by short resin life and unpredictable results. The disposal of the concentrate from the regeneration step is also a concern. From a scientific viewpoint, this solid waste can be incinerated. However, public resistance to incineration has halted the use of this method in some communities.

Activated carbon systems are used a manner similar to resin systems. They too remove color well, and since activated carbon has been used for the treatment of wastewater for a number of years, there is more understanding of its capabilities. However, there have been problems with biological growth and plugging in columns. There have also been questions concerning the how well the carbon can be thermally regenerated for reuse.

Precipitation of color from bleach plant effluents is a frequently used color treatment method. Typically, precipitation is initiated with substances such as lime or organic polymers. The precipitants are usually cheap, and the process is fairly simple, however, waste disposal and chemical recovery are usually the drawbacks.

Membrane filtering techniques such as ultrafiltration and reverse osmosis have been utilized to separated out the color in BPE, but the aggressive compounds found in effluents cause serious membrane fouling problems. Both techniques work very well in removing color, however, the high cost associated with replacing the membranes make them undesirable to some mills.

The use of fungus or ozone to degrade color in bleach plant effluents seems very appealing due to the fact that the problem of waste disposal usually associated with add-on color treatment systems is eliminated. However, ozonation brings the disadvantage of high

cost, while, at this date, the use for fungi, such as white rot fungus, has been limited by the difficulty in developing a full scale process that can handle the delicate operation of fungal growth.

Since most of the color problems are a direct result of lignin chlorination, a pulping process change known as extended delignification has been developed to remove the lignin before it can reach the bleaching process. This process is carried out by modifying the pulp cooking process. There can be as much as a 50% drop in the amount of color formed by using this method. However, an increase in processing time is often required.

The other process modifications listed in Table 2 entail replacing or partially substituting chlorine with another bleaching agent, such as chlorine dioxide. While there may be a reduction in the amount of color and chlorinated organics formed, there is sometime a decrease in pulp strength and/or brightness.

In general, the add-on color removal systems offer the following advantages and disadvantages:[8]

Advantages	Disadvantages
1. Excellent color removal	1. High cost
2. Product quality unharmed	2. Do not solve cause of the problem
3. Can compliment process modifications	3. Often have solid waste to dispose

Process modifications have the following advantages and disadvantages:

Advantages	Disadvantages
1. Decrease effluent color formation	1. Pulp quality sometimes harmed
2. Reduce/eliminate formation of toxic material	2. Not immediately implementable in some mills

It is difficult to judge one color treatment system over another. It is really a question of what type of system would fit the best in a specific mill.

B. Evaluation of Treatment System Attributes

There are a number of factors that determine which color reduction system is right for a specific mill.[6] Among them are:

1. Location of mill
2. Age of mill
3. Set-up of mill
4. Type of receiving streams
5. Nature and composition of effluent
6. Regulations/degree of treatment required
7. Operating cost
8. Product quality required
9. Future of mill

These factors were used to come up with attributes on which a color treatment system may be evaluated by its potential users. The main attributes and definitions are given below:

1. **Color Removal** - The required level of color removal may be different for each mill depending on state regulations, location of mill, etc. Also, whether it is desired for the system to remove color from the effluent or prevent color formation in the first place is an issue.
2. **Toxic Removal** - The same consideration hold for toxic material as for color. Prevention or treatment is the key question.

3. **Product Quality** - Some process modification systems alter the quality of the product formed, i.e. the strength and/or whiteness of the product may be compromised.

4. **Long-Term Benefits** (timing) - Some mills have immediate needs to meet requirements, while others have long-term goals, like dioxin-free products. Some experts think, in the long run, it is better to prevent the problems of color and toxicity in effluents rather than just treating them after they are formed.

5. **Cost** - It is already understood that all color treatment systems are expensive, however, some mills may be willing to spend more than others to meet their objectives. Acceptable levels of initial costs and operating cost to meet reduction goals are not known.

6. **Ease of Operation** - The issue of how compatible a treatment system is with the existing facilities is important. The less equipment and chemicals that have to be purchased, the better. Also, it is important for the system to offer some flexibility, especially for add-on systems, because the nature and composition of effluents often vary.

7. **By-Product Handling** - This is a very important issue when there is sludge and/or toxic material handling involved, which is the case for a lot of the add-on processes. Systems that degrade the toxic material to non-harmful components are looked upon positively for this reason.

The color treatment method being studied falls in the add-on technology category. It entails pretreating the bleach plant effluent by sand filtering out any suspended solids and then running it through a column of macro porous ion exchange resin beads, on which the color bodies are adsorbed. When the resin be comes loaded with color bodies, the resin is regenerated with caustic solution. A more detailed process description will be given later. It was the aim of this investigation to develop this process so that it would offer the following advantages to existing systems:

1. Make it be easier to integrate it into the pulp and paper mills. (i.e. use available chemicals and equipment).
2. Make it more cost effective.
3. Have it remove color more effectively and efficiently.
4. Make it more flexible in allowing for a wider range of effluent conditions.
5. Use a resin that will have a longer operating life than existing resin systems.
6. More effectively regenerate the resin to improve reuse value.

Table 3 presents some color treatment systems and their rating on a scale of 1-5, for providing the above mentioned attributes. A rating of 5 represents a system that has the attribute in the most desired fashion. Assuming these features are the determinant attributes for the buying behavior of the pulp mill companies towards waste water treatment processes, the proposed process may offer advantages over some of the other treatment technologies in terms of ease of operation and decolorization ability. Compared to process modifications, the add-on technologies have an advantage in product quality, but may have a considerable disadvantage in cost and waste byproduct handling. It was the goal of this study to maximize the advantages and minimize the disadvantages and hopefully create a useful bleach plant decolorization system.

Thus, this study focused on understanding the mechanism which controls the decolorization of bleach plant effluent, and how the composition of the effluent affects the decolorization process. By understanding these points the process can be tailored for improved color removal and ease of operation by having the proper resin (one that not only decolorizes well, but also allows for greater flexibility in effluent composition) and optimal operating conditions.

Table 3 Attributes of Color Treatment Systems (Rating scale 1-5) 5 most desirable

METHOD	COLOR & TOXIN REMOVAL	PRODUCT QUALITY	LONG TERM BENEFITS	INITIAL COST	OPERATING COST	EASE OF OPERATION	BYPRODUCT HANDLING
Resin Processes	4	5	3	3	3	3	2
Activated Carbon	4	5	2	4	4	3	2
Chemical Coagulation	4	5	2	4	4	3	1
Organic Polymers	4	5	2	4	4	3	1
Ultra filtration	4	5	3	2	3	2	2
Reverse Osmosis	5	5	3	2	2	3	2
Fungi	4	5	3	2	2	4	5
Ozonation	4	5	3	2	2	4	5
Extended Delignification 5		4	4	5	3	3	3
Oxygen Delignification 5		3	3	4	2	3	4
Peroxide Bleaching	4	3	4	2	2	4	4
Ozone	4	3	4	2	2	4	4
Chlorine Dioxide	3	3	4	2	2	5	4
Propose Process	5	5	3	3	4	5	2

CHAPTER III

LITERATURE REVIEW

A few pulp effluent decolorization methods have been developed in the past that utilize ion exchange or adsorbent resins. The Rohm & Haas, Billerud, and Dow processes will be discussed here, along with a few more studies that have been done on BPE color reduction with resin. A summary of the processes can be seen in Table 4.

Table 4 Resin Treatment Systems

Author	Sorbent	Effluent Type	pH	Flow rate	Regenerant	%Color Removed
Sanks '73	20 ion exchange resins	Ditchwaste	7.6	20 BV/hr	NaOH	80% after 20 BV
Rock,et al '74	XAD-8	C/E1 (3:1)	2.2	12 BV/hr	weak wash or white liquor	75% after 36 BV
		C/E1 mix	2.5	12 BV/hr	"	80% after 24 BV
		E1 acidified with H_2SO_4	<2.5	8 BV/hr	"	70% after 16 BV
Chamberlin '75	XD-8704	E1	5.0	2 BV/hr	weak wash	95% after 50 BV
		C/E1 mix	5.7	7.8 BV/hr		82% after 25 BV
Lindberg '80	E.I./ads	E1	2-4		caustic	90% after 16 BV
Stevens '90	adsorbent	BPE	4.5	6 BV/hr	NaOH	79% after 42 BV

A. Ion Exchange Resin Study

Sanks (1973) studied 20 ion exchange resins to determine there ability to decolorize ditchwaste (85% chlorination effluent, 15% caustic extract effluent) from a soft wood pulping process.[9] It was reported that weak base porous resins with phenolic matrices performed the best. As for regenerants, weak wash, 1 N NaOH, and ammonia all seemed to sufficiently restore the resins for reuse.

While this study was quite thorough in its testing of the resins, as represented by the adsorption isotherms and breakthrough curves for most of the resins tested, it should be noted that the BPE used was pretreated with lime to precipitate some of the color before decolorization with resin was done.

B. Rohm & Haas Process

The Rohm & Haas process, as reported by Rock et al. in 1974 utilizes a resin named XAD-8 to decolorize bleach plant effluents.[3] The resin is a highly crossed-linked, hydrophilic, porous adsorbent. Different effluent compositions were studied.

For one case, since the chlorination production volume is three times the caustic extract volume, a 3:1 mixture of C:E was used to study the resin's decolorization capabilities. For a flow rate of 12 bed volumes per hour (BV/hr) and a pH of 2.2, 75% decolorization was obtain after 36 bed volumes. For a second case, when E and C streams were combined to produce a mixture with a pH of 2.5, there was 80% decolorization after 24 bed volumes were treated. Another case investigated the decolorization of a caustic extract (E1) stream that was acidified to a pH of 2 with H_2SO_4. About 70% decolorization was achieved after about 16 BV, with a flow rate of 8 BV/hr.

Though this study investigated the treatment of various bleach plant effluent streams and mixtures of streams, no reason was given for why the results varied when the effluent makeup varied.

C. Dow Process

In a study by Chamberlin et al., a mixture of E and C stage effluents were decolorized by an experimental resin called XD-8704 that was developed by Dow Chemical Co.[10] The two effluent streams were mixed to reach a pH of 5.7. With a residence time of 7.7 minutes and a temperature around 30-35ºC, there was 82% reduction of color after 25 bed volumes had been treated. There appeared to be no slack in resin performance after regenerating with caustic.

The uniqueness of this resin was stated as being its flexibility - namely in effluent pH (2 to 9). The study seems to indicate that flexibility in pH is needed because of the pH differences in the various bleach plant effluent streams and mixtures of streams. While the appearance of color in bleach plant effluents is known to be vary dependent on pH (the higher the pH, the darker the effluent color), the molecular weight distribution is not. It is the bases of this thesis that more flexibility in the molecular weights of the color bodies is what is really needed.

D. Billerud-Uddeholm Process

Much has been written about the Billerud-Uddeholm process.[11] The initial focus of this process was to decolorize the E-stage effluent. An ion exchange resin capable of adsorption was able to reduce the effluent color by an average of 90%. After 16 bed volumes, a rapid decrease in resin performance occurred. The resin was regenerated with caustic. Later, the treatment of the C-stage effluent stream was added to the process. It was determined that the chlorination effluent could be decolorized while activating the resin at the same time. The exact operating conditions were not given.

This process was put into full scale operation in Sweden in 1980. However, it was shut down after a few years because of unexpected high cost caused by short resin life and variability in the performance of the resin.

E. Dow Patented Adsorbent Resin

The most recent process was reported by Stevens.[12] The process involves the use of an adsorbent resin made from a macro porous copolymer functionalized with hydrophilic groups. The resin was developed to be highly porous and easily regenerated.

The process entails contacting bleach plant effluent with the adsorbent resin in a packed bed. Optimal operating conditions were stated as being a flow rate of 2-6 BV/hr, a temperature of 69°C, and an effluent pH of 4.5. Resin regeneration was done with sodium chloride or other standard regenerants. Activation was done with hydrochloric acid.

It was reported that this resin has a higher adsorptive capacity than conventional anion-exchange resins. For example, after 42 bed volumes, almost 80% of the color was still being removed.

As mentioned in the previous chapter, the main problems with these resin processes have been stated as being short resin life and variability of performance. However, none of these processes are reported completely from a chemical engineering point of view. The composition and nature of the color bodies are not reported for most systems. Therefore, it is difficult to compare these processes, or, in fact, verify that they will work on any E or C-stage feed stream. One of the goals of this thesis is to identify possible feed stream variables which will affect adsorption processes.

CHAPTER IV

EXPERIMENTAL MATERIALS & METHODS

As stated before, the objective of this experimentation was to determine the ability of an experimental resin to decolorize bleach plant effluents, and report how the composition of the effluents affect adsorption. The method chosen to generate the desired information incorporated obtaining system equilibrium information by developing adsorption isotherms, and carrying out continuous flow adsorption in a resin packed column at various flow rates and effluent compositions. This section provides information on the materials and methods utilized during this experimentation.

