Sorption of organics from Kraft bleach wastewater
by Robert Lindsay Anderson

A thesis submitted to the Graduate Faculty in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE in Civil Engineering
Montana State University

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The second object of the research was to characterize the raw and treated wastewaters with respect to molecular size in order to determine the effect of molecular size on sorption. The raw and treated wastewaters were fractionated by gel permeation chromatography on Sephadex gels. GPC on Sephadex G-10 fractionated the samples into three fractions, all of molecular sizes less than 500 MW. There was no attempt to identify the three fractions.

That all fractionated molecules were of a size less than MW 500 confirmed reports that lime precipitation removes larger molecules.

The ratio of TOC applied/TOC eluate was different for each sample. This inconsistency could not be explained by the effects of pH and aromaticity.

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ROBERT LINDSAY ANDERSON

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ABSTRACT

The Kraft industry is responsible for large quantities of wastewater. This wastewater is characterized by its high color, BOD, suspended solids, and possible toxicity. Of these parameters, color is perhaps the most difficult to remove and has been the object of intensive research in the last decade.

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CHAPTER I

INTRODUCTION

The pulp and paper industry is the fifth largest industry in the United States (32, 90) and is estimated to use over 2,100 billion gallons of water annually (13, 91).

Sixty percent of the pulp produced in the United States is manufactured by the Kraft (sulfate) process (13). Though this process recycles the water and chemicals which are used for pulping, the water used for make-up and for washing and bleaching the pulp averages 33,000 gallons per ton of product pulp (96). This large usage results in a significant wastewater pollution problem. This thesis investigates one aspect of this problem.

A. THE KRAFT PROCESS

In the Kraft process, which has been in use since before the year 1900, wood is cooked for four to twelve hours at temperatures from 165 - 175°C in a solution of sodium hydroxide and sodium sulfide. The result is wood pulp, with about eighty percent of the lignin removed (60), and a solution of degraded lignin and spent chemicals. This solution is known as "black liquor" and is processed for the recovery of chemicals.

1. Bleaching

Pulp from Kraft cooking has high mechanical strength (Kraft is a German word for strong), but it also may be dark because of the residues of lignin degradation and other products. Kraft pulp may undergo a series of washing and bleaching processes which oxidize and dissolve these residues (66, 69). The result is a strong pulp and large volumes of highly colored wastewater. The wastewater is the source of a pollution problem toward which this research was directed.

2. Hoerner Waldorf Kraft Mill

The Hoerner Waldorf Corporation pulp plant is located at Frenchtown, eighteen miles NW of Missoula, Montana, and 236 miles from Bozeman, Montana. The plant, which is considered to be of "medium" size, was constructed in 1957 and was expanded in 1960 to a daily production of 450 tons/day of Kraft paperboard and 150 tons/day of bleached Kraft pulp. Unbleached pulp production increased to 900 tons/day in 1966 (74).

The bleaching process at Hoerner Waldorf consists of four stages: 1) chlorination, 2) caustic extraction, 3) sodium hypochlorite, and 4) chlorine dioxide. Each stage is followed by washing. Due to extensive countercurrent water reuse, the wastewater flows from these processes consist of about 3000 gpm from the chlorination washer, 450 gpm from the caustic washer, and small sporadic flows from spills, leakage and wash-down operations (74).

Since this Kraft mill and its bleaching processes are considered "typical", research on its wastewater pollution problems is not only significant from a local viewpoint, but also from one which is nation-wide.

B. WASTEWATER POLLUTION PROBLEMS FROM KRAFT BLEACH MILLS

Wastewater pollution problems associated with Kraft bleach mills may be classified with respect to four general pollutants:

1. Suspended solids
2. Biochemical oxygen demand (BOD)
3. Color
4. Toxicity

1. Suspended Solids

Suspended solid matter in Kraft bleach wastewater, which includes fibers and other dispersed insoluble wood components and process chemicals, can form bottom deposits in receiving streams. These deposits can be unsightly, odiferous, and deleterious to aquatic life (32, 34). On decomposition, they contribute to biochemical oxygen demand.

2. Biochemical Oxygen Demand

Two of the major dissolved organic components of Kraft bleach wastewater are lignin degradation products and carbohydrates. Lignins and lignin degradation products biodegrade very slowly and therefore contribute only slightly to BOD. Carbohydrates, such as wood sugars, on the other hand, are readily assimilated by a variety of microorganisms, and exert a significant demand on the dissolved oxygen of a stream (13, 32, 34, 60). Oxygen demanding materials also promote the growth of slime organisms on stream bottoms (34).

3. Color

In the Kraft process, a significant amount of the highly colored lignin degradation products remain attached to the cellulose fibers. The bleaching process transfers much of this colored matter from the fibers to the process water. The result is a highly colored wastewater (7, 11, 14, 21, 84).

Early pulp and paper industry spokesmen held that color, per se, was not a pollutant. However, it was recognized that color had an adverse psychological and aesthetic effect (11, 30, 40, 60), and that the industry was responsible for reducing it to acceptable levels. More recently, color has been criticized also for its pollutional effects (84):

1. Color may reduce sunlight penetration into water and inhibit the growth of desirable aquatic plants.
2. Colored components may be toxic to aquatic organisms.
3. Color may require removal before a water can be used as a potable supply or for certain industrial processes, including the Kraft process.

Furthermore, water quality regulatory agencies are becoming less tolerant of any organic material in effluents. For all of these reasons, color is now recognized as the major wastewater problem facing the Kraft industry (63).

4. Toxicity

The toxic effects of the colored components of Kraft bleach wastewater have been the subject of disagreement, mostly because of a dearth of research on the subject.

Howard and Walden (42) reported that salmonid fishes were adversely affected by Kraft effluents, but that they became acclimated, and that the effects were due mostly to pH. These authors later devised a technique which showed the toxicity of effluents to be independent of pH. Their tests showed that the test organisms (young salmon) had a Medium Survival Time (MST) of 136 minutes in 100 percent caustic extract (41).

Sprague and Drury (83) determined that salmon showed moderate avoidance to concentrations of Kraft bleach wastewater varying from 10 ppm to 10 percent.

Walden, et al (95), found that fish respiration was noticeably affected by a four percent concentration of Kraft bleach wastewater.

There is no evidence that this toxicity is due to the colored components. The question will likely never be answered because of the recognition of color as a pollutant on other grounds, because of concerted efforts on the part of the industry to remove color, and because of the difficulty of separating the colored components from the other molecules in the wastewater.

5. Wastewater Reuse

Partly because of pollution control regulations, the Kraft bleach industry already recycles much of its process water. Added advantages to water reuse are savings in heat, fiber, chemicals and the water itself (13, 32). As wastewater pollution standards become stricter, as water treatment costs rise, and as wastewater treatment technology improves, recycling of wastewater will increase. Ultimately, it seems likely that many industries, including the Kraft industry, will recycle all wastewater.

Process water used in the Kraft bleach process must meet certain quality criteria in order to maintain the quality of the pulp. Table 1 shows the ranges of desired properties for process water used in both the unbleached and bleached Kraft processes (57, 98). The most important of these properties with respect to Kraft bleach wastewater reuse are color (0-5 units), pH (6.8-7.3), dissolved solids (50-250 ppm), chloride (10-150 ppm), and chemical oxygen demand (0-8 ppm). It must be remembered, however, that the properties listed are ideals and that thousands of tons of Kraft pulp are being manufactured daily with waters that fail to meet these criteria (80, 89).

Chloride concentration has not previously been mentioned as a pollutant. It appears in high concentrations in bleach wastewaters and is important mostly from the standpoint of corrosiveness of recycled water (81).

TABLE 1

RANGES OF DESIRED PROPERTIES OF PROCESS WATER FOR KRAFT MANUFACTURE

Property	Unbleached	Bleached
Turbidity, units	5-25	0-5
Color, units	10-80	0-5
pH	6.5-8.0	6.8-7.3
Total Alkalinity, ppm	20-150	20-75
Hardness, ppm as $CaCO_3$	5-200	5-100
Dissolved Solids, ppm	50-500	50-250
Chloride, ppm	10-150	10-150
Fe, ppm	<0.5	<0.2
Mn, ppm	<0.3	<0.1
COD, ppm	0-12	0-8
BOD, ppm	0-5	0-2

A water which meets the criteria for bleached Kraft process water as listed in Table 1 may also be suitable for potable water supply. Though potable water must meet a number of criteria not applicable to bleached Kraft process water, several criteria are common to both. Table 2 lists these common criteria as proposed by the U.S. Public Health Service for potable water (92). It may be seen that, with respect to these criteria, bleached Kraft process water standards compare favorably with potable water standards.

TABLE 2

POTABLE WATER STANDARDS

Property	Concentration Limit
Turbidity, units	5
Color, units	15
Total dissolved solids, mg/l	500
Chloride, mg/l	250
Fe, mg/l	0.3
Mn, mg/l	0.03

C. STATEMENT OF THE PROBLEM

Laboratory and pilot plant investigations at the Southern Research Center of the National Council of the Paper Industry for Air and Stream Improvement (NCASI) by Berger, et al (8, 81, 88, 89), have shown that Kraft process wastewaters may be treated in a step by step process to yield a water that is completely reusable in Kraft pulp manufacture. The unit processes used are settleable solids removal, massive lime precipitation, aerobic biological oxidation, activated carbon adsorption, and demineralization.

Settleable solids are removed by plain sedimentation. This process removes seventy to ninety percent of the suspended solids, over ninety-five percent of the settleable solids, and about fifteen percent of the five-day BOD (34, 88).

Massive lime treatment, the key step in the flow sheet, is capable of removing ninety percent of the color and fifty-five percent of the five-day BOD. The effluent of this process has a pH of about 11.0, so neutralization is required to precipitate lime from the saturated solution and to yield a water that is amenable to biological oxidation (88).

After lime treatment, up to ninety-five percent of the five-day BOD may be removed by one of a number of biological oxidation processes including oxidation ponds, activated sludge or trickling filters (34, 88).

Activated carbon adsorption is used as a polishing process which may reduce five-day BOD, color, COD and turbidity to levels below ten ppm (88).

Effluents from the Kraft bleaching process are high (up to 4000 mg/1) in concentrations of chloride. Several processes such as ion exchange, reverse osmosis, or electrodialysis can be used to reduce the chloride concentration to levels which prevent corrosion and enable wastewater recycling (88).

1. Adsorption

Adsorption is the phenomenon whereby molecules adhere to a surface. If there is a chemical interaction between the molecules or particles in the fluid medium and the molecules or groups on the surface, then the process is called chemical adsorption or chemisorption. This type of adsorption involves strong bonding and is essentially irreversible (39, 47, 60, 62).

Contrasted to chemisorption is physical adsorption. In this process there is no chemical interaction. The bonding between the solute molecules and the surface is due to van der Waäl's forces and is relatively weak and reversible. Physical adsorption is the type which reduces the concentrations of dilute solutions of organic molecules in water and wastewater treatment. This process allows for regeneration or reactivation and reuse of the adsorbent (39, 47, 60, 62).

A process closely related to adsorption is ion exchange. In this process, a solute molecule or ion is attached to a surface at a site previously occupied by another molecule or ion. The binding results from the greater affinity of the site for the solute molecule or ion than for the molecule or ion originally on the site. When it is not clear whether the solute molecule adheres through adsorption or ion exchange, or both, the general term "sorption" is often used.

In this thesis, the term sorption is used generally to mean physical adsorption, but use of the term will not imply that the mode of mechanism or the adherance is understood, nor that the adherance does not involve ion exchange.

The classic sorbent is activated carbon (activated charcoal). This material has been used for centuries for water purification, but the mechanisms and kinetics of the process are not yet completely understood (39, 47). Activated carbon generally refers to a carbon whose sorptive properties have been purposefully increased by man-made operations. Activated carbon is manufactured from a number of materials including wood, coal, bone, nut shells, peat and petroleum base residues. Mostly because of the large surface area of activated carbon, up to 2500 square meters per gram, this material can sorb over ten percent of its weight of sorbate. Because of this effectiveness, activated carbon is widely used in water and wastewater treatment.

2. Other Sorbents

Despite its effectiveness, the use of activated carbon is limited by its cost. The first phase of this research was directed at investigating the sorptive properties of a number of other sorbents which might be more economical than activated carbon because of greater effectiveness or because of ready availability in Montana or in the Rocky Mountain area. The sorbents tested were local sorbents, filter aids, and resins.

Local sorbents were alumina, fly ash, bentonite, coal, and hog fuel ash. Alumina (aluminum oxide) is used as the raw material by the Anaconda Company aluminum reduction plant at Columbia Falls, Montana. Conceivably, the alumina could be used as a sorbent at Hoerner Waldorf and then shipped to Columbia Falls. The alumina could still be reduced to aluminum; the sorbate would be oxidized in the process.

Fly ash is the residue from coal combustion at steam power generating plants. It is available in large quantities throughout the United States (10). The Montana Power Company steam generating plant at Billings, Montana produces from seventy to 180 tons/day and has a two-year supply on hand (64). If the fly ash could not be reactivated after sorption, it would have the disadvantage of presenting the same solid waste disposal problem it does now.

Bentonite is an aluminum silicate clay found in the Rocky Mountain area, particularly Wyoming, which forms a viscous gel with water. It could also present a solid waste disposal problem if regeneration proved difficult.

Coal is readily available throughout the Intermountain West. If successful as a sorbent, it would have the advantage of its utility as a fuel afterwards.

Hog fuel ash is the ash which remains after bark and rejected chips are burned as fuel at pulp mills. Large quantities are available at most mills. The Hoerner Waldorf mill produces about seven tons per day and has about 2500 tons on hand (101).

Filter aids which were tested were diatomaceous earth and two products marketed by Johns-Manville Corporation, Celkate and HyfloSupercel. All of these could present a sludge disposal problem.

Resins are synthetic organic polymers which may also aid in ion exchange demineralization. Those tested were Duolite resins A-6, S-37 and LAD-500.

Activated carbon was used as a standard for comparison with all other sorbents.

3. Artificial Ditch Waste

Wastewaters from the Hoerner Waldorf plant are collected in four ditches. Ditch 1 carries wastewater from the clear water chest in the paper mill plus fresh water overflow. Ditch 2 carries wastewater from the floor drains, evaporators, the Kamyr operation, and the recovery process in the pulp plant. Ditch 3 carries all of the wastewater from the bleaching operation plus leakage and wash water from the bleach, recausticizer, and kiln areas, possibly some black liquor, and paper machine waste (73, 74). This is the wastewater of primary concern and is known as "ditch waste". Ditch 4 carries wastewater from the floor drains and the cloudy chest in the paper mill.