A. Materials

The resin, named XUS, was developed by Dow Chemical Co. It is a macroporous ion exchange resin, capable of adsorbing color bodies from bleach plant effluent streams. More information about the resin, such as how it is functionalized, was not available due to the resin's experimental status.

The bleach plant effluents used for this investigation were a chlorination stage effluent, where 30% of the chlorine was substitution with chlorine dioxide (C_D effluent), and an alkali extract effluent from the first caustic stage (E1 effluent). They were acquired from a soft wood pulp mill. It should be noted that all effluents streams were sand filtered before using in order to remove any suspended solids.

Since the C_D effluent stream at mills is typically produced at around three times the volume of E1 effluent streams, it was decided that this ratio of C_D:E1 (3:1) would be the effluent mixture of focus. The effluent streams had the following averaged properties:

	C_D (c.u./ml)	E1 (c.u./ml)	C_D/E1 (3:1) (c.u./ml)
pH as received	1.13	9.12	1.30
Color Units at rec'd pH	1497	5273	2844
Color Units at pH -7.6	2840	4859	3383

A unit of color is defined as the same amount of color that would be produced by 1mg/l of platinum, in the form of chlorplatinate ions.

B. Equipment

The equipment used during experimentation is listed below:

Equipment	Model
pH Meter	Orion digital pH/millivolt meter 611
Combination Electrode	Orion Model 9104BN
Magnetic Stirrer	VWR Model 310
Spectrophotometer	Perkin Elmer Lambda 3A UV/Vis

C. Color Measurement Method

The color of bleach plant effluents is highly dependent on pH; usually the higher the pH, the darker the color. Therefore, in order to insure that color is measure in a uniform way, a standard procedure has to be followed. The standard color measurement procedure presented by NCASI Technical Bulletin #253 was used to determine the amount of color in the effluents.[13] The procedure incorporates the following steps:

1. Adjustment of the pH of the BPE to 7.6 with either HCl or NaOH.
2. Measurement of the absorbance of a standard 500 color unit platinum-cobalt solution at 465nm by spectrophotometry, against distilled water.
3. Measurement of the absorbance of the adjusted BPE sample at 465nm. against distilled water.
4. Determination of the correlation between absorbance and color units.

5. Determination of the color units of the BPE.

D. Laboratory Procedures

In order to construct adsorption isotherms, various amounts of resin, from 0.1 grams to 30.0 grams, were mixed into 30.0 grams of effluent and stirred by magnetic stirrer for an hour. After the resin beads were filtered out, the change in the effluent color was determined by absorbance readings using a spectrophotometer. The experimentation was carried out on a CD/E1 (3:1) mixture at 22°C, and a pH of 1.3.

The rest of the experimentation was carried out in a packed bed configuration at room temperature, unless otherwise stated. A pipette with a inner diameter of 0.75 inches was used as the column. Gravitational flow was the means of effluent transport. The diagram in Figure 2 illustrates the column setup.

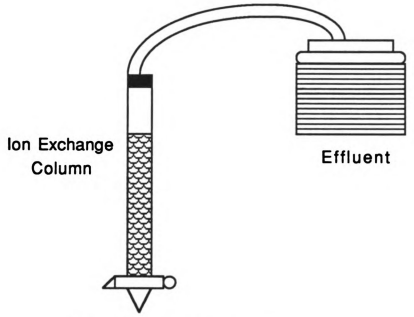


Figure 2 Ion Exchange Column

The experimental BPE decolorization procedure was as follows:

1. Presoak resin beads in water.
2. Pack column with desired bed volume of resin (usually 30 ml).

3. Sand filtration of effluents.
4. Combine E-stage and C-stage effluents in desired portions.
5. Measure pH and color of effluent mixture.
6. Run effluent mixture through column by suction & gravitational force.
7. Adjust pH to 7.6 with HCl or NaOH.
8. Measure change in color by spectrophotometry.

The experimental resin regeneration procedure was as follows:

1. Prepare NaOH solution to desired concentration and temperature.
2. Run solution through column by gravitational flow.
3. Adjust effluent to pH of 7.6.
4. Measure the amount of color eluted from the resin by spectrophotometry.

E. Limitations

The difficulties encountered during experimentation mainly were caused by limited supply of bleach plant effluent, and the challenge to regulate the flow of the effluent through the column due to the lack of a pump.

CHAPTER V

PRESENTATION OF RESULTS

The objective of this thesis is to report how feed stream variables, namely the effluent composition and flow rate, affect bleach plant effluent decolorization, using an experimental resin, XUS, as the adsorbent. By determining the rate controlling mechanism and evaluating how the variables affect it, a better understanding of adsorption systems for decolorization of bleach plant effluents can be gained.

This section reports the adsorption equilibria for this system, and its rate controlling mechanism. Results from regeneration experimentation are also presented here.

A. Adsorption Isotherms

A batch experiment was done to determine the process equilibria between the BPE and XUS resin by relating the amount of color that could be adsorbed for various amounts of resin. This experimentation was carried out at 22ºC, using an effluent mixture of C_D and E1 at a ratio of 3:1, which produced a pH of 1.3. A contact time of one hour between the effluent mixture and the resin was allowed. This time was deemed adequate for equilibrium conditions to occur by substantiating that longer contact times could not remove any more color.

A representation of this adsorption isotherm, as seen in Figure 3, was prepared by graphing the amount of color adsorbed per gram of resin, q, versus the amount of color remaining in the solution after adsorption, y.

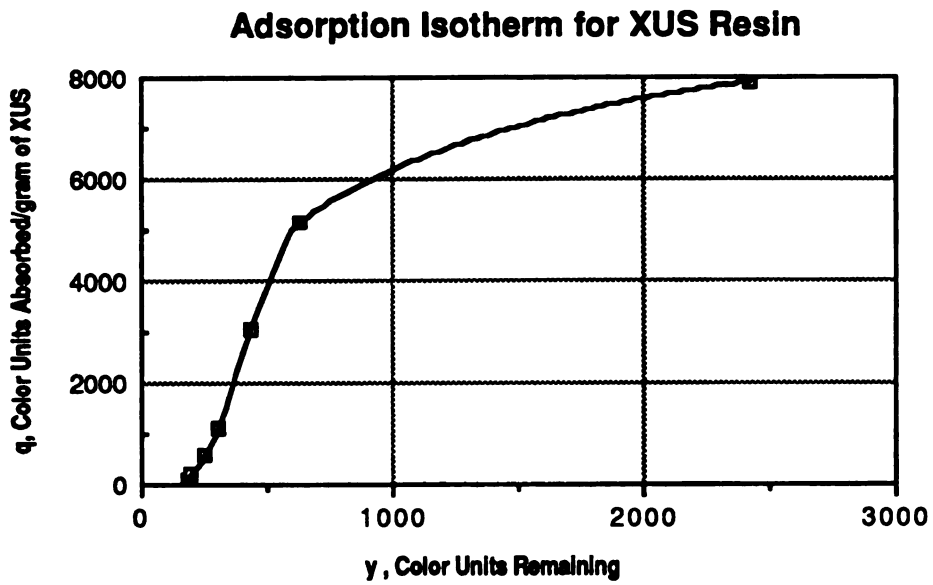


Figure 3 Adsorption Isotherm

From Figure 3, it appears that adsorption is unfavorable for q under 1500 (i.e mixing the BPE with an increased amount of resin does not increase the decolorization rate at this point, as noted by the slight concave up nature of the curve), and favorable at low to moderate dosages of resin (i.e., there is an increase in decolorization rate with increasing the resin dosage up to some point , as noted by the concave down nature of the curve).

It should be stated here that for some of the experimentation that will be presented later, it was assumed that the equilibria is linear at low concentrations (i.e. under 1000 C.U.). Thus, for that case, the distribution coefficient obtain from the graph for this region was determined to be 11.57 cm^3/gram.

The data were fitted to the Freundlich isotherm equation, given by $q = K y^n$, to gain further information about the process equilibria. This isotherm represented the data fairly well, as indicated by the straight line obtain in Figure 4, when ln (q) was plotted against ln (y). The slope of the line is equal to the value of n, which was determined from the graph to be 3.12. This value indicates that adsorption is not favorable for all the color constituents in the bleach plant effluents, since a value over 1 means that increasing the adsorbent dose may not significantly improve color adsorption. This may be due to the fact

that some of the color bodies seem to be unremovable regardless of the amount of resin used.

When an excessive amount of resin (30 grams) was contacted with 30 grams of BPE, 5% of the color remained. Thus, it is this percentage of color bodies that makes this system seem slightly unfavorable. However, despite the fact that this process may be slightly unfavorable, useful information still can be gained from studying it.

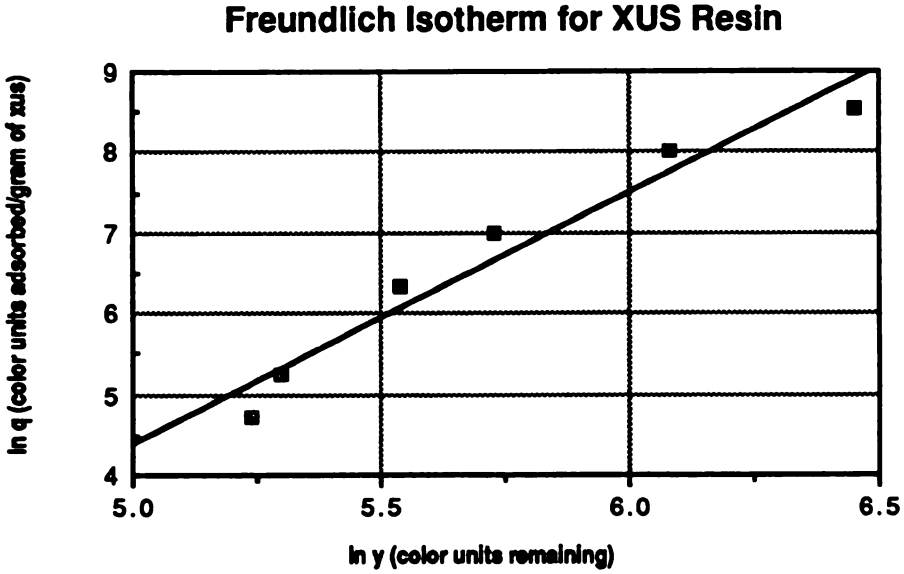


Figure 4 Freundlich Isotherm

The the data were also fitted to the Langmuir isotherm equation. However, the system was not represented well by this isotherm.

B. Determination of Rate Mechanism

In order to evaluate how certain process variables related to the success of an adsorption decolorization system, a process model was needed. Thus, it was necessary to determine the rate controlling mechanism for the adsorption of color from bleach plant effluents on XUS resin. Liquid-film diffusion control, solid diffusion control, chemical reaction control, and combination effects were investigated. Figure 5 is a representation of these mechanisms.

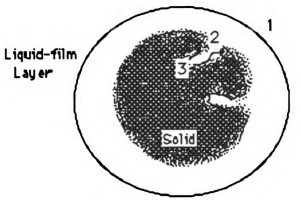


Figure 5 Adsorption Steps in Porous Solid

Point 1 indicates mass transfer of the color bodies in the liquid solution to the external surface of the adsorbent. If this is the rate controlling step, the accumulation of color on the adsorbent can be represented by:

$$dq/dt = k_L s\,(C - C_i^*) \qquad [5\text{-}1]$$

where q is the concentration of color adsorbed, $k_L s$ is the liquid mass transfer coefficient multiplied by the adsorbent area, C is the concentration of color in the bulk solution, and C_i^* is the color concentration in the liquid phase that would be in equilibrium with the concentration of the color on the surface of the adsorbent.

Point 2 illustrates diffusion within the pore of the adsorbent. If this mechanism is rate controlling, a representative equation is as follows:

$$\partial q/\partial t = \mathcal{D}a / r^2\,[\partial / \partial r\,(r^2\,\partial q / \partial r)] \qquad [5\text{-}2]$$

where $\mathcal{D}a$ is the effective diffusivity, and r is the radial distance from the center of the pellet.

Position 3 illustrates the adsorption of the color bodies on the adsorbent, which, if rate controlling, would result in equation 5-3.

$$dq/dt = k_1\,(a - q)\,C_o - k_2\,q\,(C_o - C) \qquad [5\text{-}3]$$

The variable k is the rate constant, and a is the saturated resin capacity. C_o is the initial amount of color in the effluent mixture.

Each mechanism is evaluated below to determine its importance to describing this adsorption system.

1. Liquid-film Mass-transport Control

A liquid-film mass-transport control model developed by Carberry was used in order to determine if the diffusion of the color bodies through the effluent to the resin surface is the rate determining mechanism.[14] The model assumes a favorable non-linear equilibrium, which does not seem to be the case over the entire concentration range for the system being studied. Therefore, when analyzing the experimental results with this model, care was taken to stay within the concentration range that produced favorable adsorption.

The model was developed using the following variables:

a - saturated resin capacity, C.U. / g resin

C - concentration of unadsorbed color, C.U. / ml

Co - initial amount of color in effluent, C.U. / ml

k_L - liquid-film coefficient, cm / min

q - adsorbed color, C.U. / g resin

s - external surface area of resin per mass of resin, cm^2 / g resin

V - volumetric flow rate, ml / min

x - weight of used resin bed, grams

y_L - liquid volume treated, ml

where C.U. stands for color units.

The liquid phase transfer of color bodies when strong adsorption occurs (i.e. C_i^* is negligible) and the overall material balance can be represented by the following equations, respectively :[14]

$$d\,q / d\,t = k_L s\, C \qquad [5\text{-}4]$$

$$\partial\,(C/C_o) / \partial x + a / C_o\ \partial\,(q/a) / \partial y_L = 0 \qquad [5\text{-}5]$$

The manipulation and integration of the above equations gives the following model for liquid-film mass-transport control :

$$\ln (C/C_o) = (k_L s\, C_o / a\, V)\, y_L - (k_L\, s\, x / V - 1) \qquad [5\text{-}6]$$

An attempt was made to fit data from continuous flow runs in a resin packed column (where the flow rate was varied for each run), to the above model in equation 5-6. The data was in the form of the fraction of color leakage (C/C_o) as a function of the amount of effluent treated.

The model indicates that there should be a linear relationship between the ln C/C_o vs. the volume of treated effluent. Thus, a straight line would indicate a process that can be modeled with the above equation. However, to confirm liquid-film mass control, the mass transfer coefficient, $k_L s$, should be proportional to the flow rate raised to the 0.5 power, while being independent of the bed height, based on the correlation for the mass transfer coefficient in a packed bed:[15]

$$k_L = 1.17\ (d / \nu)^{-0.42}\ (\nu / \mathcal{D})^{-0.67}\ U^{0.58} \qquad [5\text{-}7].$$

From Figure 6, for the decolorization of a C_D/E1 (3:1) mixture at 33.4 BV/hr and x = 25.95 grams, it can be seen that other mechanisms must play a role in the adsorption. A line is obtained from $C/C_o = 0$ to about $C/C_o = 0.35$, after which time the line begins to curve.

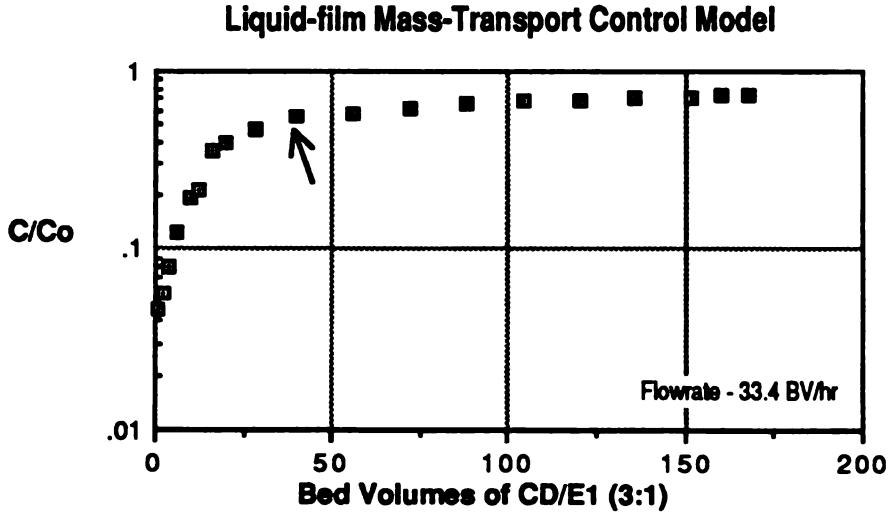


Figure 6 Liquid-film Mass Transport Model - 33.4 BV/hr

The curve levels out at about C/Co = 0.5, indicating that over 50% of the color bodies cannot be adsorbed after the resin reaches a certain saturation. Figures 7 and 8, illustrating the liquid control model at 21.4 BV/hr and 12.25 BV/hr, respectively, show a

similar leveling off in the adsorption rate. However, the lower the flow rate, the greater the volume of effluent that can be treated before this breakthrough of color begins. An understanding of the effluent mixture's makeup is needed to understand one of the explanations for what is happening.

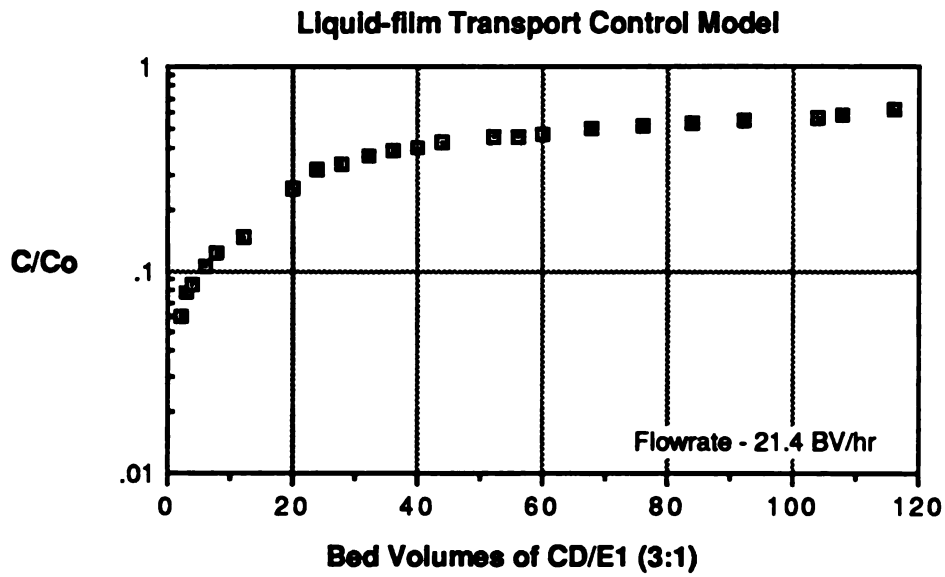


Figure 7 Liquid-film Mass Transport Model - 21.4 BV/hr

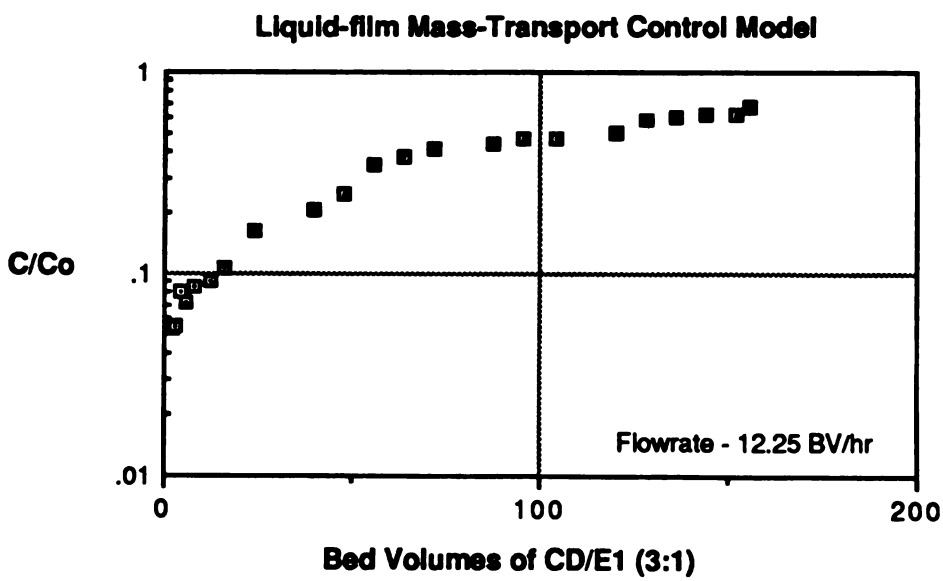


Figure 8 Liquid-film Mass Transport Model -12.25 BV/hr

The E-stage effluent contributes about 36% of the color to the mixture, and, as stated earlier, it contains a lot of high molecular weight material. Also, from previous experimentation, it is known that the XUS resin can treat large volumes of C_D-stage effluent at high flow rates before color leakage occurs (see Figure 9). Thus, it appears that at low resin saturation, most of the color materials in both the E and C_D -stages are adsorbed. Then, at higher resin saturation, it appears that it becomes difficult to adsorb the high molecular weight material, and thus, the breakthrough of that material occurs.

Though the existence of solid diffusion resistances will be discussed in the next section, it is important to note that the improvement in adsorption with lower flow rates may occur due to the fact that longer contact times assist the diffusion of the larger molecular weight molecules into the pores to a vacant site for adsorption.

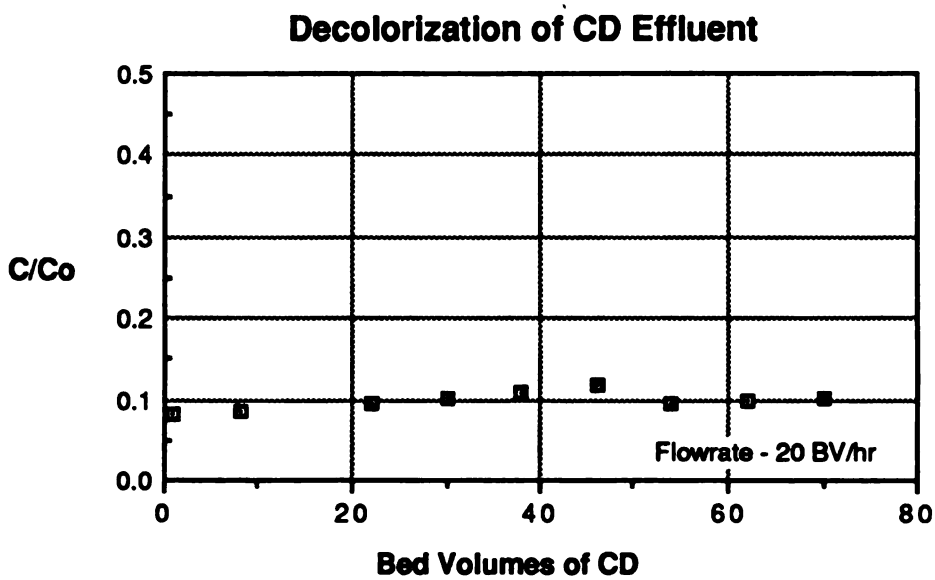


Figure 9 Decolorization of C-stage Effluent

In Figure 9, 70 bed volumes of C_D effluent can be treated with only 10% leakage of color. After the same volume of 3:1 C_D/E1 mixture, there is over 50% leakage of color, as shown in Figure 7.

When the liquid-film control model given by equation 5-6 is applied to the color leakage range from $C/C_o = 0$ to 0.36, graphical solutions such as Figure 10, 11, and 12 are

obtained. With ($k_L s\ x/V - 1$) being the y-intercept and ($k_L s\ C_o / aV$) being the slope of the line, values for $k_L s$ were determined for various flow rates, as shown in Table 5.