With a color value of 10,000 to 25,000 CU the caustic extraction stage effluent contributes about ninety percent of the color load from the bleaching operation of a typical Kraft mill. The bleach plant effluent usually accounts for eighty to ninety percent of the total color load (7, 30, 60, 87). This emphasizes the importance of the ditch waste. The components of the ditch waste are about fifteen percent caustic extract and about eighty-five percent chlorine waste. A wastewater called "artificial ditch waste" was made by blending fifteen parts of caustic extract with eighty-five parts of chlorine waste. This eliminated wastes from other parts of the mill and yielded a wastewater which was more consistent in composition than the actual ditch waste. Artificial ditch waste was used for this research.

a. Massive Lime Precipitation The artificial ditch waste, as it was received in the laboratory, had a color of about 3,000 CU. The waste was precipitated with enough lime so that, upon recarbonation to pH 7.6, the water had 300 CU. This 300 CU water was the raw wastewater used for this research.

4. Gel Permeation Chromatography

Both the rate and capacity of adsorption are dependent, among other things, on the molecular weight or size of the adsorbate (53, 107). The second phase of this research was aimed at characterizing the raw wastewater and the wastewater treated with various sorbents with respect to molecular size. The technique used was gel permeation chromatography.

In gel permeation chromatography, a sample is applied to a porous gel, usually in a column. The pores in the gel are of such a size that molecules above a certain size cannot penetrate into the gel; they are therefore carried down through the column in the fluid passing around the gel beads and they emerge quickly. Other molecules may enter the pores. These molecules diffuse down through the column, through the pores, but at a slower rate than the larger molecules, The molecules are thus separated on the basis of size (23, 78).

The purpose of the gel permeation chromatography (GPC) was to determine if certain sorbents are specific for certain sized sorbates. It this is true, then perhaps sorbents can be used in combinations to produce a treated water which no sorbent could produce by itself.

In summary, the research described in this thesis was an attempt to replace activated carbon in the massive lime precipitation flow sheet with a sorbent which improved either the efficiency or the

the economics of the color removal process. Gel permeation chromatography was used in an attempt to characterize the effectiveness of the sorbents with respect to molecular size.

CHAPTER II

LITERATURE SURVEY

A. COLOR

1. Definition of Color

Color is a human visual response to light reflected from or transmitted through a body. Three aspects of color are hue, brightness and saturation (102).

Hue refers to the name of the color and is dependent upon the dominant wavelength or the combination of wavelengths of light perceived. Most colored natural waters and wastewaters strongly absorb the blue wavelengths (350 to 480 mu) of incident white light. The remaining primary colors, red and green, add and are perceived as yellow (102).

Brightness is a measure of the light intensity or energy (102).

Saturation refers to the purity of the color, that is, how much white light is mixed with the colored light. The smaller the amount of white light mixed with a color, the greater is the degree of saturation (102).

The term "true color", which is synonymous with color in water and wastewater testing, means color caused by substances in solution in the water. "Apparent color" is caused by suspended matter as well (76).

Two common methods for measuring color are visual comparison methods and spectrophotometric methods. With the visual comparison methods, an observer compares the color of a sample with the color of an arbitrary standard or with a glass disc which has been calibrated with an arbitrary standard. A spectrophotometer electronically measures the intensity of transmitted monochromatic light. This transmission may then be compared to the transmission through the standard (76).

The color standard used for this work is the widely accepted platinum-cobalt standard. The unit of color is that produced by 1.0 mg/l of platinum in the form of chloroplatinate ion (85).

Lambert's Law states that each layer of equal thickness of a medium absorbs an equal fraction of the light which travels through it; that is, monochromatic light intensity decreases exponentially as the length of the medium increases. Beer's Law states that the intensity of monochromatic light decreases exponentially as the concentration of the absorbing medium increases. These two laws are combined as the Lambert-Beer Law, which may be expressed mathematically as (76):

$$T = \frac{I}{I_o} = 10^{-kcl}$$

$$\text{or} \quad A = \log \frac{I_o}{I} = kcl$$

where T = transmission

A = absorbance

k = extinction coefficient, a constant for a particular solution

c = concentration of the solution

l = length of the absorbing medium

If, for a particular solution, plots of absorbance versus concentration for constant path length and absorbance versus path length for constant concentration yield straight lines, then the solution obeys the Lambert-Beer Law.

2. Causes of Color in Kraft Bleach Wastewater

Almost every pulp component or Kraft bleach reaction product has been accused of being the cause of color in Kraft bleach wastewater (38). Most often blamed are lignins and lignin degradation products (7, 14, 28, 38, 40, 58, 60, 68, 70, 84). Other suspects have been tannins (7, 106), carbohydrates (21, 38, 58), and other dissolved extractives (38, 58).

Hartler and Norrström (38) showed in Kraft pulps from spruce, ninety percent of the color is due to lignin, ten percent to carbohydrates, and less than one percent to dissolved extractives.

Christman and Ghassemi (16) isolated seven compounds which are degradation products of color in natural waters. These are vanillin, vanillic acid, syringic acid, catechol, resorcinol, protocatechuic acid and 3,5-dihydroxybenzoic acid. All of these aromatic compounds may be derived from lignin.

Pew and Conners (68) suggested phenyl substituted benzoquinone and coniferaldehyde groups are major contributors to the color of wood lignin.

Falkehag, et al (28), suggested Kraft lignin is the likely coloring matter in Kraft pulp and color is caused primarily by CH=CH double bonds conjugated with the aromatic ring and by quinone-methides and quinones. Minor contributions to color may be caused by chalcone structures, free radicals, and metal complexes with catechol structures.

3. Lignin--Definition and Structure

Wood is a heterogeneous material made up of three major components: cellulose, the hemicelluoses, and lignin (77). Lignin, which accounts for twenty to thirty-five percent of wood (71), has been the subject of intensive investigation by organic chemists for over a century, yet its structure and reactions have still not been completely elucidated. Originally defined as a compound, lignin is now considered to be a collective term for a whole series of similar, very large, structurally related molecules, perhaps analogous to other natural polymeric classes of compounds such as cellulose, starch, or protein (77).

Freudenberg (29) has summarized the concept of lignin on the basis of morphology: "Lignin is a substance which permeates the membranous polysaccharides and the spaces between the cells, thereby strengthening them. Its presence brings about physiological death of the tissue. It is a functional component of wood, and it occurs in mature wood as a preformed, completed substance."

The monomeric unit of lignin is considered to be the phenylpropane unit (66, 71, 75, 77), shown in Figure 1. Also shown in Figure 1 are the structures of coniferyl alchohol and guaiacyl propane, thought to be the precursors of lignin (16, 66, 75, 77).

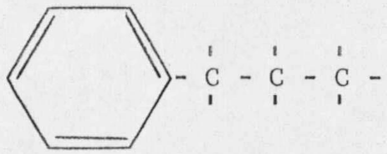
In the lignin macromolecule, the monomeric phenylpropane units may be linked in a variety of ways both by ether and by carbon-to-carbon linkages (66, 75, 77). Carbon-to-carbon linkages may be phenyl-phenyl, phenyl-propyl, or propyl-propyl, and are highly resistant to chemical degradation. Multiple points of attachment may involve both ether and carbon-to-carbon linkages.

4. Kraft Reactions

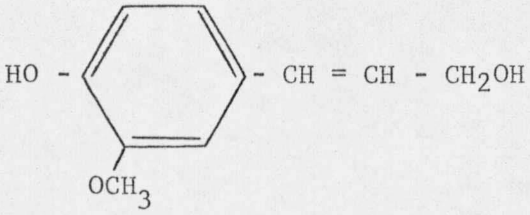
Though the Kraft process has been used commercially since before 1900, its reactions are poorly understood.

Heating lignin with alkalai solutions is thought to cause the splitting of certain phenyl-propyl ether linkages as well as propyl-propyl carbon-to-carbon linkages (66, 75). These reactions are common to the soda and Kraft processes.

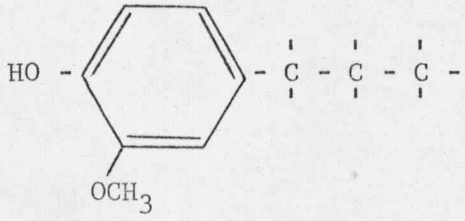
In the Kraft process, sodium sulfate is added to make up losses of alkalai in the soda process. Sodium sulfate is reduced to sodium sulfide in the recovery furnace. The resulting solution contains both sodium hydroxide and sodium sulfide as active alkalais (66). It is thought that nucleophilic attacks by sulfide, hydrosulfide, and methyl mercaptide ions cause cleavage of ether bonds in the lignin polymer (26). The reaction products have not been completely elucidated.



a. Phenylpropane unit



b. Coniferyl alchohol



c. Guaiacyl propane unit

Figure 1. Monomeric units and precursors of lignin

5. Bleach Reactions

In the bleaching process, the chlorination stage is the most important. The dominant reactions in this process are (66, 75):

1. Chlorine substitution on the aromatic ring.
2. Electrophilic displacement of the propyl side chain.
3. Chlorine-catalyzed hydrolysis of ether groups.

These and other accompanying reactions, such as further chlorine substitution and oxidation to quinones, yield a complex mixture of various small molecules which are soluble in water and especially in alkalai.

Caustic extraction is the solution and removal of the lignin degradation products formed in the chlorination stage (71).

Reactions and products in hypochlorite and chlorine dioxide bleaching are largely unknown (66, 75).

In summary, the colored compounds in Kraft bleach wastewater are thought to be lignin degradation products and that these products are mixtures of relatively small chlorine substituted propyl and etherified phenyl compounds.

B. SPECTROPHOTOMETRY

It is widely accepted that almost all native lignins have characteristic ultraviolet absorbance spectra with a maximum absorbance at 280 mu (66, 71, 75, 77), and that the 280 mu maximum persists in spite of such alterations as methylation acetylation, and treatment with sodium hydroxide (77). Falkehag, et al (28), verified that Kraft lignin from spruce exhibits the 280 mu maximum. In fact, absorbance at 280 mu is used as a standard measure of lignin concentration in solutions (71).

Figure 2 shows the ultraviolet absorption spectra determined by Falkehag et al for Kraft lignin (28).

Despite the universal acceptance of the 280 mu maximum, Pew (67) showed that coniferyl alchohol, thought to be a lignin precursor, has a maximum at 265 mu, and that other phenylpropane lignin model compounds have maxima ranging from 273 mu to 341 mu.

No reports were found in the literature on ultraviolet absorption spectra for Kraft bleach waste lignin, although many investigators have used absorbance at 280 mu for quantification.

C. KRAFT BLEACH WASTEWATER TREATMENT

A variety of unit processes have been used for treatment of Kraft bleach wastewater, some in research, some in actual operating systems.

1. Mill Operation Modification

Perhaps the best approach to the Kraft bleach wastewater pollution problem is prevention, if it can be achieved without compromising the quality of the product pulp (63). Warner and Miller (97) reported that bleach plant color can be reduced by seventy-five percent by eliminating the caustic extraction stage, and that color may be reduced by reversing the sequence of bleaching steps. Unfortunately

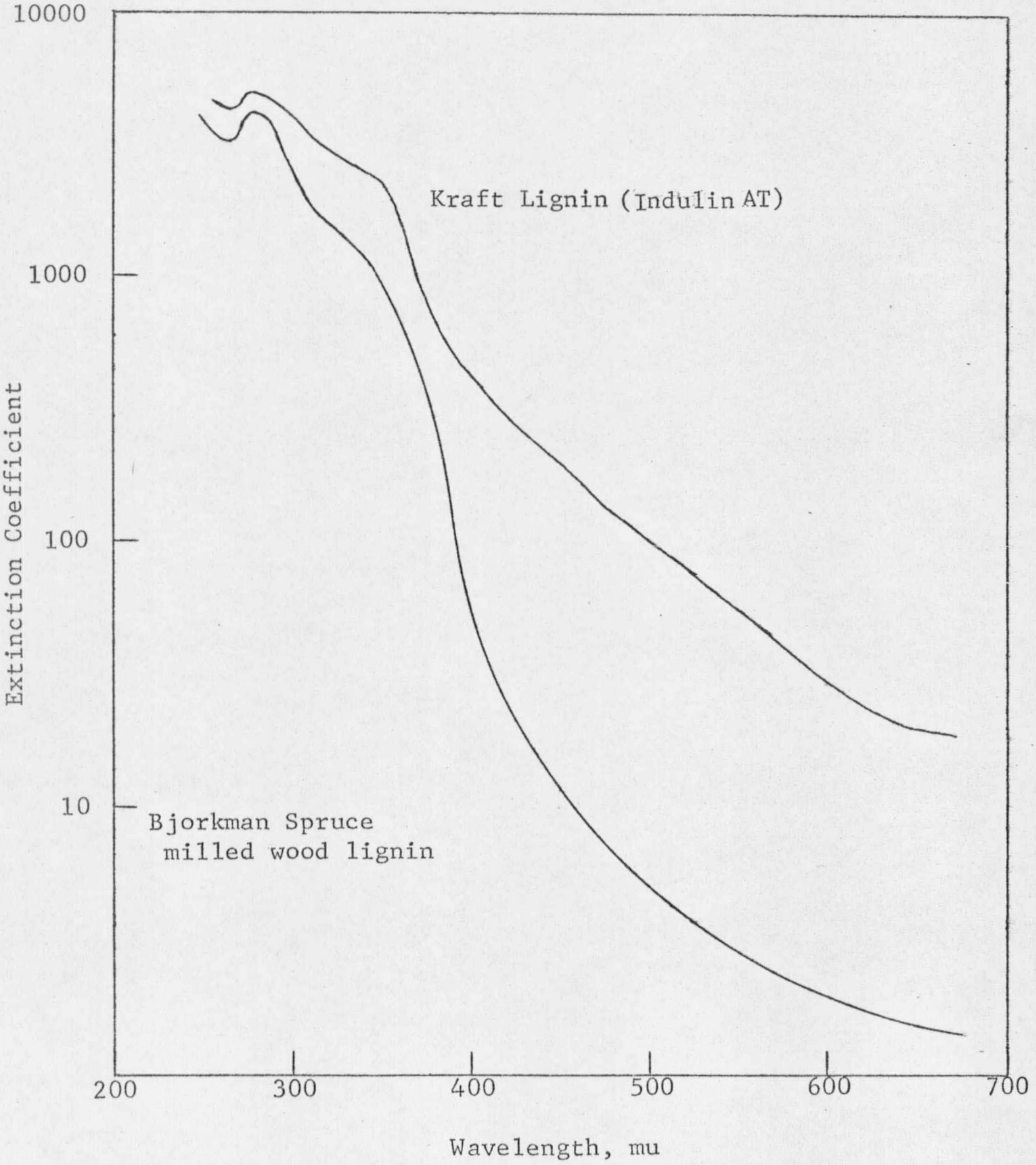


Figure 2. Absorbance spectra of lignin

both of these remedies result in a more highly colored pulp.