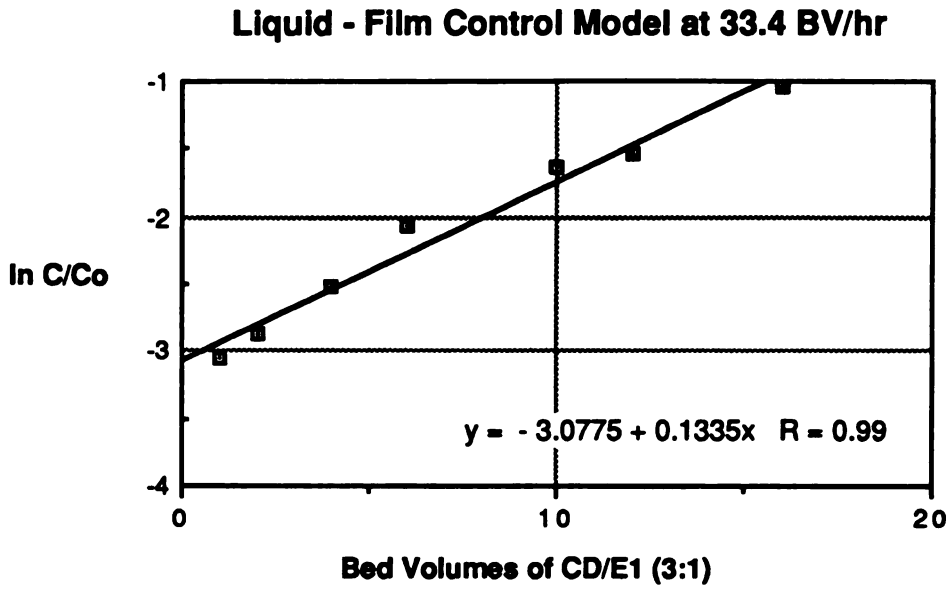


Figure 10 Liquid Diffusion Control Model - 33.4 BV/hr

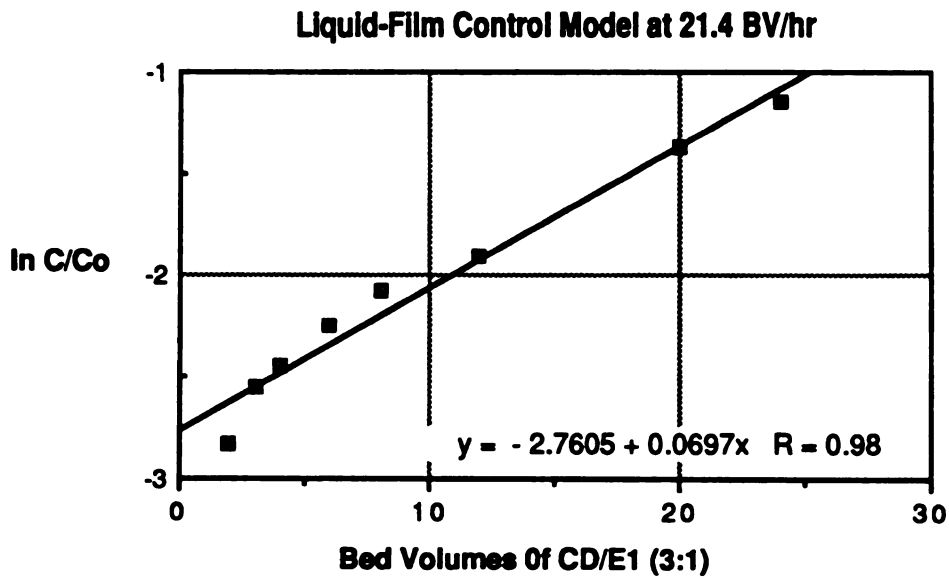


Figure 11 Liquid Diffusion Control Model - 21.4 BV/hr

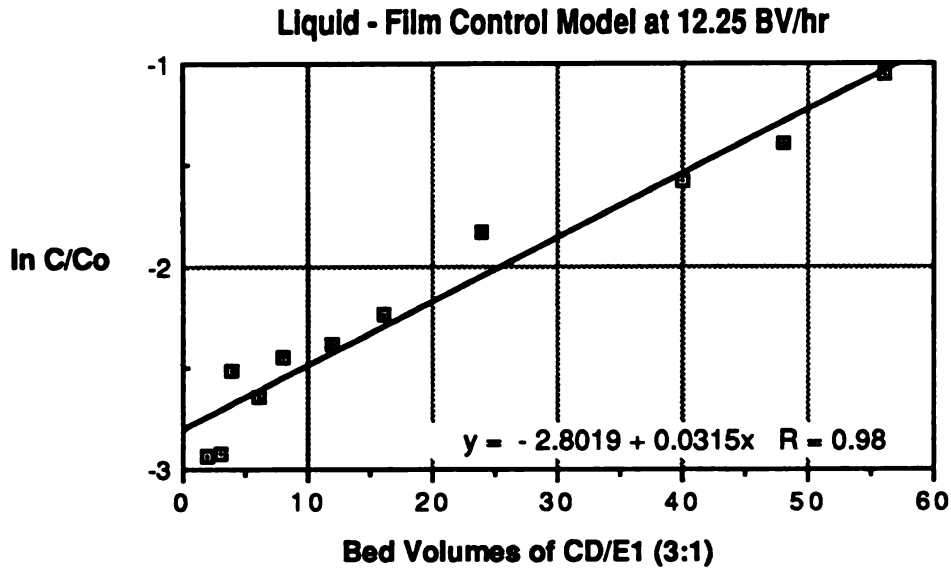


Figure 12 Liquid Diffusion Control Model - 12.25 BV/hr

Table 5 Mass-Transport Coefficients for Various Flow rates

BV/hr	V (ml/min)	Slope	Intercept	$k_L s$ (cm^3/g-min)
12.25	6.1	0.0315	-2.802	0.425
21.4	10.7	0.0700	-2.761	0.726
33.4	16.7	0.1335	-3.078	1.336

While straight lines where obtained from the graphs of ln (C/C_o) versus the volume of treated effluent, it was still necessary to determine what relationship the mass transfer coefficient has with velocity and bed height before it can be said that liquid-film mass transport controls this process.

In Figure 13 a graph of $k_L s$ as a function of flow rate was constructed. From this graph it was determined that $k_L s$ is nearly directly proportional to the volumetric flow rate. This relationship indicates that the system being studied is not solely liquid-film mass transport controlled.

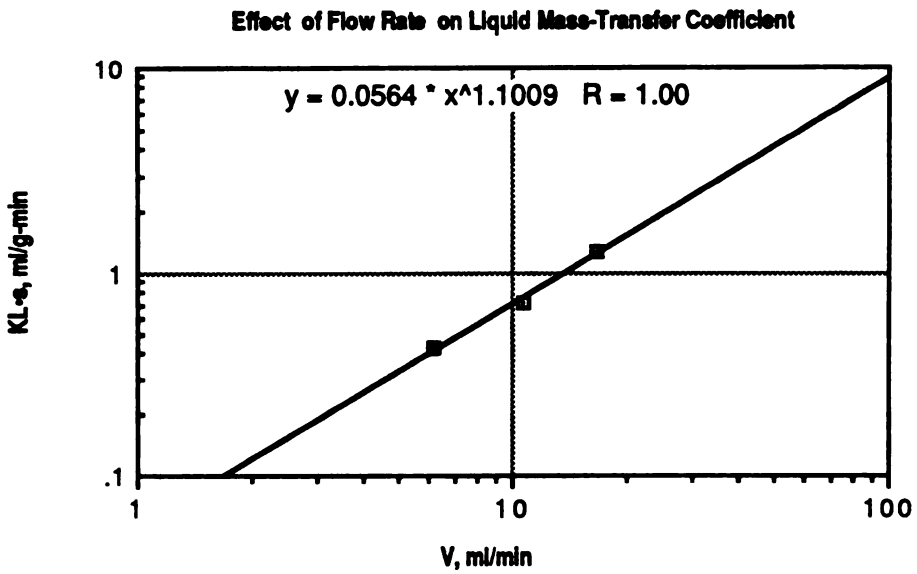


Figure 13 Mass Transfer Coefficient as a Function of Flow rate

Theoretical Mass Transfer Coefficients

The mass transfer coefficients calculated in Table 5 (determined from eqn. 5-6) are actually overall mass transfer coefficients. The liquid-film control model used to derive the coefficients assumes that the overall mass transfer coefficient, $K_o s$, is equal to the liquid mass transfer coefficient, $k_L s$. By using a mass transfer correlation for mass transfer in the liquid phase in packed beds, it can be seen to what degree liquid-phase diffusion plays a role in the overall rate mechanism. The following mass transfer correlation was used:[15]

$$k_L / U = 1.17 (d U / \mathcal{V})^{-0.42} (\mathcal{V} / \mathcal{D})^{-0.67} \qquad [5\text{-}8]$$

where,

d - diameter of pellet

$\mathcal{D}$ - diffusion coefficient

$\mathcal{V}$ - kinematic viscosity

U - Velocity

The average particle size was taken to be 0.039 cm, the diffusivity assumed to be $1X10^{-5}$ cm^2/sec, the kinematic viscosity was calculated to be 0.01 cm^2/sec, and the density of the resin to be 0.865 g/cm^3. The external area of the resin pellet per mass of resin, s, was

calculated from $s = 6(1-\varepsilon)/\rho d$, where ε and ρ are the porosity and density of the bed, respectively.

The value of $k_L s$ at various flow rates was calculated and compared to the values obtained experimentally. If the experimental mass transfer is assume to really represent the overall mass transfer coefficient, and the mass transfer coefficient calculated from the correlation is assume to be the true liquid-phase mass transfer coefficient, an estimate of the solid-phase mass transfer coefficient can be obtained from the relationship that $1/K_o s = 1/k_L s + 1/k_x s$, with $k_x s$ being the solid-phase mass transfer coefficient. The values of the mass transfer coefficients are listed in Table 6.

Table 6 Comparison of Mass Transfer Coefficients

BV/hr	U (cm/min)	$k_L s$ (experimental) (cm^3/g-min)	$k_L s$ (correlation) (cm^3/g-min)	$k_x s$ (cm^3/g-min)
12.25	2.15	0.425	6.26	0.456
21.4	3.75	0.726	8.96	0.790
33.40	5.86	1.336	11.22	1.520

From the results obtained, liquid-phase diffusion for the system being studied is not likely to be the controlling mechanism. The experimental mass transfer coefficients are an order of magnitude lower than those predicted by the correlation. This could be due to an underestimation of the diffusion coefficient and/or serve as an indication that solid phase diffusion plays a key role in this system.

Bed Height Effects

To determine if the resin bed height has an effect on adsorption, the same column was packed to heights of 10.5 and 17.6 cm on two different occasions. Running 3:1 C_D/E1 effluent mixture through the different bed heights at nearly the same volumetric flow rate (10 ml/min) to minimize velocity effects, the amount of decolorization was measured. While Figure 14 shows that the longer bed decolorizes the effluent better, based on Figure 15, constructed from the liquid control model of equation 5-6, the mass transfer coefficient

for that bed is 0.465 cm^3/g-min, as compared to 0.726 for the shorter column. Thus, the mass transfer coefficient is nearly inversely proportional to the resin bed height.

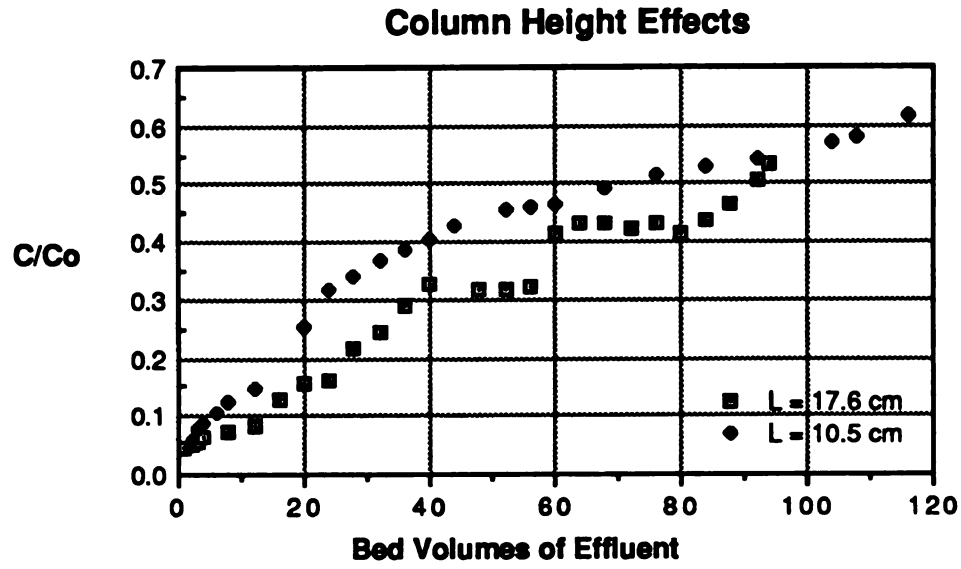


Figure 14 Effects of Resin Bed Height On Adsorption

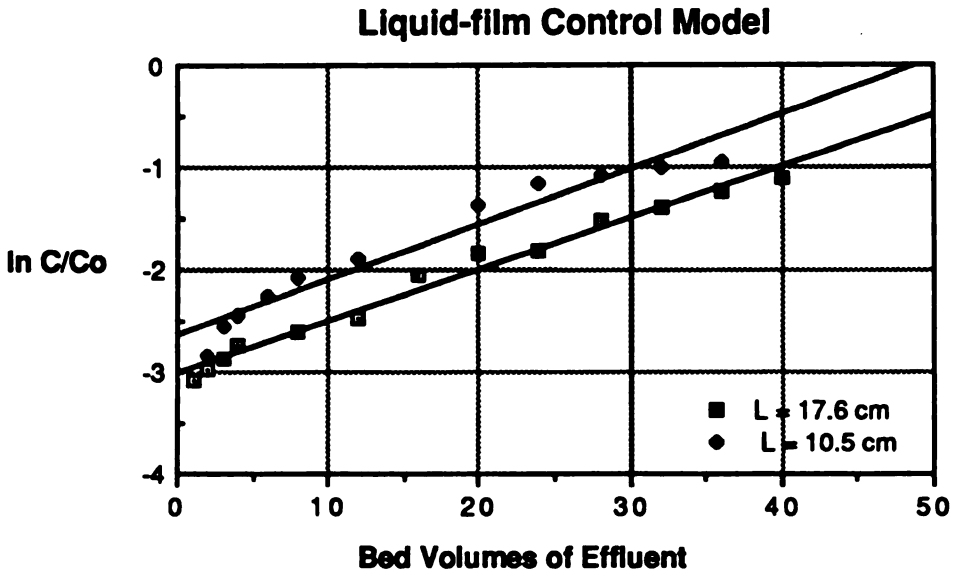


Figure 15 Effects of Height on Liquid Phase Transport

Again, the chance of liquid-film mass transfer being the primary rate controlling mechanism is diminished due to the fact that the traditional mass transfer coefficient model, as shown in equation 5-7, is independent of bed length for non linear equilibrium if fluid

properties are assumed constant (which is a reasonable assumption considering the low concentration levels of the color bodies). However, the existence of solid diffusional resistances could explain the bed height effects.

Effluent Composition Effects

Two effluent mixtures having the same pH of 4.5 but different compositions (one containing all E1 effluent, the other containing a 1:4 ratio of C_D/E1) were decolorized at 6 BV/hr. The results are shown in Figure 16 as a graph of the fraction of color remaining in solution after treatment (C/C_o) verses the number of bed volumes treated. The mixture containing only E1 adsorbs, on the average, 10% less than the mixture containing some C_D. It is known that the chlorination stream contains compounds that tend to be of lower molecular weight than compounds found in an alkaline extract stream. Thus, the effluent containing C_D may appear to be more decolorized by the XUS resin due to the fact that it may be easier to adsorb the lower molecular weight material.

When an all C_D effluent is decolorized with XUS resin, over 100 bed volumes can be treated before there is any detectable, amount of color remaining in the treated effluent, as was shown in Figure 9.

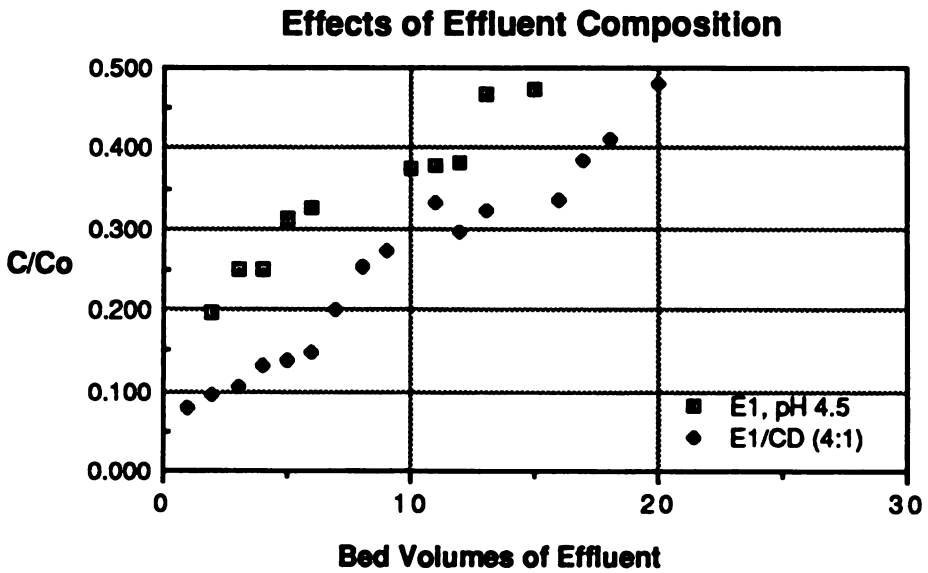


Figure 16 Effect of Effluent Type on Adsorption

To determine how much an effect the composition of the effluent has on the mass transfer rate, the mass transfer coefficient was calculated for the decolorization of the bleach plant effluent containing only the E-stage effluent. The liquid-film control model was applied up to 50% leakage of color (unlike the 36% limit utilized for the C_D/E1 mixtures). From Figure 17, $k_L s$ is 0.068 cm^3/g-min. This value is much smaller than those obtained for the 3:1 C_D/E1 mixtures, leading to the belief that the adsorption of the color bodies in the E-stage effluent is rate limiting.

The mass transfer coefficient was also calculated for the 1:4 mixture of C_D/E1 which was decolorized. When the results were fitted to the liquid control model, the value of $k_L s$ was calculated to be 0.156 cm^3/g-min with the aid of Figure 18. So just by adding a small amount of CD to the effluent stream, the mass transfer rate almost doubles. As stated earlier, the high molecular weight compounds in the E-stage effluents could be the cause of this high resistance to mass transport.

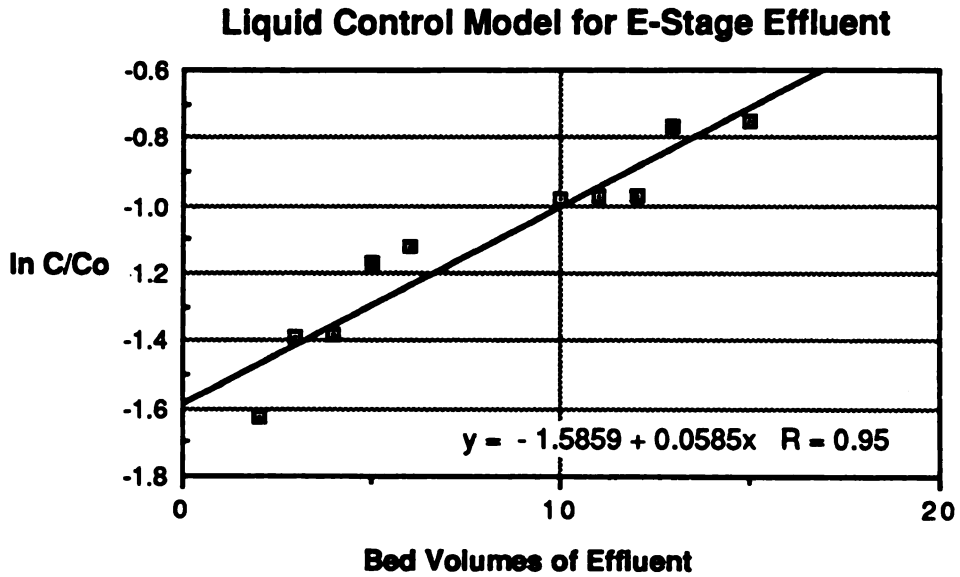


Figure 17 Effects of Composition - E-stage Effluent

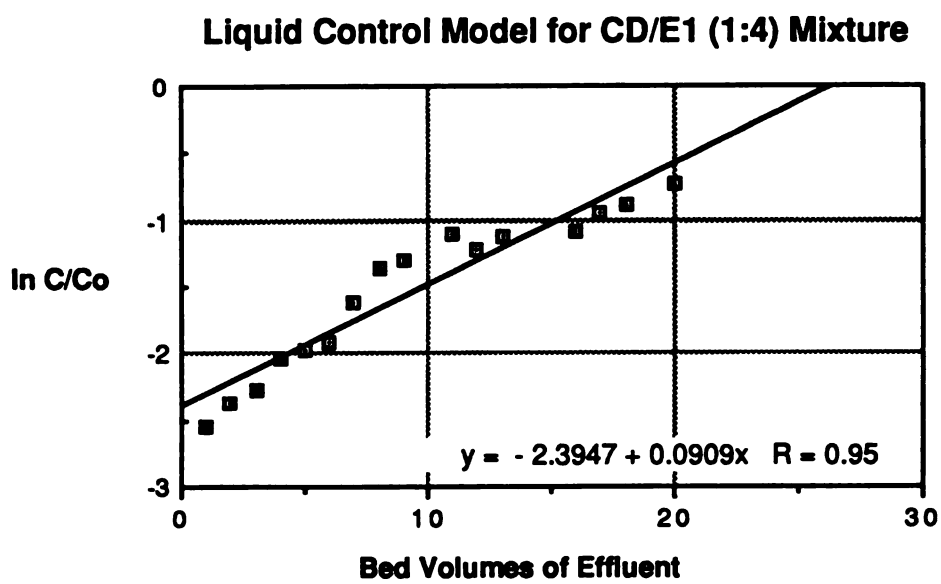


Figure 18 Effects of Composition - C_D/E1 1:4

While the model being studied appears not to be liquid-film mass transfer controlled, this model should be adequate to describe some of the process dynamics for regions of low color leakage.

Adsorption studies done with other adsorbents are presented in Appendix A.

2. Chemical Reaction Effects

One way to determine the whether chemical-reaction has any significant effect on the overall rate mechanism is to make a Wilson line plot.[16] The resistance to mass transfer, $1/k_LS$ is plotted against the inverse of the relationship that the volumetric flow rate has with the mass transfer coefficient. The idea behind the plot is that if k_LS is the true mass transfer coefficient then at very high flow rates there will be no resistance to mass transfer, and so the line should pass through zero, thus indicating that the chemical reaction must be extremely rapid.

In Figure 19 the Wilson line plot of this system has a y-intercept of close to zero. This indicates that the rate of chemical reaction (or adsorption in this case) has a negligible affect on the overall rate mechanism.

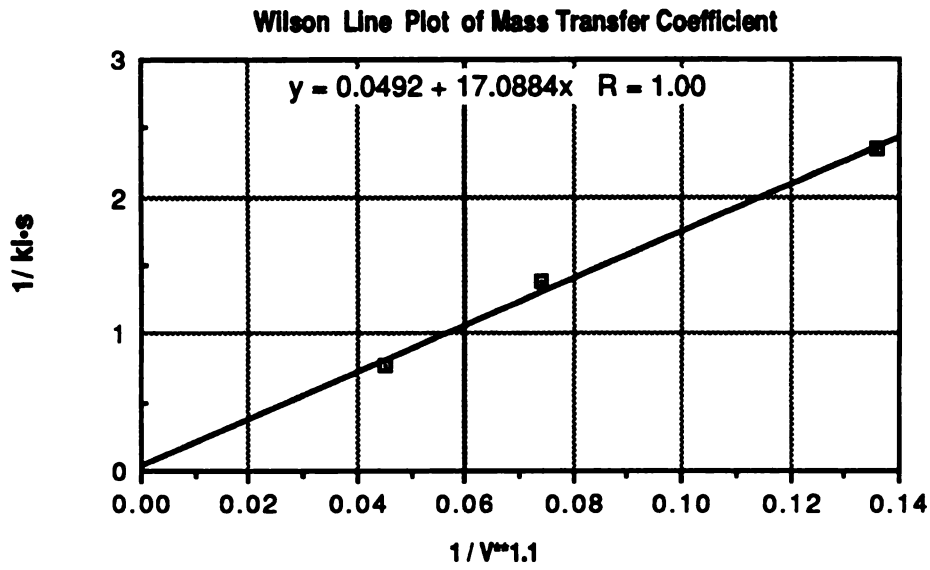


Figure 19 Wilson Plot of Mass Transfer Resistance

3. Internal Diffusion Effects

If solid diffusion has an affect on the rate mechanism, one other way for detecting its affect is to interrupt the feed of the effluent to the packed column for a short time and see how that affects adsorption. If solid diffusion gradients are present, the adsorption rate would increase after the feed is reintroduced to the column due to the equalization of the gradients during the interruption period.[17] Thus, a discontinuity of the adsorption curve will result, as evidenced by a decrease in color leakage.

A decolorization experiment was discontinued for 2 days. The results of the experiment, represented by Figure 20, gives a strong case for solid diffusion having a controlling effect on the rate mechanism, because discontinuity in the curve is present after feed interruption.