2. Suspended Solids Removal

Suspended solids are most often removed from Kraft effluents by plain sedimentation, but occassionally by flotation or filtration. Sedimentation removes seventy to ninety percent of the total suspended solids and over ninety-five percent of the settleable solids (32, 34, 88).

3. Biooxidation

Biological oxidation is perhaps the most common unit process used for treatment of wastewaters and has been applied extensively to Kraft bleach wastewaters.

Gehm (32, 33) reported that, after settleable solids removal, one or a combination of the biological oxidation processes may reduce the five-day BOD of Kraft bleach wastewater by eight-five to ninety percent. Among the processes are stabilization ponds, aerated lagoons, activated sludge, and trickling filters.

Thirumurthi, et al (90), attested to eighty percent five-day BOD removal from Kraft mill effluents by aerated lagoon treatment.

Charles and Decker (15) reported activated sludge treatment of Kraft bleach wastewater with nutrient supplementation produced an effluent which met standards requiring five-day BOD be reduced by sixty percent and the effluent, when diluted to sixty-five percent concentration, support 100 percent survival of yearling salmon after ninety-six hours.

Lignin degradation products, because of their biological resistance, contribute little to five-day BOD. Traditional biological oxidation processes effectively remove carbohydrates but have little effect on lignin degradation products and color (7, 40, 84).

One contradiction to this position is a study by Woodard, et al (106), which showed activated sludge, acclimated to lignin, could remove ninety percent of the lignin from a synthetic solution. Surprisingly, this line of research has not been pursued.

A group of Basidiomycetes known as "white rot fungi" are the only organisms known to degrade lignin (66, 77). Marton, et al (50), demonstrated Polyporus versicolor, a white rot fungi, when preconditioned to Kraft lignin, can completely discolor Kraft lignin in three days.

4. Foam Separation

There are two types of foam separation processes: foam fractionation and ion flotation. Foam fractionation relies on the surface activity of a solute such as lignin degradation products. The surface activity causes the solute to migrate to air-water interfaces (bubbles) and to be removed at the liquid surface in the resulting foam (105).

Ion flotation relies on the soluble anionic lignin degradation product reacting stoichiometrically with a cationic surfactant to form an insoluble precipitate. The precipitate is adsorbed on the liquid film and removed with the foam (105).

Studies with foam fractionation have shown it to be moderately effective for ABS removal (86), but ineffective for color and lignin removal (59, 105). Wilson and Wang (105) have shown ion fractionation can remove ninety percent of the color from synthetic lignin preparations.

5. Electrolysis

Campbell, et al (14), in a unique study, hypothesized that an electrolytic cell which produces chlorine at the anode and polyvalent metal ions at the cathode may be effective in removing color by oxidation of smaller molecules and coagulation of larger ones. Color removals of ninety-five to ninety-seven percent were demonstrated.

6. Coagulation

Davis, et al, reported up to ninety-two percent of the color in chlorination stage bleach wastewater (18) and 96.5 percent of the color in caustic extraction wastewater (87) may be removed by coagulation with Al^{+3} or Fe^{+3}.

Thirumurthi, et al (90), demonstrated ninety-three percent color removal from Kraft mill waste using alum coagulation.

7. Reverse Osmosis

Beder and Gillespie (6) investigated the ability of reverse osmosis to manufacture reusable water from caustic extraction wastewater and massive lime treated wastewater. Although reverse osmosis was not able to reduce COD or BOD to the desired levels, they showed low pressure reverse osmosis with polyelectrolyte membranes appears more effective than massive lime treatment for color removal from caustic extraction wastewater and high pressure reverse osmosis with cellulose acetate membranes can reduce the solids content of both raw wastewater and massive lime treated wastewater to the level of reusability.

Ammerlaan, et al (5), reported reverse osmosis may be effectively used to treat chlorination stage effluents but further development is needed to reduce costs and extend membrane life. The process is promising, however, because it reduces chloride concentration as well as color.

8. <u>Massive Lime</u>

A most significant advance in Kraft bleach wastewater color removal has been the development of the massive lime process. In this process, developed and patented by Berger, Gehm and Herbet for the National Council of the Paper Industry for Air and Stream Improvement (8), the mill's total lime requirement is slaked and reacted with the highly colored effluent. The resulting sludge is settled, dewatered, and then used to causticize green liquor. The color bodies which are dissolved in the resulting white liquor eventually find their way into the recovery furnace where they are burned. The clarified, decolorized effluent is carbonated with lime kiln stack gases to precipitate and recover calcium carbonate (7, 8, 40, 63, 80, 89).

The massive lime process is effective for gross color removal-- about ninety percent for highly colored effluents (7, 40, 80, 89). Advantages of the process include (7, 63):

1. Lime is readily available at Kraft mills at low cost.
2. Highly-developed recovery techniques, utilizing conventional recovery equipment, are available at Kraft mills.
3. Kraft mill operating personnel posses the necessary background and knowledge for successful operation of lime reactions and recovery.
4. An average of forty-five percent of the five-day BOD is removed.

A shortcoming of the process is the further treatment required to reduce color to the levels required for reuse.

NCASI studies (58, 61) on caustic extraction stage and chlorination stage effluents have shown the massive lime color removal process is a chemical rather than physical mechanism and color removal is dependent on the presence of enolic and phenolic hydroxyl groups. Furthermore, lime was found to precipitate the higher molecular weight fractions in the effluents.

Presently, one operating Kraft mill is using the massive lime process and several others are either operating or planning modifications of the process (36, 58, 63, 65, 84).

9. Sorption

Because of its ability to reduce dilute concentrations of organic materials in water, sorption has received wide acceptance in wastewater treatment. Activated carbon is the traditional sorbent used for this purpose, but other materials have also been used.

a. Activated Carbon Activated carbon sorption of organics, particularly ABS, in secondary sewage effluents has been widely researched (53, 54) and widely applied (39).

Kraft bleach wastewaters contain such a high concentration of organics that activated carbon treatment alone is uneconomical because of the large quantities of activated carbon required to reduce organics to an acceptable level. Development of the massive lime process, however, has opened a new avenue for sorption. The effluent from the massive lime process is too highly colored for reuse as process water but dilute enough for economical application of sorption. Berger (8, 81, 88, 89) and others (30, 51, 62, 91) have shown activated carbon sorption, preceded by settleable solids removal, massive lime precipitation, and perhaps biooxidation, can produce a completely reusable process water from Kraft wastewater. Demineralization would also be required for Kraft bleach wastewater to reduce chloride concentrations.

But activated carbon sorption is not without its disadvantages. Granular activated carbon, easily applied in columns and easily regenerated, cost twenty-five to fifty cents per pound in 1966. Powdered activated carbon, the most effective form, cost seven to nine cents per pound in 1966, but an effective regeneration process has not yet been fully developed.

Timpe, et al (91), have indicated an effective activated carbon can be manufactured at Kraft mill sites from black liquor. After sorption, this activated carbon could be completely burned and reintroduced into the pulping process. The potential of this process rivals that of the massive lime process.

Weber, et al (53, 82), have reported the effectiveness of activated carbon is determined primarily by: the large surface area (up to 2500 square meters per gram), the presence of acidic or basic functions in the active surface, and the molecular size of the sorbate. The larger the sorbate molecule, the lower is the rate at which it diffuses through the pores in the sorbent, hence the lower is the rate of sorption.

Zuckerman and Molof (107) reported activated carbon sorption of ABS is effective for smaller organic molecules, probably those with a molecular weight of under 400.

b. <u>Resins</u> The sorptive properties of synthetic resins were investigated as early as 1936. However, early resins did not have the porosity required for diffusion of high molecular weight compounds through the resin matrix. As a result, the surface area was relatively low and sorption of organics was modest. Furthermore, the successful development of resins for ion exchange tended to obscure their sorptive properties (2). The "fouling" of resins by organic molecules was generally viewed as a disadvantage rather than a potential treatment process.

More recently, attention has returned to resins as sorbents. Abrams has reported on the effectiveness of resins for decolorizing sugar solutions (86), for removing organic contaminants from municipal water supplies (2, 3), and for wastewater reclamation (2).

Dickinson and Barrett (25) considered resins and activated carbons, not as competitors, but as complementary systems which together might be more effective than either separately.

Sanks (72, 74) has shown that several resins are effective in decolorizing massive lime precipitated Kraft bleach wastewater.

Use of resins as sorbents appears to be promising in a variety of applications because of the increasing ability of manufacturers to produce "tailor-made" resins. Other advantages include the ease of chemical regeneration in most cases and the long life of resins (1). Disadvantages include the high cost of resins, disposal of regenerant, and decrease of activity due to irreversible sorption.

c. Hog Fuel Ash Hog fuel ash, also called bark boiler ash, hogged fuel ash, and fly ash, is the ash which remains after bark and rejected chips are burned for production of heat and power at Kraft mills. Surprisingly, the ash, though it resembles activated carbon, has been largely ignored as a sorbent and has merely been considered a solid waste.

Warner and Miller (97) reported that the ash completely decolorizes both black liquor and caustic extraction effluent and may be used as an excellent filter aid.

Robinson (70) reported that hardwood ash could almost completely decolorize caustic filtrate but that pine ash is much less effective.

d. Coal Coal has received some attention as a sorbent but, because of the wide variety in the characteristics of natural coal, results have been inconclusive.

Johnson, et al (45, 46), reported coals sorbed about four percent of their weights in removing COD from secondary municipal effluents using repetitive contacts. The best coals appeared to be about one-fourth as effective as activated carbon, but since coal costs only 1/100 as much as activated carbon, coal may be a competitive sorbent. Costs for coal sorption were reported to be two to 3.5 cents per 1000 gallons.

Shannon and Silveston (79) reported that coals have very low sorptive capacities and that costs for coal sorption may approach $2.00 per 1000 gallons.

e. Alumina Alumina has been shown to be an effective sorber of phosphate ions (4), but it is probably a poor sorber of organic molecules.

Volk and Jackson (93) reported that hydroxy aluminum gels readily adsorbed both ABS and LAS.

Morris and Weber (54) showed activated alumina to be a poor sorber of ABS. Another study (86) showed that both alumina and bauxite are ineffective for removal of COD from secondary municipal effluents.

f. Fly Ash Fly ash, not to be confused with the hog fuel ash (sometimes called fly ash), is the ash remaining after pulverized coal is burned, usually at steam power generating plants. Limited research has shown that fly ash may be an effective sorbent.

Deb, et al (22, 49), showed fly ash is moderately effective in removing ABS from a synthetic waste and COD from a secondary municipal effluent.

Williamson, et al (104), reported fly ash removed about thirty percent of the COD from secondary municipal effluents in batch tests.

Johnson, et al (46), reported some fly ashes in batch tests removed as much as sixty-six percent of the COD and seventy-six percent of the ABS from secondary municipal effluents.

Eye and Basu (27) demonstrated a thirty percent reduction of COD from secondary municipal effluent using fly ash.

g. Clay Research on clay as a sorbent has been limited.

Murphy, et al (55), reported fluorite was moderately effective in removing color from Kraft bleach wastewater, but regeneration costs made the process uneconomical.

Williamson, et al (104), achieved thirty-six percent removal of COD from secondary municipal effluent using Wyoming bentonite.

Huang and Liao (43) reported 100 ug/l of DDT, dieldrin, and heptachlor were instantaneously adsorbed on kaolinite and illite in batch tests.

h. Diatomaceous Earth Williamson, et al (104), reported up to twenty-eight percent removal of COD from secondary municipal effluent using diatomaceous earth in a batch test.

10. Demineralization

Where demineralization is required to reduce dissolved solids, particularly chloride from Kraft bleach wastewater, the Kunin Process or another of the ion exchange processes or one of the membrane processes may be used (80, 88).

D. MOLECULAR WEIGHTS OF LIGNIN AND LIGNIN DEGRADATION PRODUCTS

Molecular weights of lignins are difficult to determine because it is hard to isolate natural lignins without altering their chemical structures.

Brown, et al (12), isolated natural lignin by employing brown rot fungi to degrade the cellulose fraction of wood and by fractionating the residue by gel permeation chromatography on Sephadex G-50. They reasoned lignin is a finite sized polymer rather than an infinite structure and the size depends on the location in the cell wall.

Sarkanen (75) summarized information which showed molecular weights of some lignin preparations varied from 420 to 138,000, depending on the source and the degree of degradation during isolation.

McNaughton, et al (52), summarized conflicting data which reported the molecular weights of Kraft lignin to vary from 1000 to 48,000,000. They reasoned the tendency of Kraft lignin to agglomerate in solution may account for the discrepencies. They showed the average molecular weight of Kraft lignin increases as the cooking process continues. Molecular weights of Kraft lignin approached 50,000.

NCASI studies (58, 61) showed, by vapor pressure osmometry, the average molecular weight of residues in Kraft bleach wastewaters is about 1500 and lime precipitation is more effective for the larger molecules in these mixtures.

1. Gel Permeation Chromatography

Gel permeation chromatography (GPC), also called gel filtration and gel chromatography, has gained wide acceptance as a technique for fractionating molecules on the basis of molecular weight or size and for determining the molecular weight or size of unknown molecules. The technique is beginning to find applications in water and wastewater treatment because of theories that such processes as sorption, lime precipitation, and biooxidation are dependent on the molecular size of solutes.

Zuckerman and Molof (107), using Sephadex G-15, fractionated domestic sewage effluent into two fractions, one of MW > 1200 and one of MW < 400. They claimed "hydrolysis" with lime broke the larger molecules into smaller ones which were more effectively removed by activated carbon sorption.