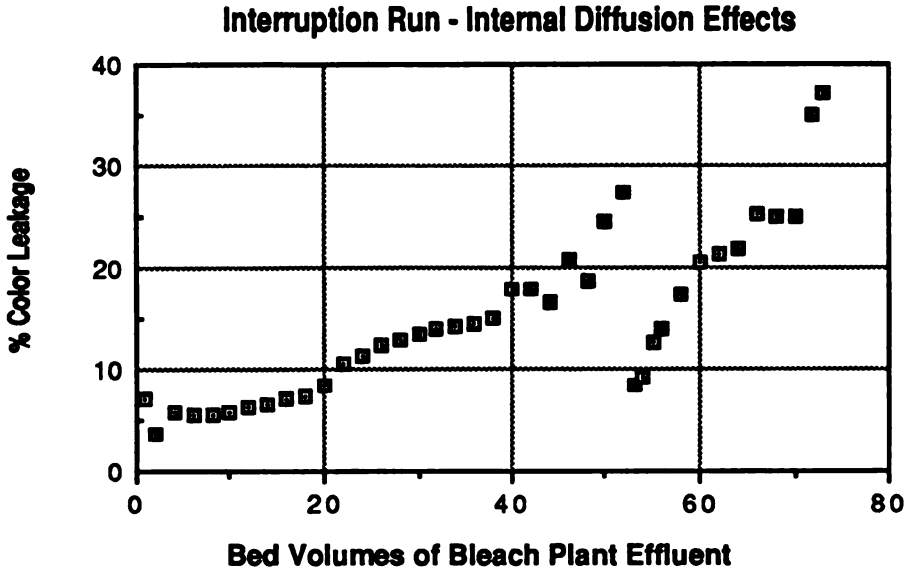


Figure 20 Solid Diffusion Effects

Upon continuing the experiment, the resin was able to decolorize the BPE almost as if the resin were new for the first few bed volumes. However, after treating 40% of the bed volumes that had been initially treated on this resin, the percentage of color leakage returned to the level it was at the point of interruption.

4. Film Resistances and Intraparticle Diffusion

The indications from the previous sections suggest that the process being studied may be controlled by both film resistance and intraparticle diffusion. Rosen developed a model for this case, with a restriction to linear equilibrium isotherms.[18] While the isotherm for this process is not linear over the entire concentration range, it is linear in the concentration range of interest.

The model is a function of time and bed length and is given in the following form:

$$C/C_o = 1/2 \{ 1 + \mathrm{erf}[(3Y/2X) - 1/(4v/X)^{1/2}] \} \qquad [5\text{-}9]$$

where

$v = \mathcal{D}_a K_D \rho / R K_f$ (film-resistance parameter)

$X = 3 \mathcal{D}_a K_D Z / m U R^2$ (bed-length parameter)

$Y = 2 \mathcal{D}_a (t - Z/U) / R^2$ (contact-time parameter)

$m = \varepsilon / (1 - \varepsilon)$

The experimental data for an effluent mixture of C_D/E1 of 3:1 at a flow rate of 33.4 BV/hr (or U=5.86 cm/min) was used to compare the system being studied to the Rosen model.

The value for the distribution coefficient, K_D, was assumed to be constant at low concentrations, and from the adsorption isotherm in Figure 3, was taken to be 11.57 cm^3/g. The overall mass transfer coefficient, K_f, was assigned the value of $1.93X10^{-4}$ cm/min calculated from the liquid-film control model. Z, t, and ε are the bed length, contact time, and bed void fraction, respectively. Since the value of the effective diffusivity, $\mathcal{D}_a$ is unknown, data provided by the Rosen model were fitted to the experimental data in order to find the value of X, which in turn gives a value of $\mathcal{D}_a$.

With the value of v/X is not being dependent on the diffusivity directly, it was calculated to be 0.168. The values of v/X provided in the article by Rosen that are closes to the experimental value are v/X=0.1 and 0.2. Fitting the theoretical data, X was determined to be equal to 5. From this value, the effective diffusivity was calculated to be 3.16×10^{-7} cm^2/sec. The effective diffusivity is probably much lower at higher resin saturation as it becomes increasingly difficult for the large molecular weight color bodies to diffuse into the pores.

Figure 21 shows that this model adequately describes this adsorption system for C/Co under 0.4. However, above this value the experimental model deviates greatly. While it could be that part of this deviation is caused by the assumption that the adsorption isotherm is linear, it is believed that most of the deviation is caused by the composition of the effluent.

When the model was applied to adsorption data taken at an effluent flow rate of 21.4 BV/hr (or U=3.75 cm/min) a better fit was obtain, as seen in Figure 22. An effective diffusivity value of $8.09X10^{-8}$ cm^2/sec was calculated for this system. This is probably closer to the actual diffusivity at higher resin saturations. The deviation begins to increase after $C/C_o = 0.5$. This could be because the process becomes more solid diffusion limited with higher resin saturation.

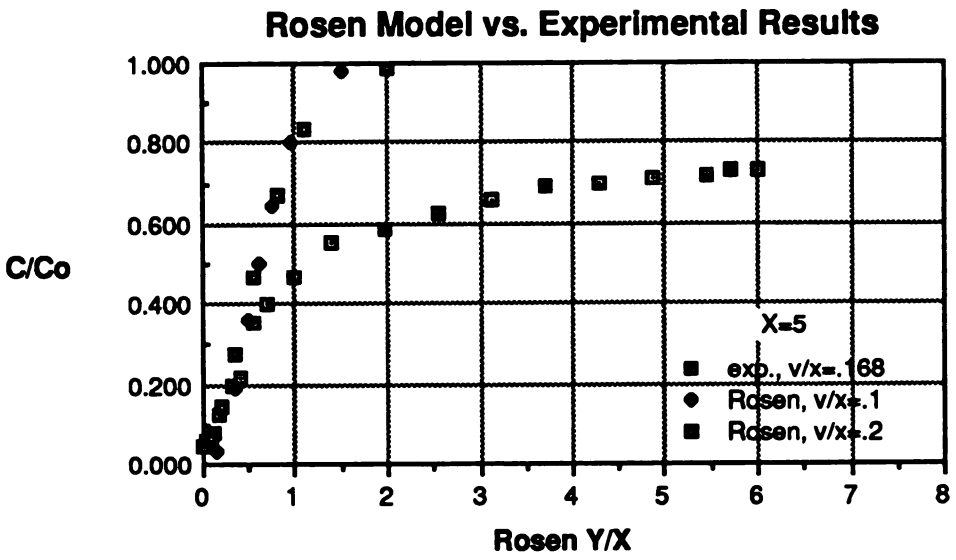


Figure 21 Liquid-phase and Solid-phase Diffusional Effects - 33.4 BV/hr

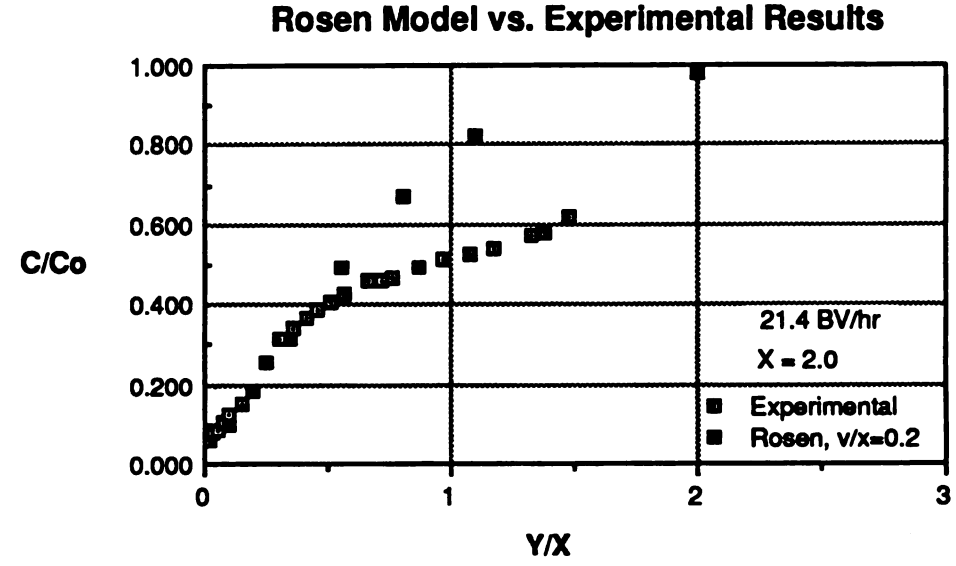


Figure 22 Liquid-phase and Solid-phase Diffusional Effects - 21.4 BV/hr

Once again, it appears that the adsorption of two different types of color bodies (high and low molecular weight) could cause the deviation in shape of the experimental curve to the theoretical curve.

It appears that the model fails to completely describe this system because some of the high molecular weight color bodies fail to be adsorbed before the resin is saturated. The low molecular weight color bodies, however, continue to be adsorbed for an extended

period of time. Thus, while the model is predicting complete breakthrough of color, nearly 40% of the color continues to be adsorbed.

The value of the diffusivity ($3.16X10^{-7}$) determined from the Rosen model was used in the correlation for the mass transfer coefficient that was given in equation 5-7. The new values determined by the correlation are give in Table 7 along with the values for the mass transfer coefficient that were obtain from the liquid-film control model of equation 5-6.

Table 7 Comparison of Mass Transfer Coefficients given by Liquid-film Model and Rosen

BV/hr	U (cm/min)	$k_L s$ (experimental) (cm^3/g-min)	$k_L s$ (correlation) (cm^3/g-min)
21.4	3.75	0.726	0.885
33.4	5.86	1.336	1.15

The mass transfer coefficient values calculated from the mass transfer correlation equation, using the an effective diffusivity value predicted by the Rosen model, are of the same order of magnitude as the mass transfer coefficient values obtain experimentally, using the liquid-film control model. This seems to indicate that the predicted diffusivity values are close to the actual values.

C. Effects of Velocity on Adsorption

When mixtures containing C_D and E1 effluents (3:1) where decolorized by the XUS resin at various flow rates, as expected, the adsorptive capacity of the resin varied (as seen in Figure 23). As the contact time decreases with increasing flow rate, the high molecular weight color bodies have less of an opportunity to diffuse into the pores of the resin.

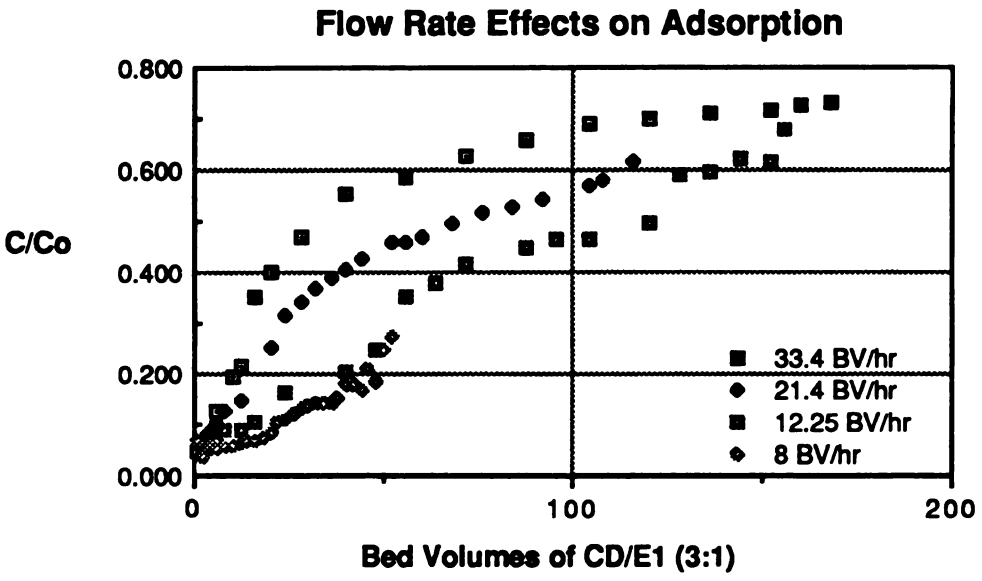


Figure 23 Effect of Flow rate on Adsorption

In Figure 24, the adsorption of the effluent mixture at 6 bed volume/hr shows that better than 90% decolorization can be obtained for over 40 bed volumes. In order to determine the optimal flow rate for a decolorization system using XUS resin, it must first be determined what degree of decolorization is desired. For an example, if only 70% decolorization is necessary, a flow rate of 12 BV/hr can be used to accomplish this for over 50 bed volumes.