Weber (100) disagreed with Zuckerman and Molof's findings, arguing: 1) hydrolysis is insignificant, 2) the mechanism of lime treatment is one of precipitation and coagulation, and 3) the larger molecules are often more effectively sorbed than are the smaller ones.

Collins, et al (19), fractionated spent sulfite liquors on Sephadex and speculated wood lignin is covalently bound to carbohydrates.

Lorås (48) achieved well defined separations of extracts from sulfite pulps with GPC on Sephadex.

Christman and Minear (17) reported separating lignins from carbohydrates in spent sulfite liquors using GPC on Sephadex.

Collins, et al (21), used GPC on Sephadex to fractionate Kraft bleach wastewater. The low lignin concentration, as measured by absorbance at 280 mu, in the fractions led them to postulate carbohydrates contribute significantly to color in pulp and Kraft bleach wastewater.

a. Aromatic Adsorption It has been well established that aromatic compounds are retarded on many gels (23, 24, 35, 78). This phenomenon is referred to as aromatic adsorption. Aromatic adsorption is particularly severe on cross-linked dextrans such as Sephadex, but less so on cross-linked polyacrilamides like Bio-Gel (24).

Gelotte and Porath (35) reported aromatic adsorption in aqueous solutions could be reduced by including urea or potassium thiocyanate in the eluent.

Determann and Walter (24) agreed urea reduced aromatic adsorption, but found the cyanate increased it.

Brown, et al (12), eliminated aromatic adsorption while fractionating wood lignin on Sephadex by eluting with formamide.

CHAPTER III

EXPERIMENTAL PROCEDURES

The experimental procedures performed consisted of: 1) tests used to determine concentration parameters, 2) batch sorption, and 3) gel permeation chromatography.

A. TESTS

1. Total Organic Carbon

TOC (Total Organic Carbon) was measured using a Beckman Model 915 Total Organic Carbon Analyzer with a Beckman Model 215A Infrared Analyzer and a Sargent Model SRLG potentiometric recorder. Samples were injected with a Hamilton Model 80550 Syringe.

2. Color

Color was determined by measuring the transmission of light with a wavelength of 422.2 mu with a Hitachi Perkin-Elmer Model 139 Spectrophotometer. The lengths of light paths through the samples were 10 mm, 50 mm, or 100 mm, depending on the intensity of the color. Distilled water was used as the standard for absence of color. A solution of 500 mg/1 of platinum (in the form of chloroplatinate ion) was used as a 500 color unit standard.

Color in water is reported to be extremely pH dependent, invariably increasing as pH increases (85). Black and Christman (9) reported that a number of surface waters with color values ranging from 42 to 330 color units at pH 2 increased in color from 30 to 105 percent when the pH was raised to 10.

To determine the effect of pH on the color of the raw waste, the pH was changed by adding sodium hydroxide or sulfuric acid. Figure 3 shows the change in color for a pH range of 2 to 12. The largest variation in color occurs between pH 4 and pH 9. In the range of interest (pH 7.6 to pH 12) the total variation in color was only about five percent.

A portion of the raw waste was diluted with distilled water until the color was thirty color units. Over a pH range of 2 to 12 variation was insignificant as shown in Figure 4. Because the effect of pH change was so small, color measurements were made throughout the experiments without regard for pH adjustment.

3. Absorbance at 265 mu

The absorbance of light with wavelengths varying continuously from 200 mu to 700 mu was measured for the raw waste and for all treated samples with a Cary Model 14 Spectrophotometer. Figure 5 shows the relationship between light absorbance and wavelength for the raw waste and activated carbon treated wastewater. A maximum absorbance was recorded at 265 mu and a minimum at 240 mu. All treated samples also exhibited the peak at 265 mu and the trough at 240 mu.

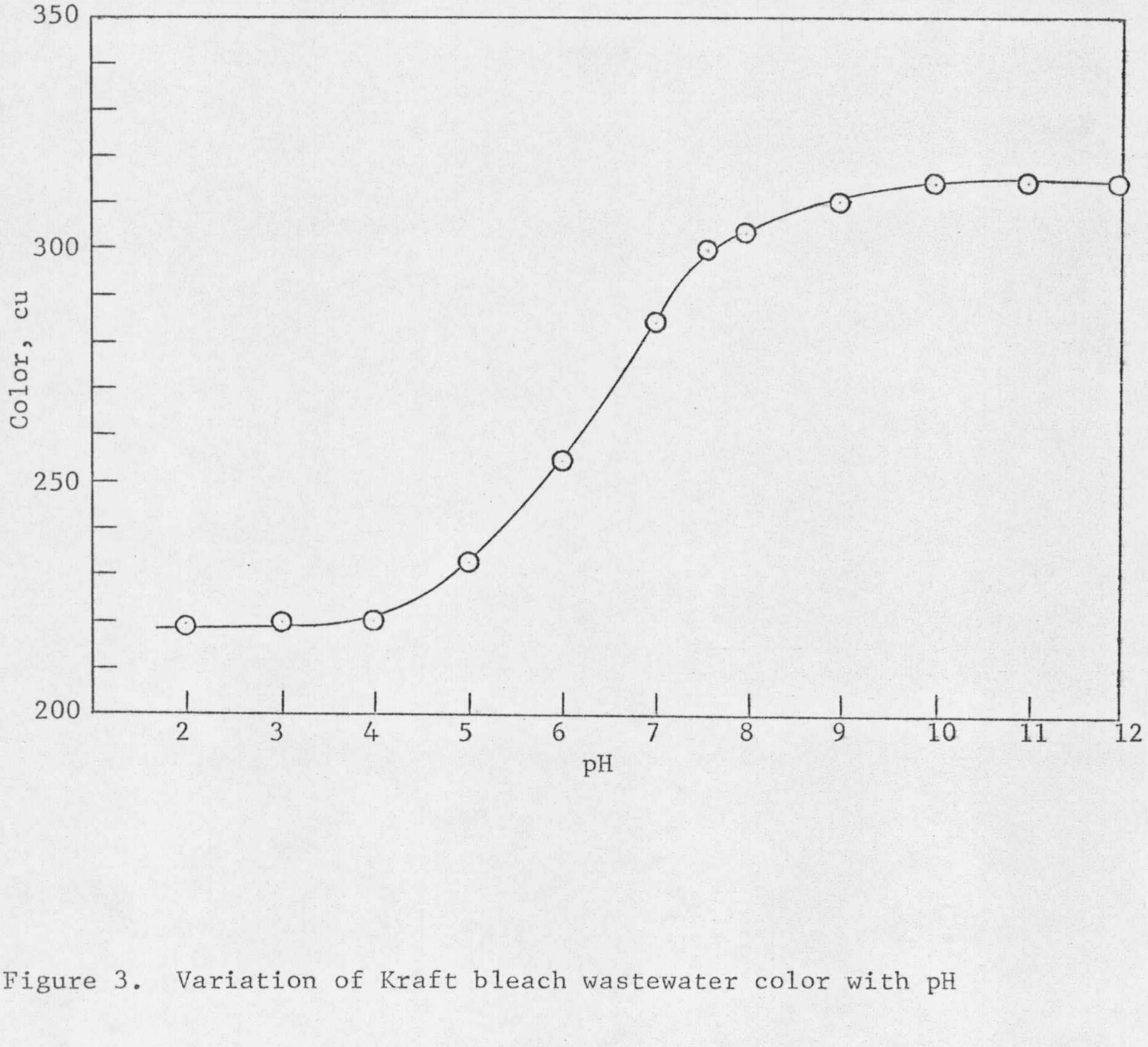


Figure 3. Variation of Kraft bleach wastewater color with pH

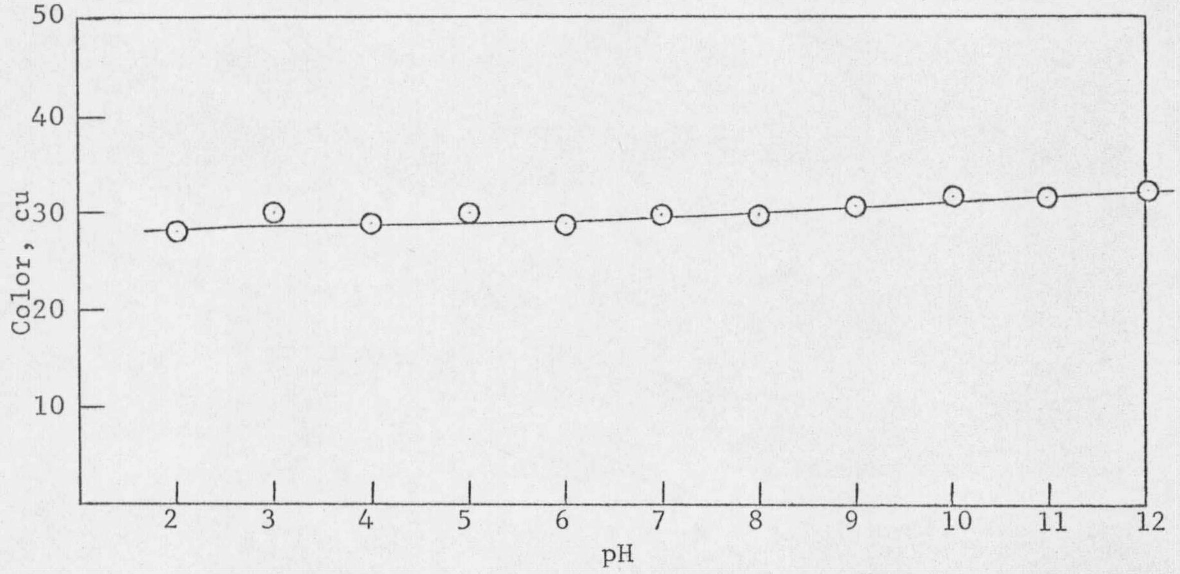


Figure 4. Variation of dilute Kraft bleach wastewater color with pH

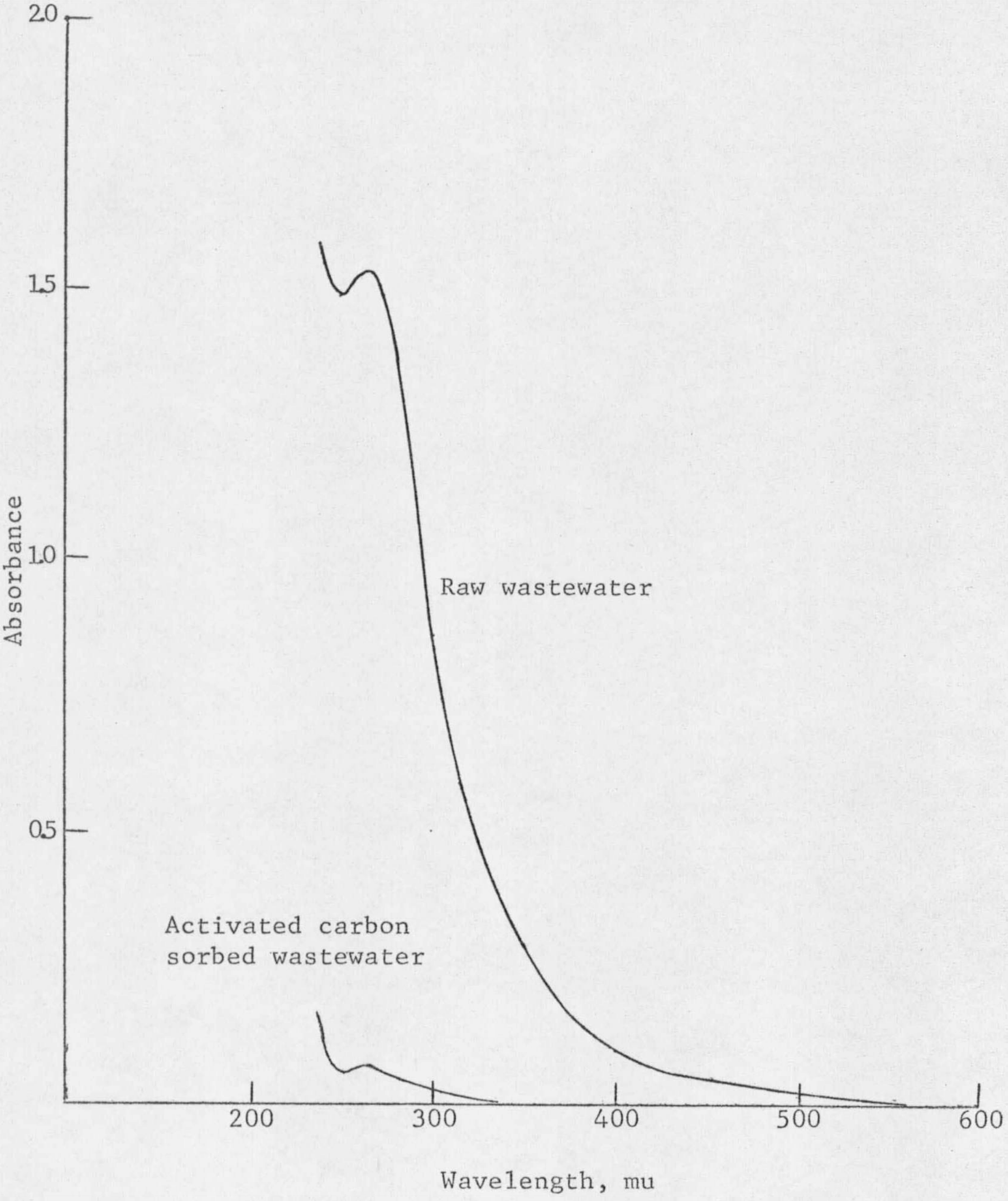


Figure 5. Variation of absorbance with wavelength

Figure 6 shows the relationship between absorbance at 265 mu and dilution of the raw waste. Because of this linear relationship between absorbance at 265 mu and dilution, and because of the absorbance peak at this wavelength, absorbance at 265 mu (referred to herein as A_{265}) was used as a concentration parameter. No attempt was made to relate this parameter to a specific mass per unit volume concentration.

B. EXPERIMENTS

The experimental work consisted of two phases. The first was batch sorption of the raw waste on the various sorbents. The second was an attempt to characterize the raw and treated wastes according to molecular size by gel permeation chromatography.

1. Batch Sorption

The sorbents chosen for this research were selected for a variety of reasons. Activated carbon was used to provide a standard because it is the classic sorbent for removing organic molecules from aqueous solutions. The activated carbon chosen for this study was Filtrasorb 400, shown by Sanks (74) to be an effective sorber of color from Kraft bleach wastewater. Alumina, fly ash, bentonite, coal, and hog fuel ash were selected, despite little available information about their sorptive properties, because of their availability in Montana or in the Rocky Mountain area. Diatomaceous earth, Celkate, and HyfloSupercel were investigated because of their proven applications as filter aids. LAD-500, A-6 and S-37 are all resins which have

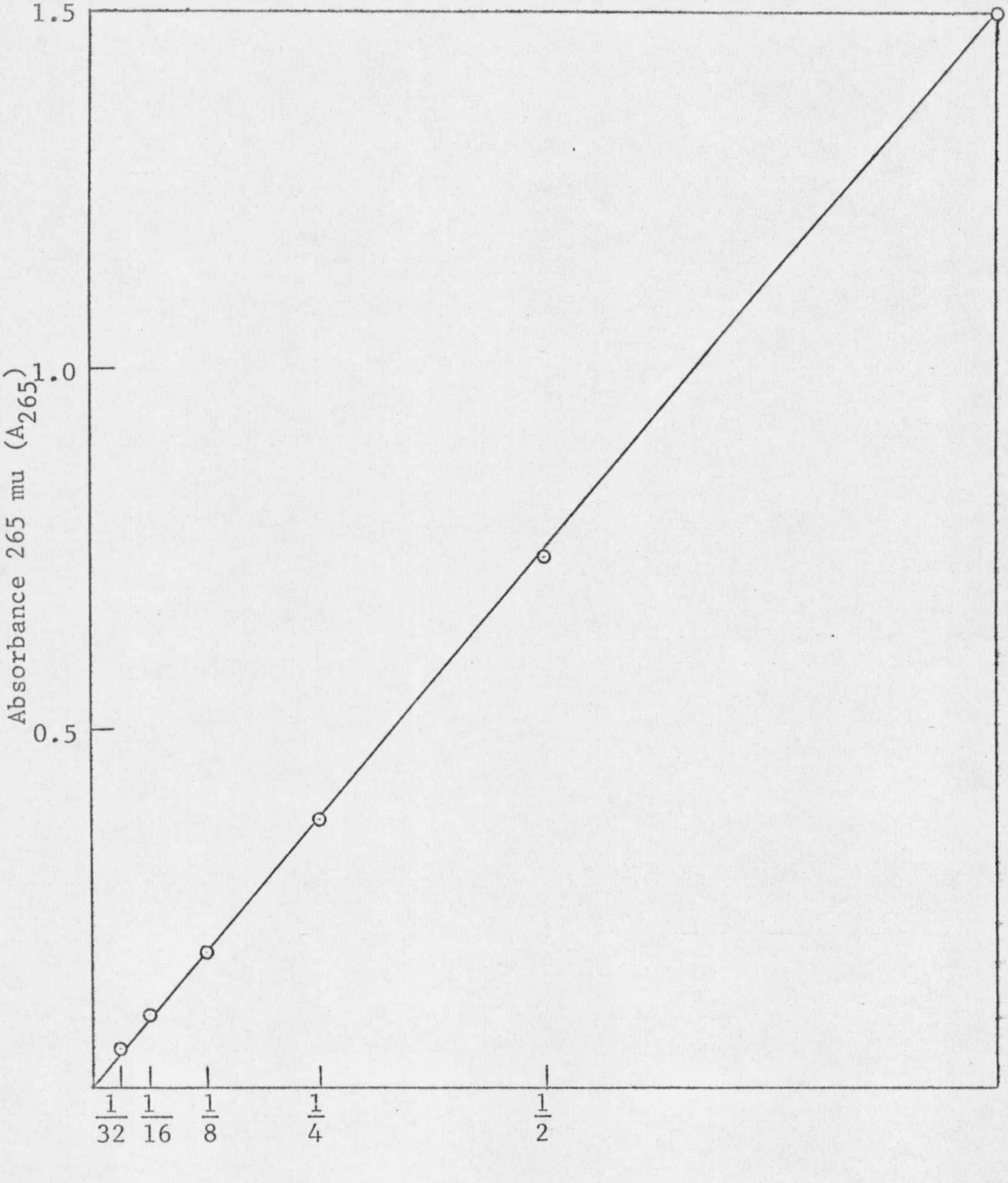


Figure 6. Variation of A_{265} with dilution

demonstrated efficient sorption of refractory organics (25, 74).

Doses of all sorbents were based on dry weights per unit volume of raw waste.

For each sorption experiment, weighed portions of the sorbent, usually 1.0, 3.0 and 5.0 grams, were placed in wide-mouthed 250 ml Erlenmyer flasks. To each flask was added 100 ml of the raw waste. The flasks were agitated in a Blue M MagniWhirl Constant Temperature Bath at 20°C and at a frequency of about 120 hz. and an amplitude of about one inch. One flask of each dosage was removed from the bath after 30, 60 and 120 minutes. The waste in each flask was immediately filtered through a 0.45 u Millipore filter and tested for TOC, color, and A_{265}.

Because of the poor results obtained initially with diatomaceous earth, Celkate, HyfloSupercel, coal and bentonite, no further experiments were performed with these sorbents.

a. <u>pH Changes</u> A Sargent Model DR pH Meter was used to measure the effect of each sorbent on the pH of the waste. Five grams of the sorbent was placed in 100 ml. of waste in a 250 ml. beaker. The suspension was stirred continuously with a mag mixer and the pH was recorded as it varied with time until equilibrium was reached.

2. Gel Permeation Chromatography

The first step in the gel permeation chromatography phase of this research was to select the proper Sephadex gel for fractionation of the Kraft bleach wastewater. Table 3 shows the permeation characteristics of the three Sephadex gels which were used (78). Each gel was calibrated by applying Blue Dextran (MW = 2,000,000), potassium ferricyanide (MW = 330) and carbonate (IW = 60) to the column. After it was determined that only on Sephadex G-10 were there separations, all chromatographic runs were made with this gel.

The chromatographic column was a Pharmacia Type K9/60, 9 mm in diameter and 60 cm long. Flow of the eluent, 0.02 M NaCl, was maintained at 10 ml/hr by a Sage Model 375 Tubing Pump.

TABLE 3

PERMEATION CHARACTERISTICS FOR
SEPHADEX GELS

Sephadex Type	Fractionation Range (MW)
G-10	0-700
G-25	100-5000
G-50	500-10,000

One ml fractions of eluate were collected by an Isco Model 326 Fraction Collector. Samples were applied in 1.0 ml portions.

Gel permeation chromatography procedure has been described by Determann (23) and <u>Sephadex, Gel Filtration in Theory and Practice</u> (78).

TOC, measured on each fraction collected, was used as the concentration parameter. Collected fractions were too small to be tested for color or A_{265}.

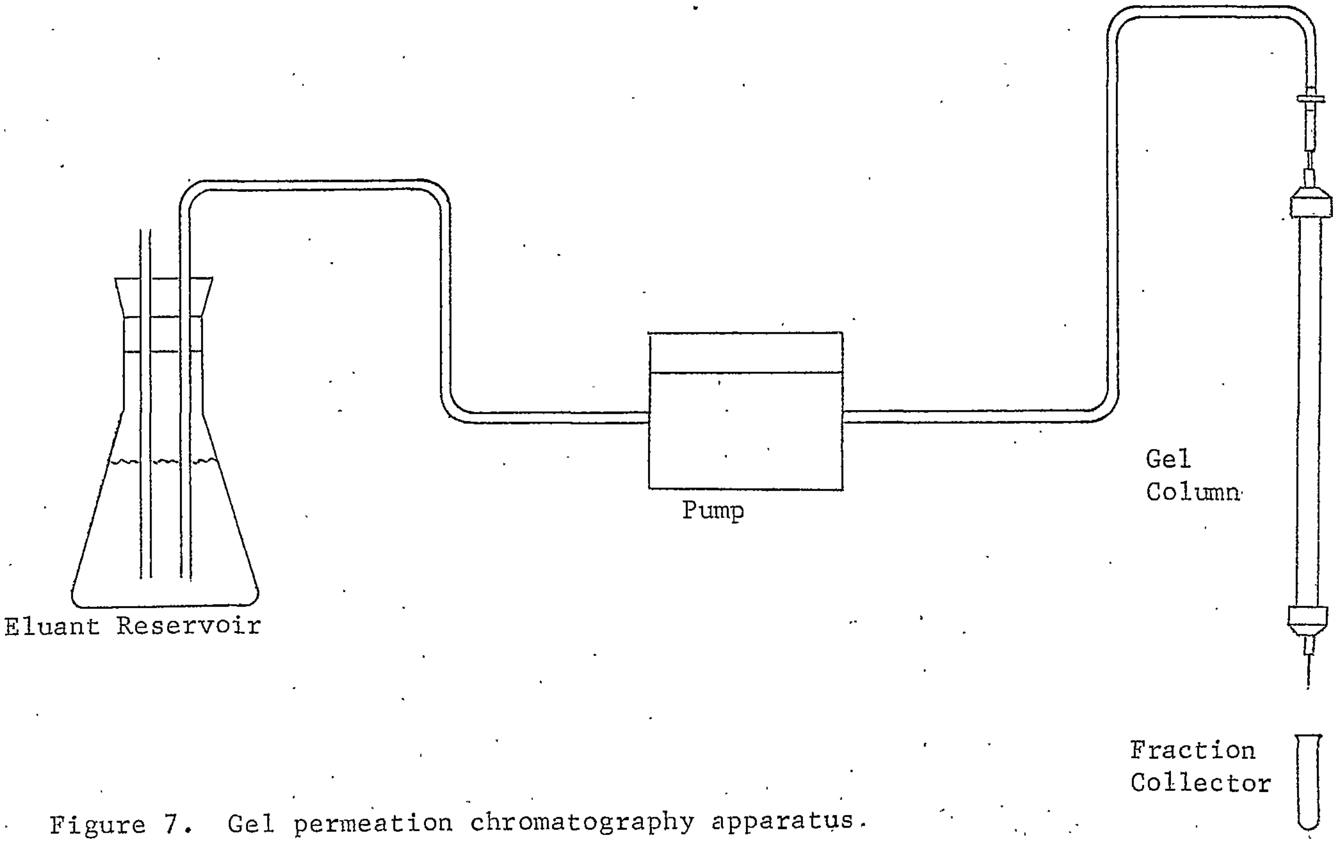


Figure 7. Gel permeation chromatography apparatus.

CHAPTER IV

RESULTS AND OBSERVATIONS

A. BATCH SORPTION

The effectiveness of the sorbents tested varied over a wide range. Some removed significant portions of color, TOC, and A_{265}. Others performed poorly. The most ineffective sorbents were coal, bentonite, diatomaceous earth, Celkate and HyfloSupercel. After initial tests showed the poor performance of these materials, they were rejected and eliminated from further consideration.

The most promising sorbents were alumina, fly ash, hog fuel ash, activated carbon, LAD-500, A-6 and S-37.

Each of these sorbents increased the pH of the wastewater. Figures 8 and 9 are typical of this pH increase. Table 4 summarizes these data. Changes in pH were minor for LAD-500, alumina, and S-37. The changes were larger for activated carbon and A-6. Both fly ash and hog fuel ash increased pH to over 12.

Figures 10 through 12 show the effect of a sorbent on the wastewater parameters of color, TOC, and A_{265} for each dosage of sorbent and for each time interval. In general, the maximum dosage (5 g/100 ml) for the longest period of time (two hours) resulted in the best removals. These data are summarized in Table 5.