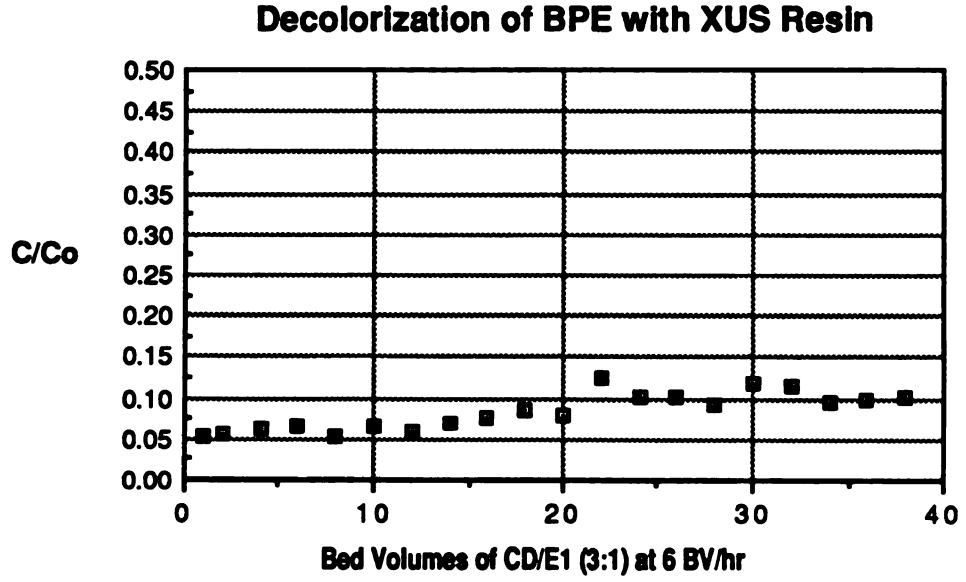


Figure 24 Fraction of Color Leakage at 6 BV/hr

D. Regeneration of Resin

As mentioned earlier, the short life of some adsorbent resins has led to their downfall, in economic terms, as components in effluent treatment systems. After becoming loaded to a certain percentage of their capacity with color bodies, the level of success achieved in restoring the resin to a reusable state determines its life and thus the value of the resin. It is for this reason that regeneration is such an important step in the decolorization cycle of bleach plant effluents.

Since caustic is usually accessible in pulp mills, sodium hydroxide was the regenerant of choice for the experimental resin. The success of regeneration was determined by the amount of color eluted from the resin and the amount of regenerant needed to elute the color. The concentration and temperature of the regenerant was varied for different runs.

In Figure 25 the results of the regeneration of the resin with 1 N NaOH at room temperature can be seen. While only about 50% of the color adsorbed during BPE decolorization eluted from the resin, the color was eluted in a form that was 10 times more concentrated. While this may provide an advantage to having less waste to dispose of, it will effect the resin life.

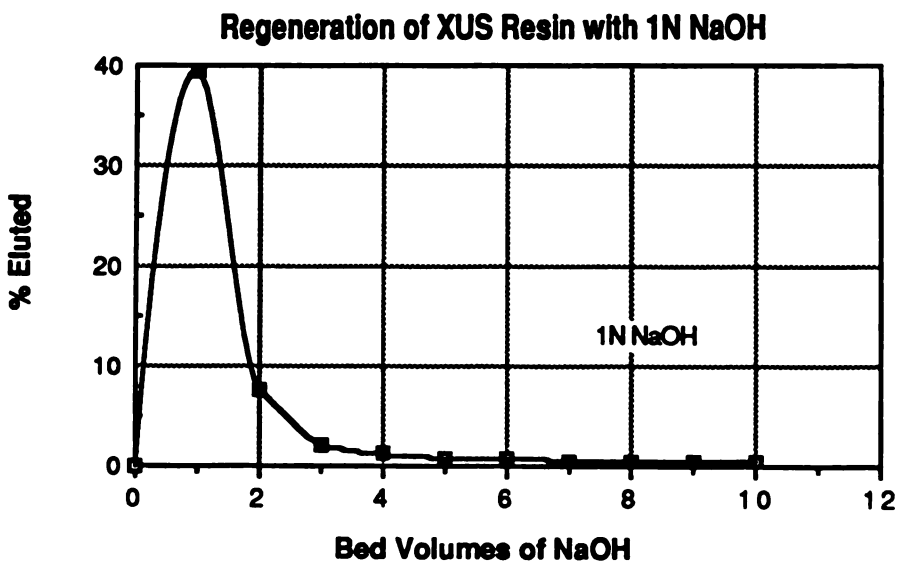


Figure 25 Regeneration with 1 N NaOH at Room Temperature

When the temperature of 1 N NaOH solution was raised to 60ºC, the amount of color eluted decreased by almost half, as seen in Figure 26. This result was unexpected since usually warmer regenerant aids resin regeneration.

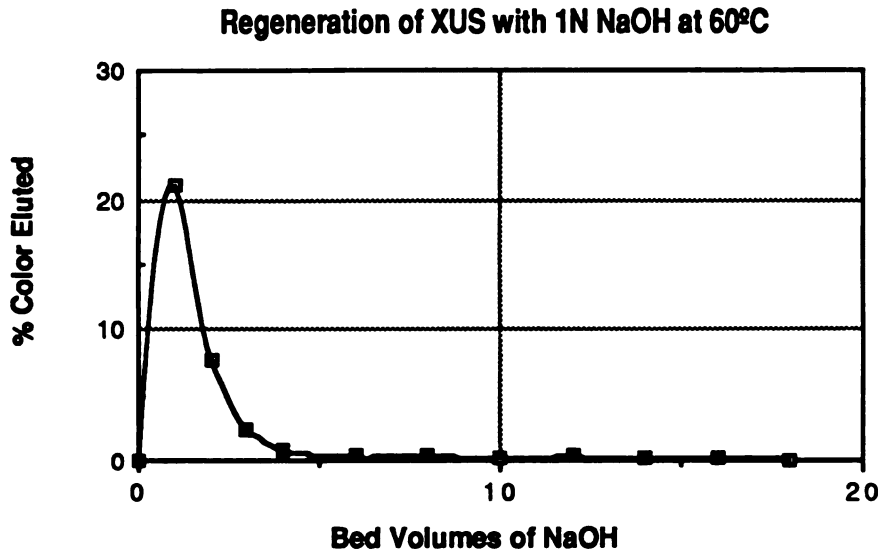


Figure 26 Regeneration with 1 N NaOH at 60 ºC

The regeneration of resin with 3 N NaOH as Figure 27 illustrates, seems to elute less color than the 1 N NaOH solution. However, one cause for this could be in the method of pH adjustment before the color measurements were made. While care was taken not to add large volumes of HCl or NaOH when adjusting the pH of treated BPE or regenerant effluent for color measurements, when 3 N NaOH was the regenerant this was sometimes unavoidable. Thus, the samples could have possibly become diluted to levels where the color measurement would be somewhat low.

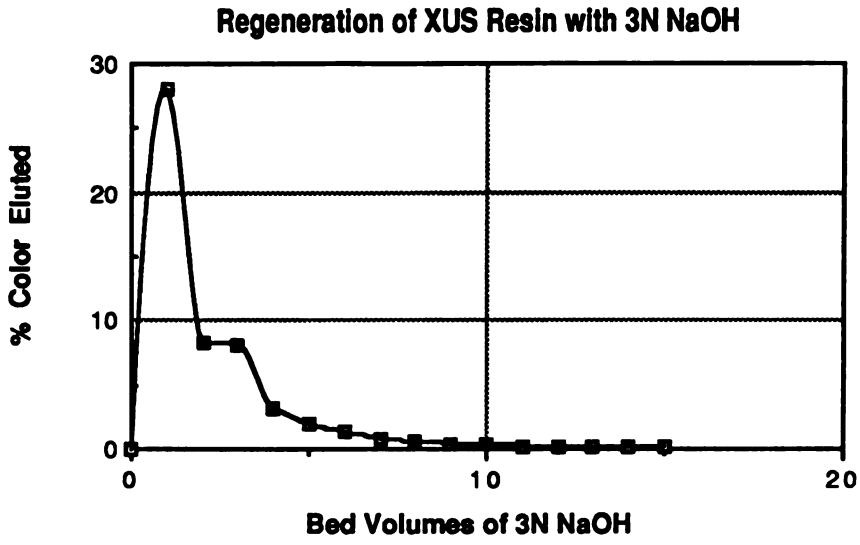


Figure 27 Regeneration with 3N NaOH at Room Temperature

CHAPTER VI

SUMMARY AND CONCLUSIONS

The hypothesis of this thesis is that the composition of the bleach plant effluent has a great impact on how successful an effluent color adsorption process will be. It is known that bleach plant effluents contain color bodies of various molecular weights. It is believed to be the high molecular weight material (MW>10,000) that must be considered when designing an adsorption system.

An effluent mixture of 3 parts C_D-stage effluent and 1 part E1-stage effluent was the focus of the investigation. Since the E1-stage effluent contains more of the highly colored material, its color contribution to the mixture turned out to be 36% of the total mixture color. From the literature it is thought that 30% of the colored material in C-stage effluent and over 75% of the colored material in the E-stage effluent have molecular weights over 10,000. Thus, a 3:1 mixture of C_D to E1 would be made up of around 50% of the colored material with molecular weights over 10,000.

From the liquid-film control model that was applied to the experimental adsorption data, it was observed that after an undetermined resin saturation, over 50-60% of the material could no longer be adsorbed. When the data were applied to the Rosen model, which takes into account both liquid and solid phase resistances, it was noted that after a certain resin saturation, solid diffusional resistances increased drastically. For both of these models, over 30% of the color continues to be adsorbed after a very large number of bed volumes have been treated, thus, the resin has not been completely saturated. It is believed that only the small molecular weight color bodies can be adsorbed into the pores during this range.

The rate controlling mechanism for this process was investigated in order to find out more information on how process variables affect adsorption. From the fact that the mass transfer coefficient varied linearly with flow rate and inversely with bed height, and that solid diffusional resistances were determined to exist from results of an interrupted decolorization experiment, it was determined that both liquid and diffusion phase resistances are controlling. The actual adsorption step was ruled to be negligible.

Even though solid diffusion is very important for the system being studied, the liquid-film control model seem adequate to describe the system. From this model, valuable information was obtained concerning how mass transfer is affected by the effluent composition. The mass transfer coefficient almost doubled when adsorption was done on a 1: 4 mixture of CD to E1 as opposed to treating a stream containing only E-stage effluent.

From the Rosen model, a value of $3X10^{-7}$ cm^2/sec was calculated to be the effective diffusivity for color breakthrough under 50%. When this value is used in a mass transfer coefficient correlation, the value obtained is close to the mass transfer coefficient values obtain from the liquid-film control model. The value is probably much lower above 50% color breakthrough, but the model was not equipped to describe this process for this range. However, for a process design, the range of interest is usually under 20% color breakthrough, so the Rosen model is adequate to interpret results.

Adsorption decreased drastically with increasing flow rate. Since solid phase diffusion plays such a major role with the high molecular weight color bodies, the shorter the contact time, the less of an opportunity they have to diffuse into the pores.

When the XUS resin's ability to decolorize BPE is compared with other ion exchange/adsorbent resins, it is competitive. At 12 BV/hr the experimental resin decolorizes 80% of the color of 3:1 C_D/E1 effluent mixture, as compared with 75% after 36 BV as reported by Rock, for the XAD-8 resin. At 6 BV/hr, the experimental resin decolorized about 90% of the color for 40 bed volumes, as compared with 79% decolorization after 42 bed volumes, as reported in the Dow patent, at the same flow rate. By noting the large volumes of bleach plant effluent the experimental resin was able to

treat, the capacity of the resin is excellent. However, if the experimental XUS resin is used at flow rates fast enough to process the large volumes of BPE that need to be processed its performance will undoubtedly be impaired.

Future experimentation should include an accurate method for determining the molecular weight distribution of the bleach plant effluent before and after treatment.

If an effective and efficient adsorption process is to be developed in the future to decolorized bleach plant effluents, care must be taken to understand the characteristics and compositions of the streams, since they may vary from mill to mill, and from day to day. Also, it may be necessary to use two types of adsorbents - one to remove the low molecular weight color bodies, and another to remove the high molecular weight material. By removing the low molecular weight material first, a larger pore adsorbent can be used to remove the rest of the color without worrying about the loss of surface area due to the larger pores.

APPENDIX

APPENDIX A

RESULTS FROM ACTIVATED CARBON AND MSA-1 RESIN ADSORPTION STUDIES

In addition to using the experimental XUS resin to decolorize bleach plant effluents, experimentation also was done with activated carbon and a resin named MSA-1 as adsorbents. While both worked well as adsorbents, regenerating them proved difficult. Thus, they were not the focus of this examination. However, results from adsorption studies utilizing them are presented here to illustrate how other adsorbents perform.

Activated Carbon

Adsorption Isotherms were constructed from experimental results to show activated carbon's ability to decolorize bleach plant effluents. Activated carbon in both powdered and granular forms was used. It should be noted that synthetic BPE made from Indulin AT (Westvaco) was used for this experimentation, so direct comparison between results presented here and results found in the body of this thesis should not be made.

For the isotherm utilizing powdered activated carbon (PAC) as the adsorbent, the pH of the effluent was 8.17, while the temperature was 22°C. The experimental procedure for obtaining the isotherm data was the same as followed in chapter 3 of this thesis, except the contact time was 1/2 hour. Figure 28 represents the Freundlich isotherm obtain with these conditions when ln q verse the ln y was plotted. A value of about 1.09 was obtained for n, which indicates favorable adsorption.