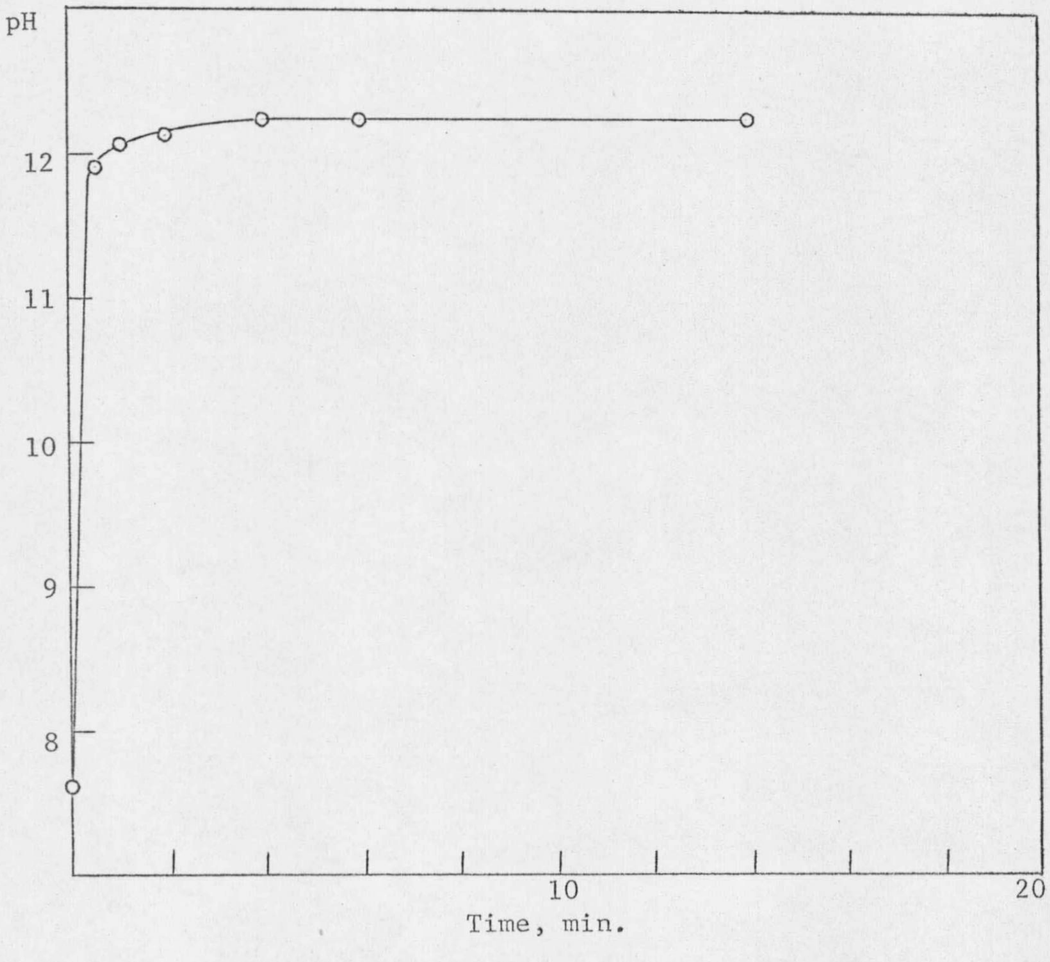


Figure 8. Variation of pH with time during hog fuel ash sorption

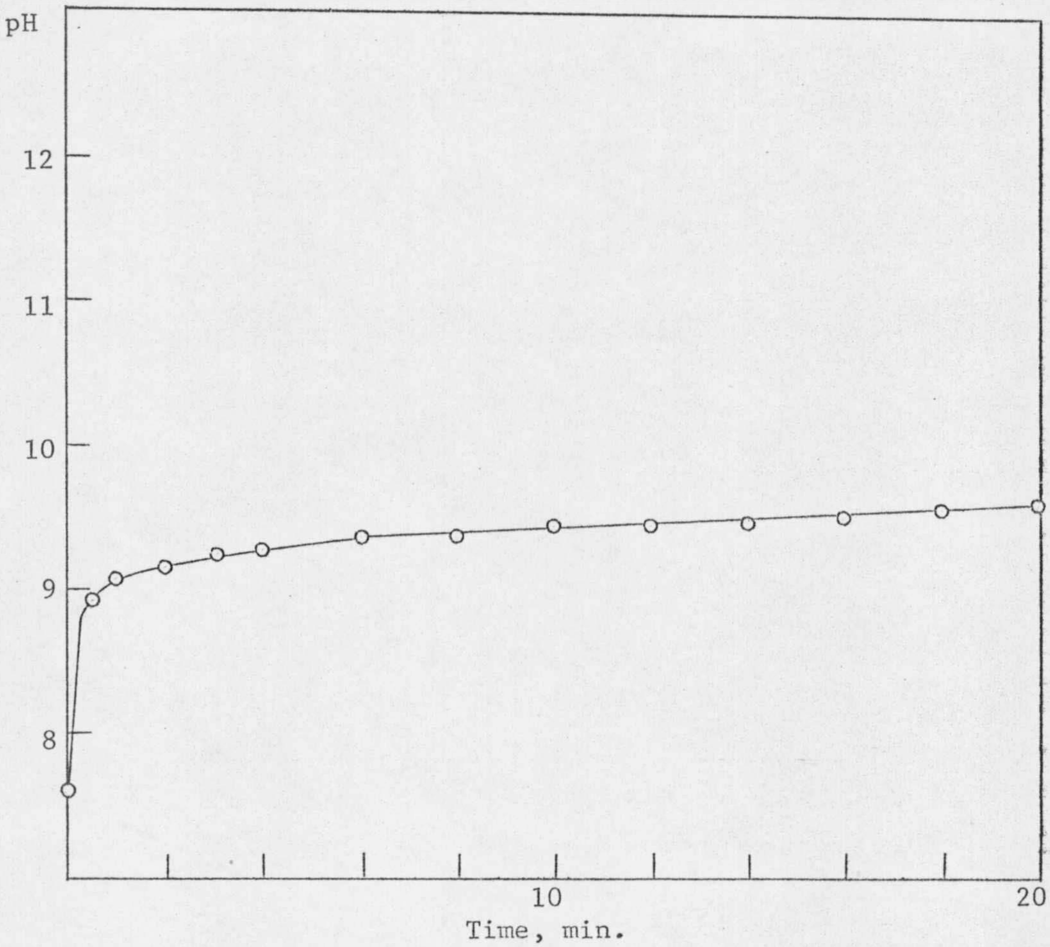


Figure 9. Variation of pH with time during activated carbon sorption

TABLE 4

pH VARIATION WITH TIME IN BATCH SORPTION

Adsorbent	Dosage, g/100 ml	Time to Equilibrium pH, min.	Equilibrium pH
Alumina	5	5	8.5
Fly Ash	5	15	12.3
Hog Fuel Ash	5	5	12.2
Activated Carbon[a]	5	25	9.7
LAD-500	1	0	8.0
A-6	5	15	10.9
S-37	5	10	9.2

[a] Filtrasorb 400

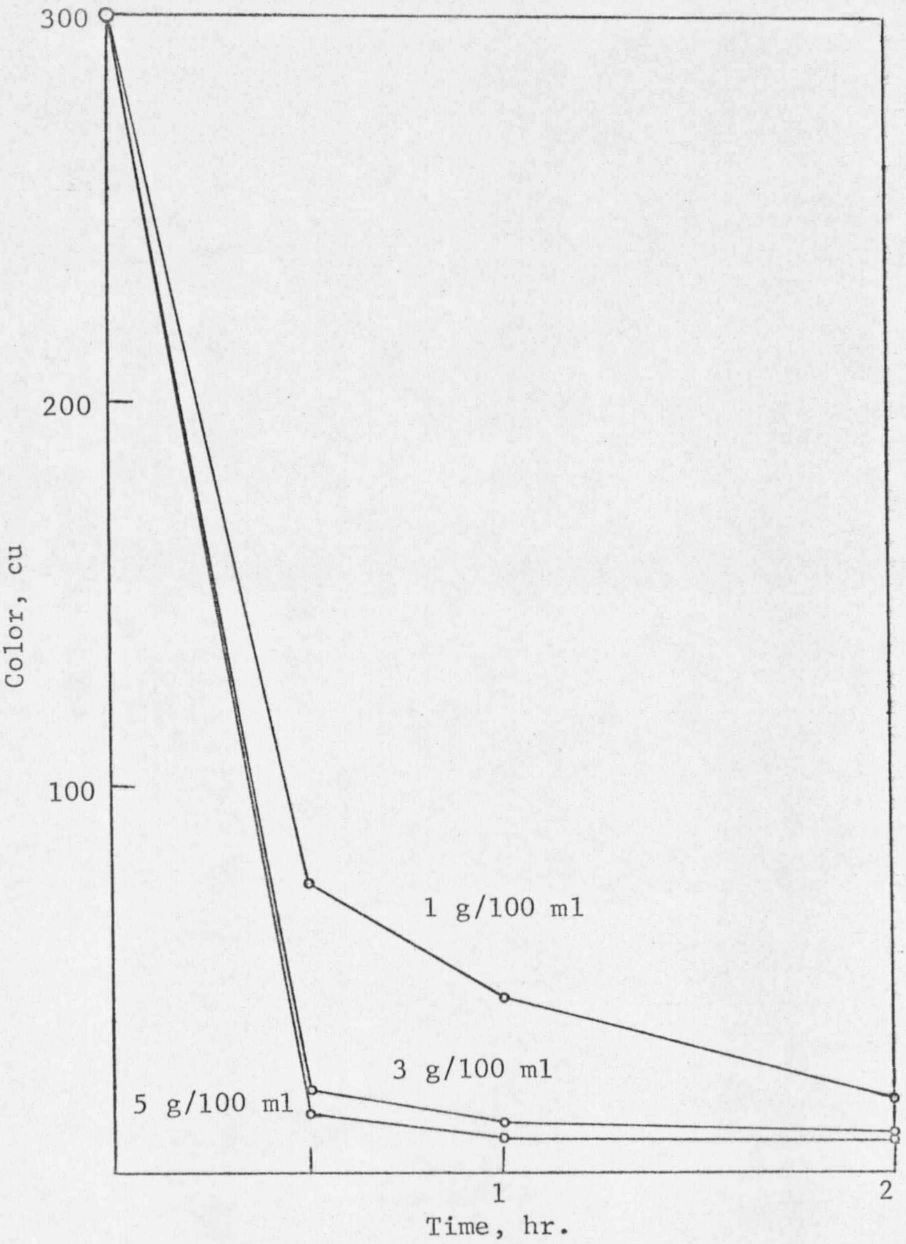


Figure 10. Batch sorption of color by S-37

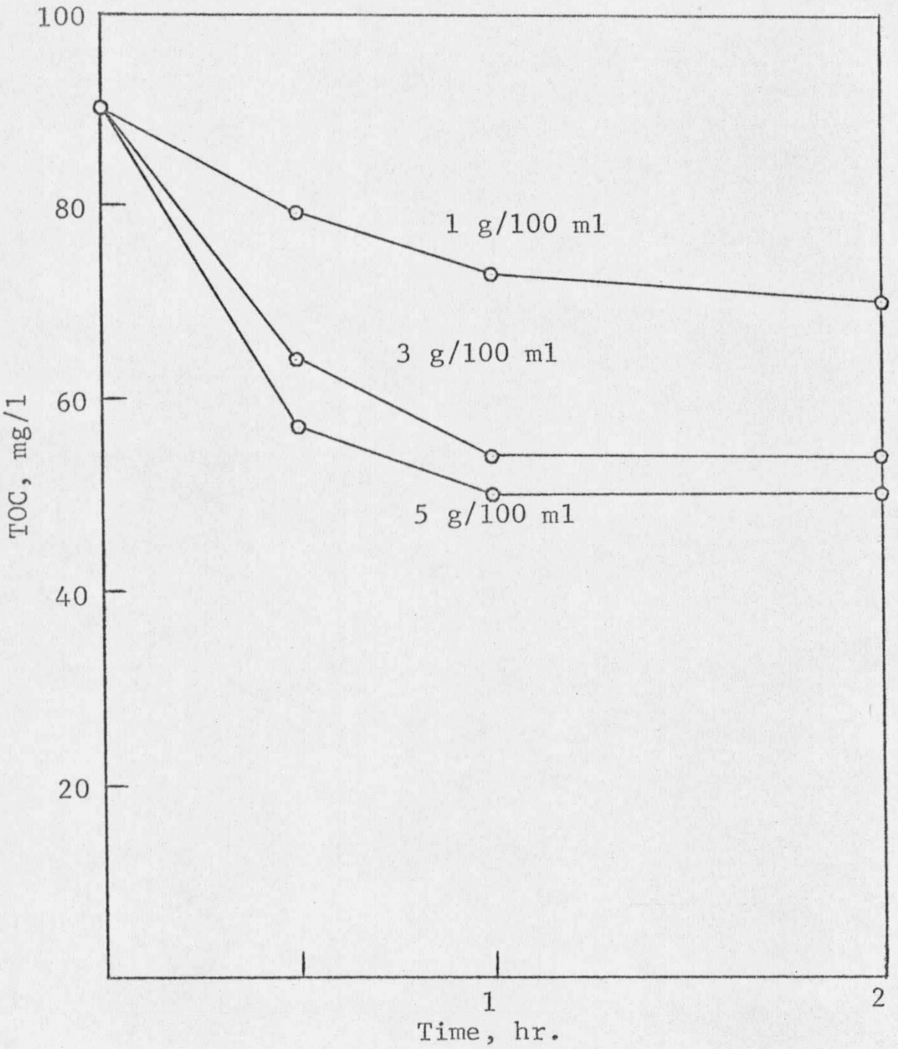


Figure 11. Batch sorption of TOC by hog fuel ash

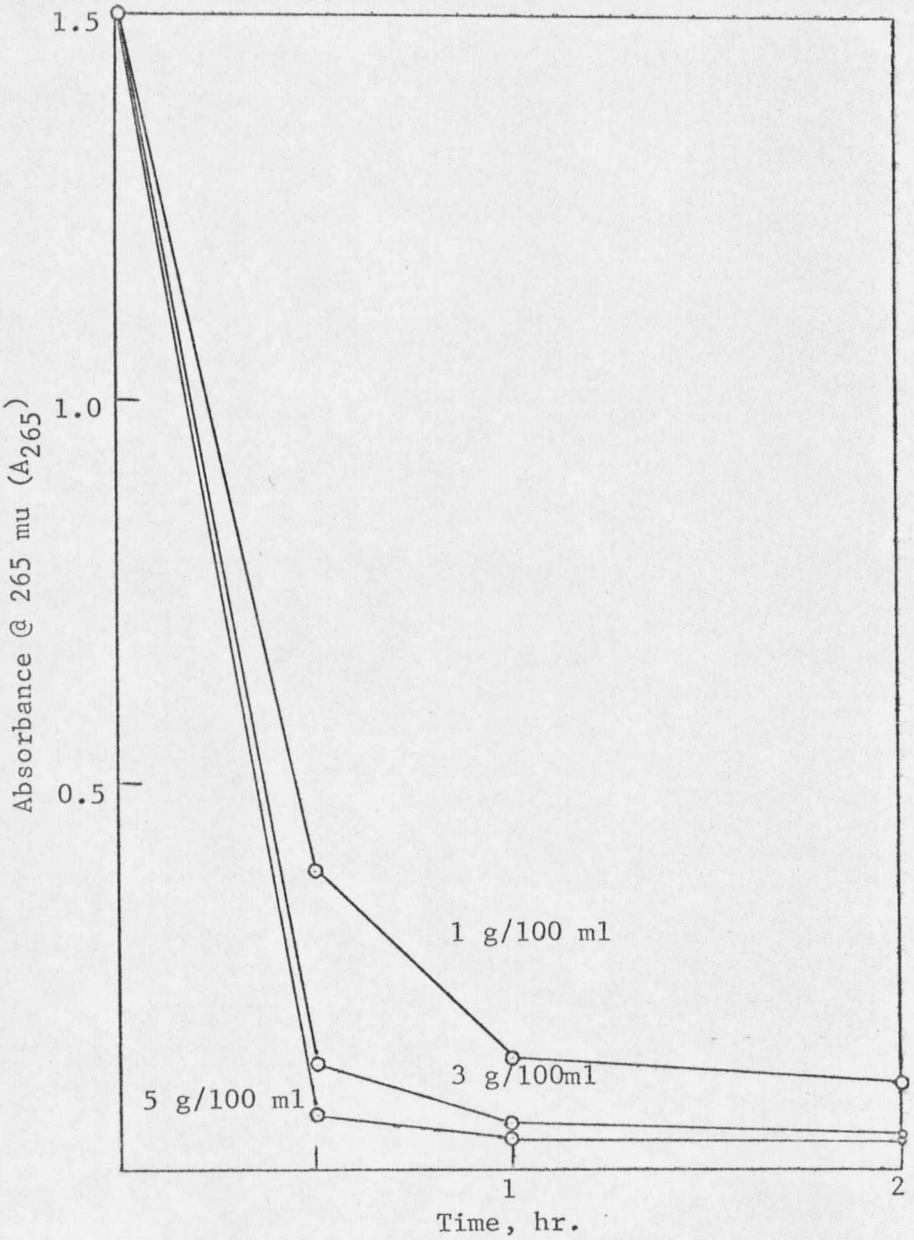


Figure 12. Batch sorption of A_{265} by activated carbon

TABLE 5

SUMMARY OF RESULTS FROM
BATCH SORPTION

Wastewater	Dosage g/100 ml	Color, Cu	TOC, mg/1	A_{265} Removal, %
Raw Waste		300	90	
Treated with:				
Alumina	5	90	62	43
Fly Ash	5	60	50	64
Hog Fuel Ash	5	37	50	70
Activated Carbon[a]	5	10	24	98
LAD-500	1	27	56	74
A-6	5	8	49	78
S-37	5	6	40	85

[a] Filtrasorb 400

The best sorbents were activated carbon, S-37 and A-6, all commercial products.

As previously stated, one of the goals of this research was to find a locally available sorbent which might compete with activated carbon in the treatment of Kraft bleach wastewater. Of the local sorbents tested, hog fuel is probably the only candidate since it performed much better than fly ash and alumina.

Examination of Table 5 shows that activated carbon was unquestionably a better sorbent than hog fuel ash in these experiments.

Hog fuel ash did not produce a water which would likely be acceptable as Kraft bleach process water. Even as unbleached Kraft process water, the TOC is probably excessive. But sorption on hog fuel ash followed by biological treatment may produce a water acceptable for the unbleached Kraft process.

Clearly, further research is needed to investigate the economics of a continuous flow system and to examine problems which were encountered in this project. For example, hog fuel ash raised the pH of the wastewater to over twelve. This pH would have to be reduced before biological treatment could be applied. Another potential problem is the observation that, in containers holding Kraft bleach wastewater which had been contacted with hog fuel ash, an extremely insoluble white precipitate formed around the containers at the meniscus after a period of a few days. The deposition of a persistent precipitate on Kraft bleach process equipment would be objectionable.

One promising aspect of the use of hog fuel ash is the ease with which the wastewater may be filtered through the ash. Most of the sorbents, activated carbon in particular, abraded in the batch tests and quickly plugged the 0.45 u Millipore filters. Hog fuel ash was an exception. This suggests the dual use of the ash as a filter media for suspended solids removal and as a sorbent for the removal of organics.

B. GEL PERMEATION CHROMATOGRAPHY

Figure 13 shows the chromatogram of raw wastewater on Sephadex G-50. Clearly there is no separation of components and apparently all components are of a size smaller than 500 MW, the lower limit of the fractionation range, since the peak lies to the right of the 500 MW calibration line.

Figure 14 shows the chromatogram of raw wastewater on Sephadex G-25. The shoulder at 15 ml hints of a separation, but apparently most of the molecules are of a size smaller than 330 MW, as shown by large peak to the right of the calibration line.

Figure 15 shows the chromatogram of raw wastewater on G-10, the Sephadex gel with the smallest fractionation range. The peak at 13 ml, the shoulder at 15 ml, and the peak at 19 ml indicate the separation of three fractions. All three fractions lie within the fractionation range of the gel.

Having chosen Sephadex G-10 as the appropriate gel, chromatography runs were made on wastewater treated with each sorbent. The chromatograms are shown on Figures 16 through 22. Each chromatogram confirms the separations with peaks or shoulders at 13, 15, and 19 ml. At first glance, the chromatograms appear to show the effect of each sorbent on each of the three separation zones.

But scrutiny of the chromatograms raises some doubt about their accuracy. For most of the sorbed wastewaters, the quantity of TOC in the eluate was quite different from the quantity of TOC in the sample.