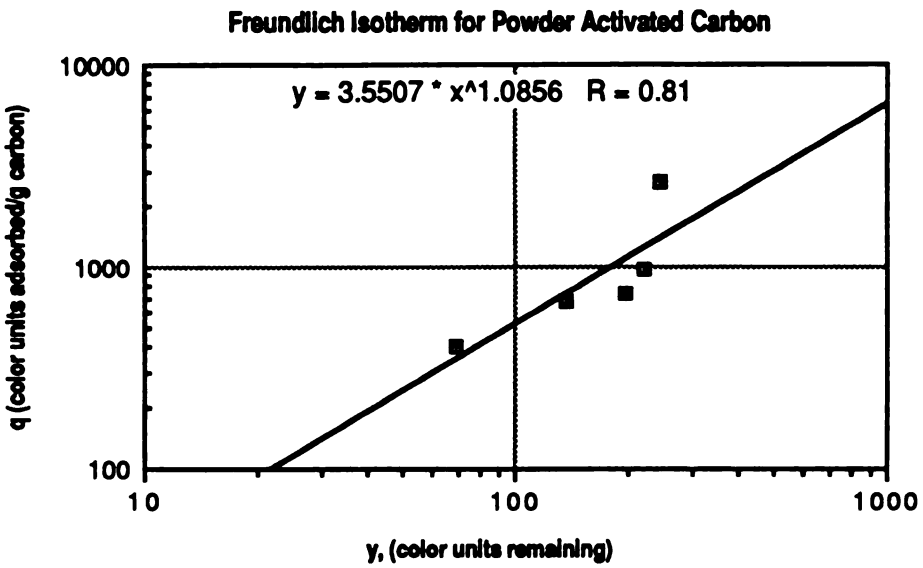


Figure 28 Adsorption Isotherm for Powdered Activated Carbon

For experimentation with granular activated carbon (12-20 mesh), the effluent had a pH of 7.0, and a temperature of 22°C. Again, the contact time between the carbon and the effluent was 1/2 hour. The results were fitted to the Freundlich Isotherm equation and Figure 29 was produced. The value for n in this case was 1.26, which is also in the favorable adsorption range.

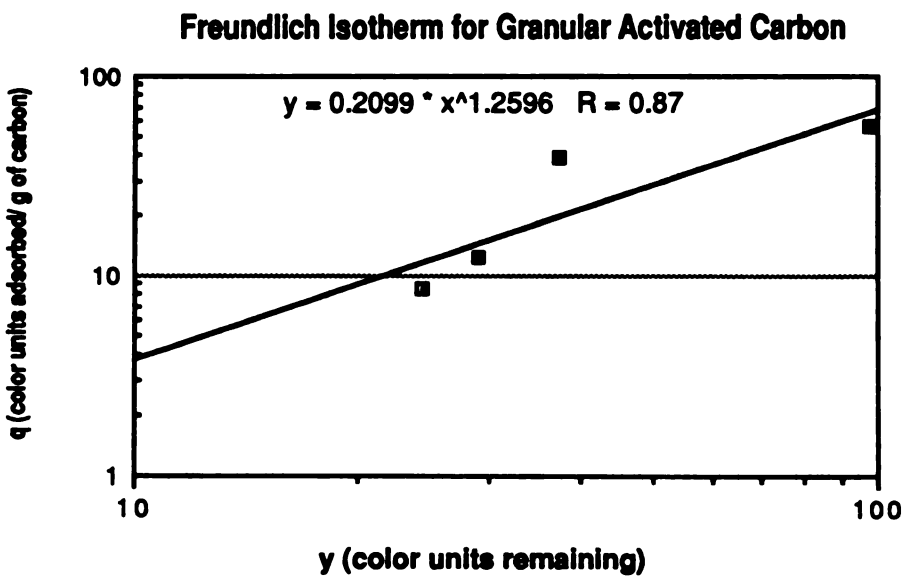


Figure 29 Adsorption Isotherm for Granular Activated Carbon

Regeneration of activated carbon usually is done by thermal heating. It is suspected that regenerating the carbon by this method may make and activated carbon

system fro decolorizing BPE too expensive, considering the large volumes of BPE that must be treated. Thus, adsorbent resins were investigated.

MSA-1 Resin

MSA-1 is a strong base macro porous anion exchange resin developed by Dow Chemical Co. Decolorization experimentation using this resin as an adsorbent was done using both the synthetic and the real BPE.

A Freundlich isotherm was constructed using results from batch experimentation utilizing synthetic BPE at a pH of 7.1 and a temperature of 22°C. The contact time was 1/2 hour. Figure 30 is an illustration of the graph produced. The value obtained for n was 0.66. This value was the smallest for the adsorbents tested.

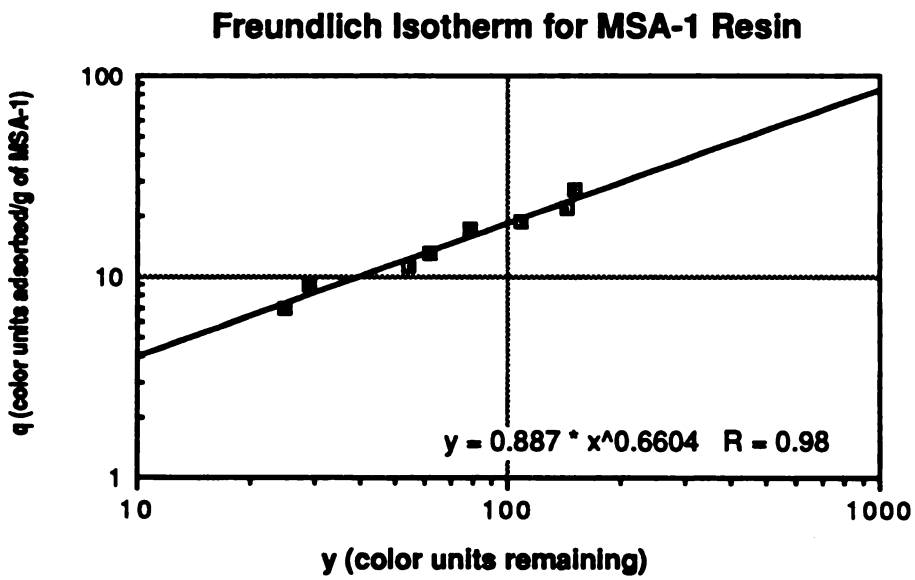


Figure 30 Adsorption Isotherm for MSA-1 Resin

Bleach plant effluent from an actual mill was used in column testing with MSA-1. Figure 31 illustrates the amount of color leakage that occurred for each addition volume of BPE treated. One curve represents the decolorization of a mixture of C_D to E1 of 1: 2, at a pH of 2, and a flow rate of 5 BV/hr. The other curve represents the decolorization of an effluent mixture of C_D to E1 of 1: 3.75, at a pH of 4, and a flow rate of 4 BV/hr through a 30 ml bed of MSA-1.

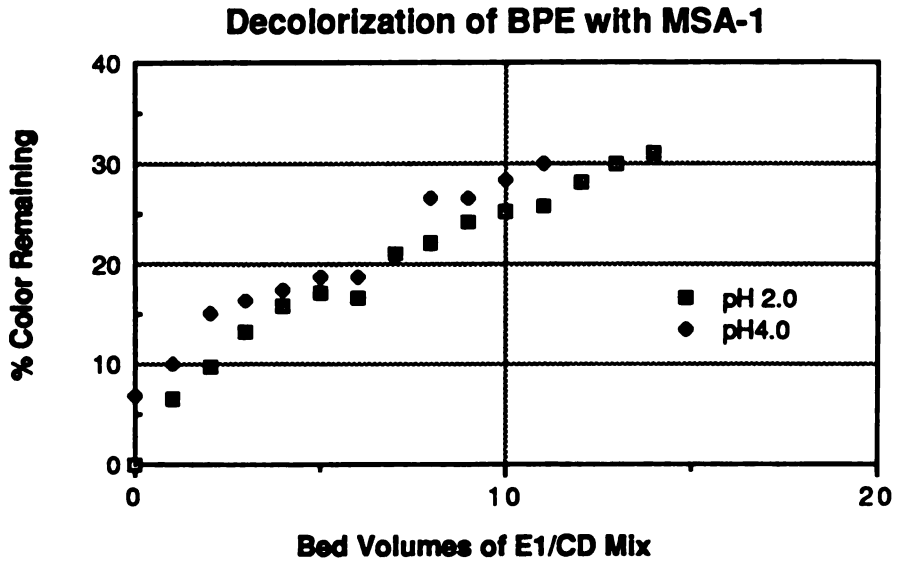


Figure 31 Decolorization of BPE with MSA-1 Resin

When this data was applied to the liquid-film control model given by equation 5-6 in this thesis, the mass transfer coefficients ($k_L s$) values of 0.137 cm^3/g-min and 0.110 cm^3/g-min were calculated from Figures 32 and 33 for the pH 2 and pH 4 mixtures, respectively. These value are comparable to those obtain for experimentation done on similarly composed effluents with XUS resin.

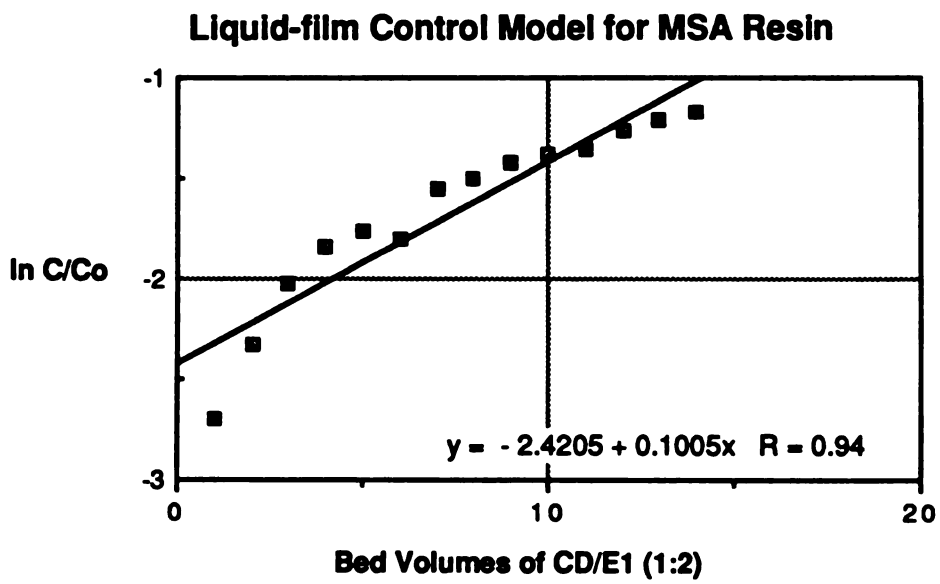


Figure 32 Liquid-film Control Model for MSA-1 Resin and BPE (pH 2)

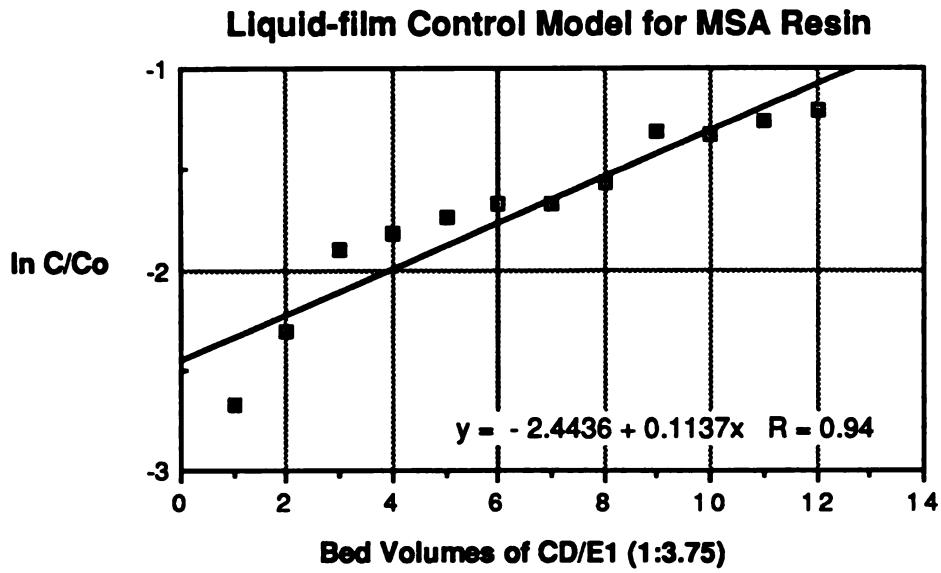


Figure 33 Liquid-film Control Model for MSA-1 Resin and BPE (pH 4)

Though the results obtain with this resin were similar to those obtained with XUS resin, regenerating the MSA-1 resin proved to be difficult, thus it was not used in further investigations. It appeared that some of the material in the effluent adsorbed so strongly to the MSA-1 resin that it could not be removed.

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