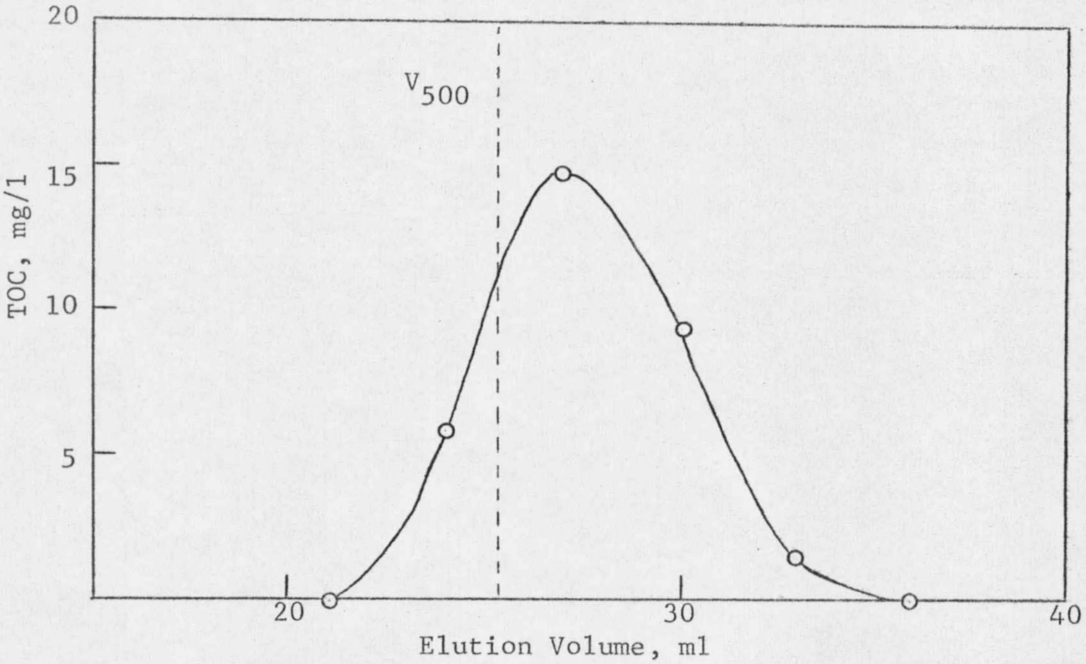


Figure 13. GPC of raw wastewater on G-50

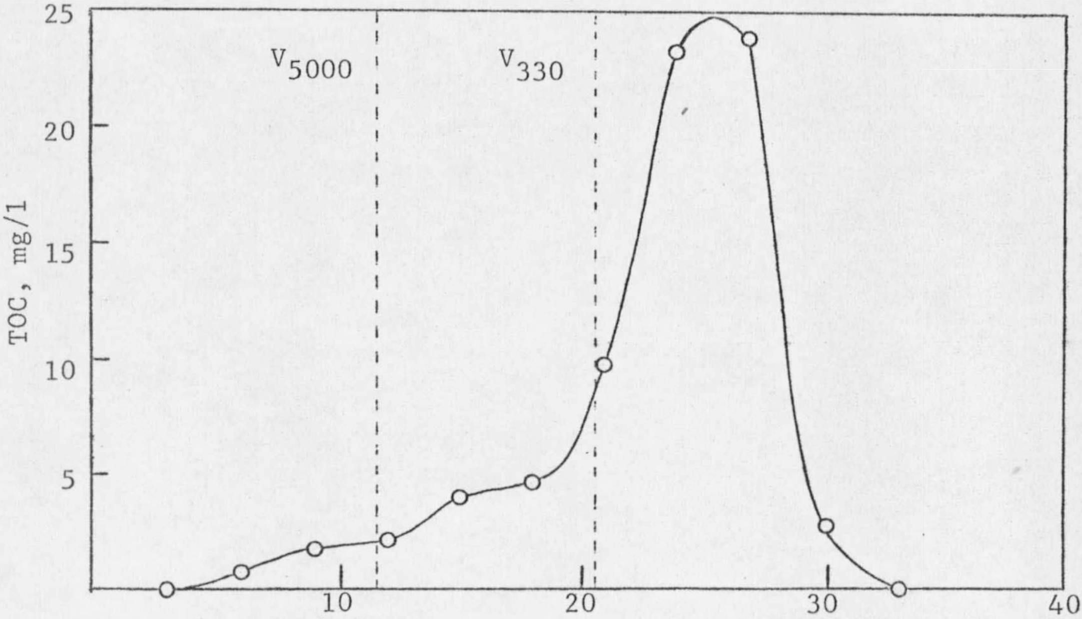


Figure 14. GPC of raw wastewater on G-25

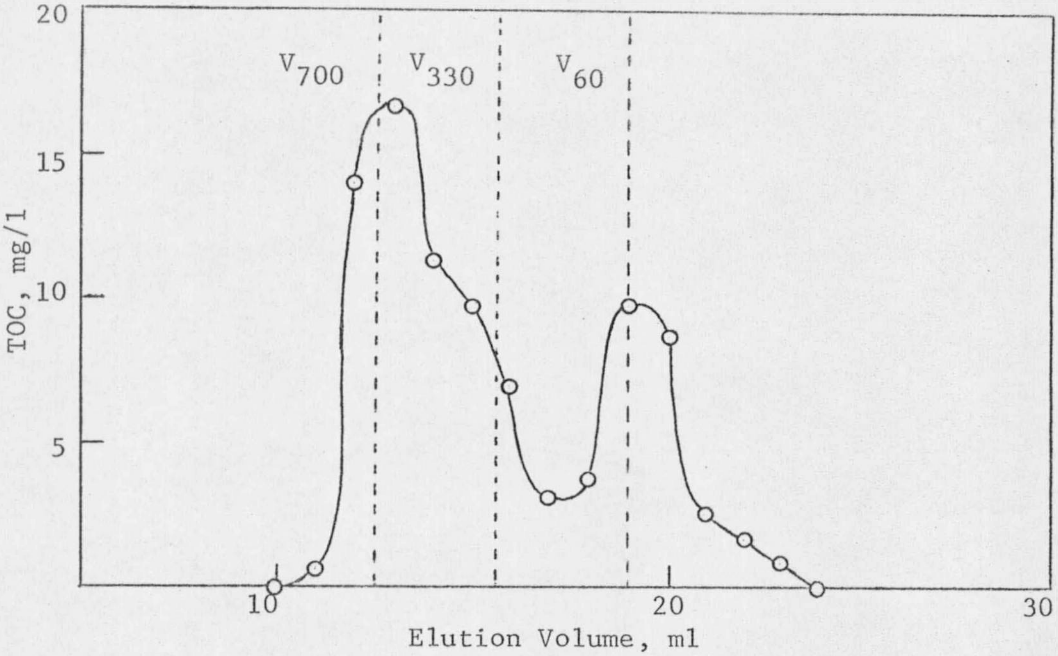


Figure 15. GPC of raw wastewater on G-10

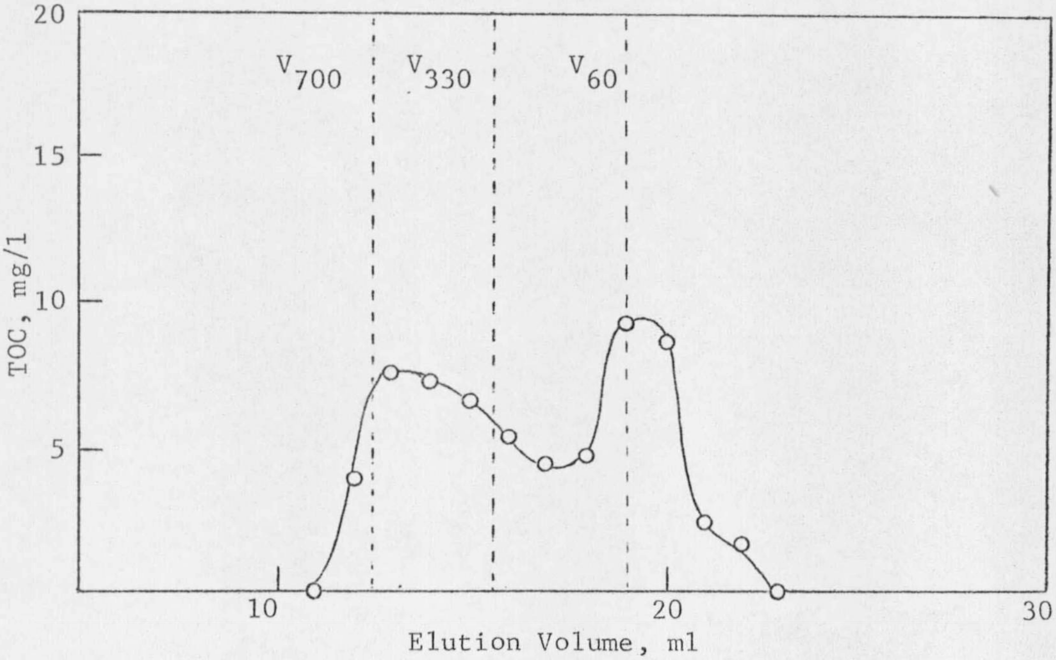


Figure 16. GPC of alumina sorbed wastewater on G-10

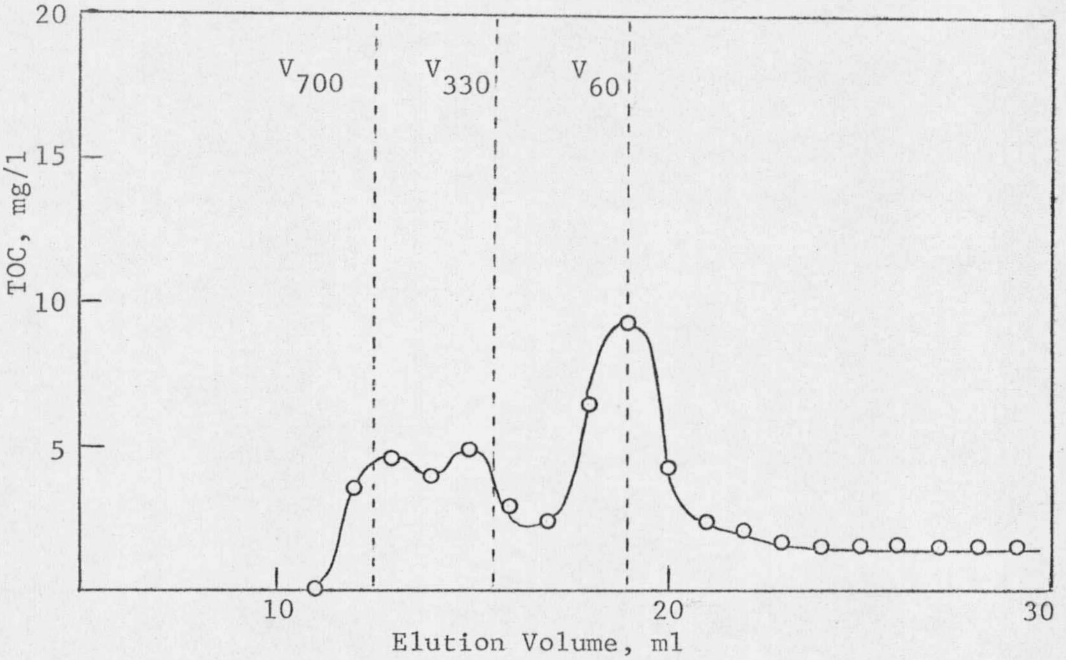


Figure 17. GPC of fly ash sorbed wastewater on G-10

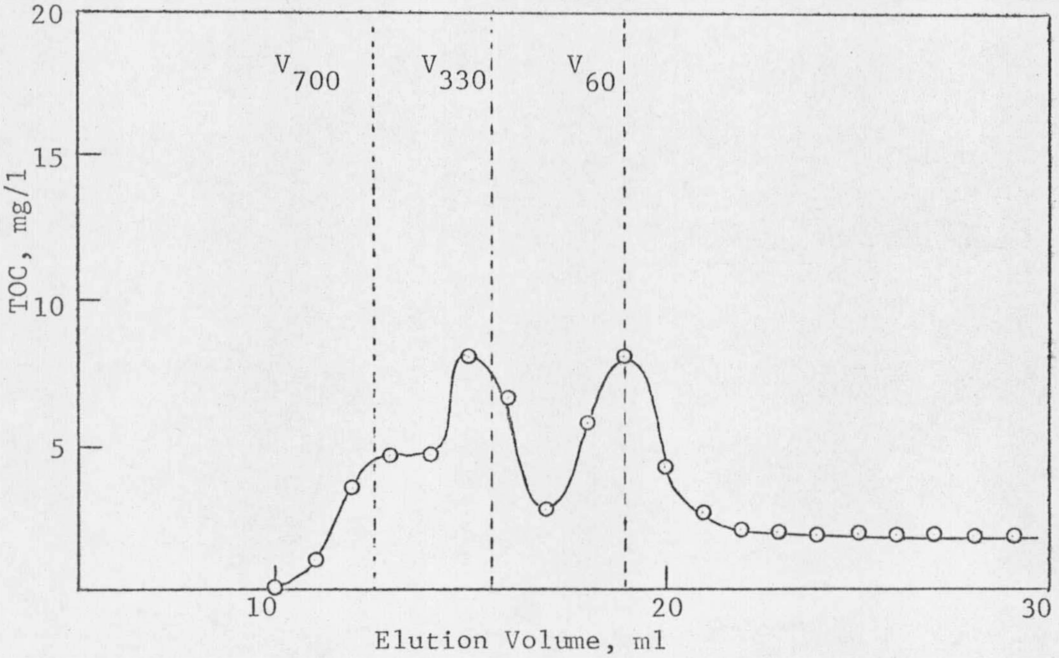


Figure 18. GPC of hog fuel ash sorbed wastewater on G-10

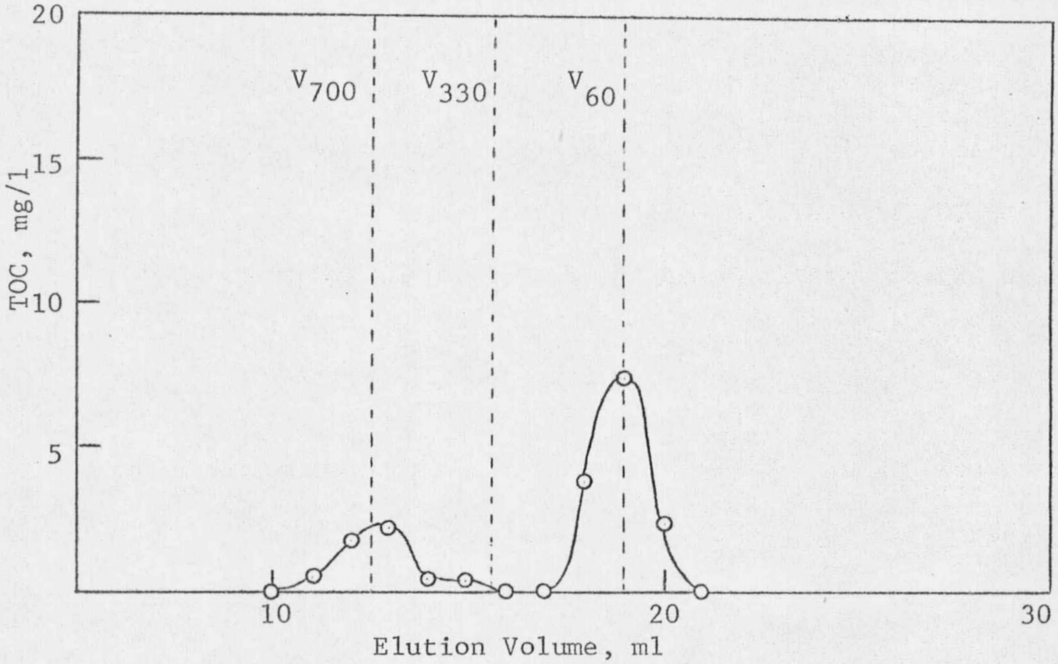


Figure 19. GPC of activated carbon sorbed wastewater on G-10

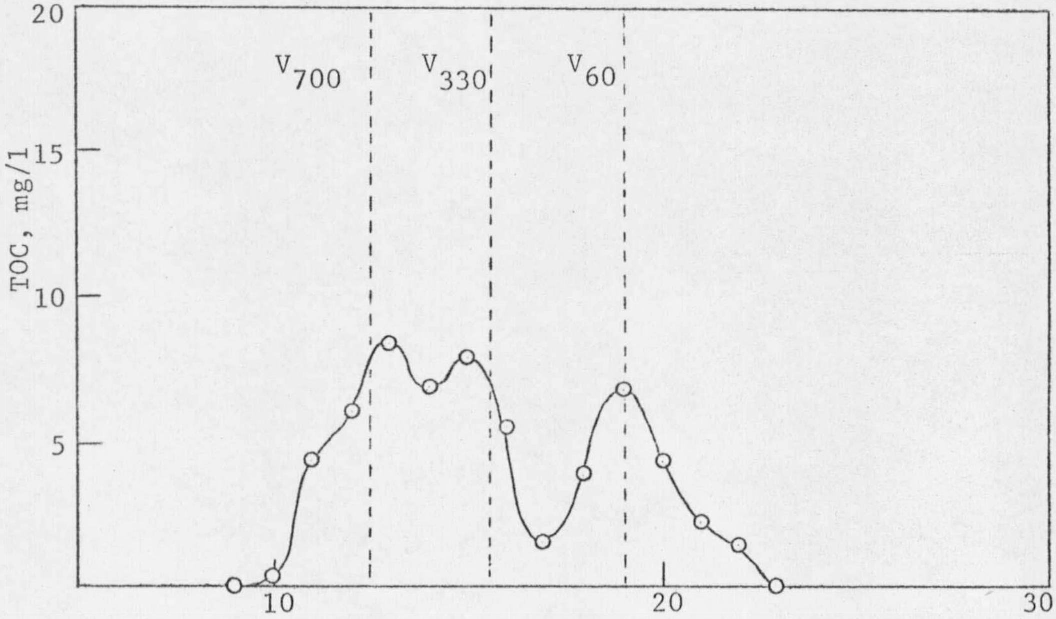


Figure 20. GPC of LAD-500 sorbed wastewater on G-10

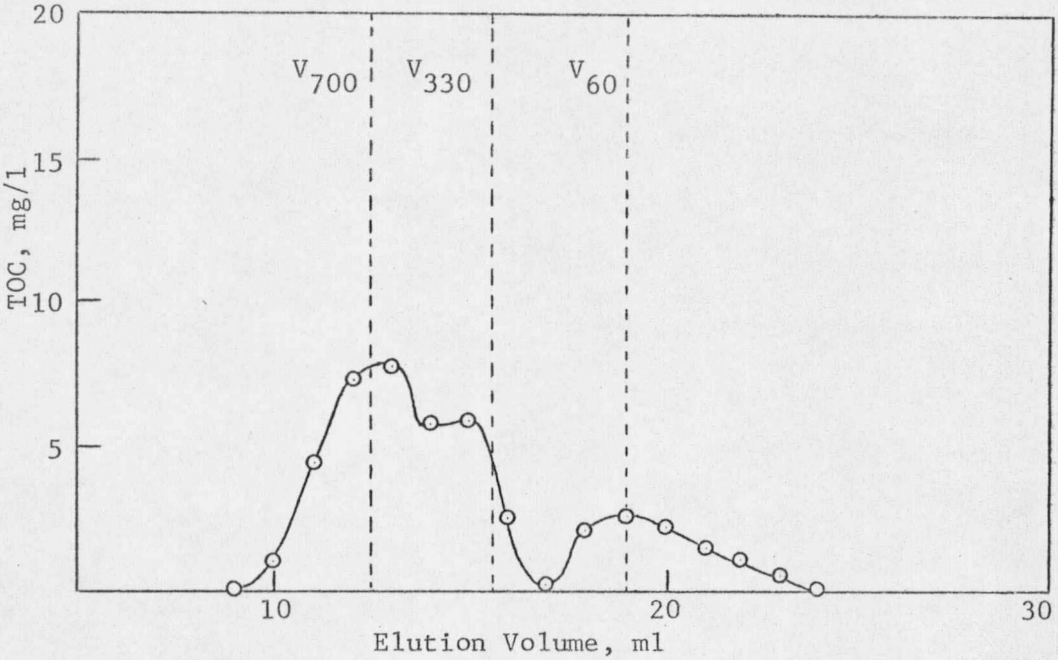


Figure 21. GPC of A-6 sorbed wastewater on G-10

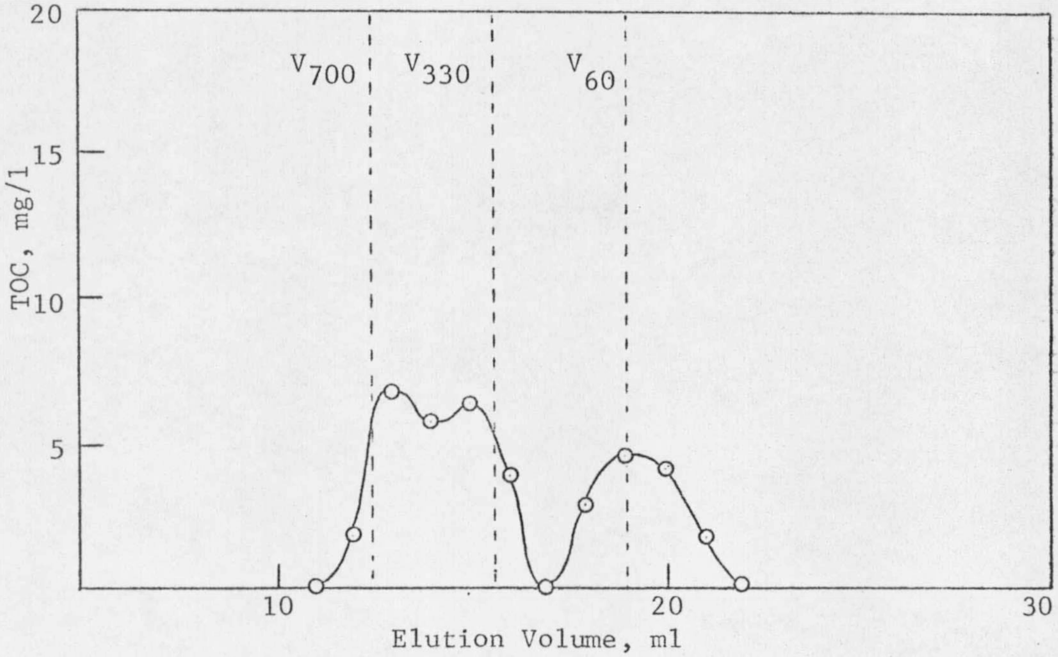


Figure 22. GPC of S-37 sorbed wastewater on G-10

As shown in Table 6, for the raw wastewater and the A-6 sorbed wastewater, the TOC in the eluate matched the sample TOC. For wastewaters treated with activated carbon and S-37, eluate TOC was considerably less than sample TOC. For the other sorbents, the eluate TOC was greater than sample TOC. For fly ash and hog fuel ash treated wastewaters, Figures 17 and 18, the eluate TOC seems to continue indefinitely.

It appears some components in some wastewaters are sorbed on the gel. The result is a chromatogram with less TOC than the sample. For other wastewaters, it appears that previously sorbed molecules are eluted with the sample resulting in a chromatogram with more TOC than the sample. Or conceivably, some organic carbon was eluted from the Sephadex gel itself.

TABLE 6

YIELD FROM GEL PERMEATION CHROMATOGRAPHY ON RAW AND TREATED WASTEWATERS

Sorbent	Yield, TOC Applied/TOC Eluate
Activated Carbon	0.58
S-37	0.71
Raw Wastewater	1.00
A-6	1.00
LAD-500	1.10
Alumina	1.23
Fly Ash	1.10+
Hog Fuel Ash	1.50+

CHAPTER V

DISCUSSION AND CONCLUSIONS

Within the stated limitations of this research, moderate success was achieved in finding a substitute for activated carbon as a sorbent in Kraft bleach wastewater treatment. Hog fuel ash may be such a substitute.

Hog fuel ash is produced at Hoerner Waldorf at the rate of about seven tons per day. Based on the wastewater flow of 3450 gpm, the hog fuel ash could dose the wastewater at about 0.014 g/100 ml. This is at least two orders of magnitude below the dosages used in this research. Obviously, hog fuel ash is not produced in sufficient quantities to provide one-time sorption of Hoerner Waldorf's wastewater.

Several other treatment schemes may be considered. One is two stage treatment. Hog fuel ash could conceivably be used as a "roughing filter" followed by an activated carbon "polishing filter". The purpose of the hog fuel ash would be to reduce the quantities of activated carbon required. An advantage of this scheme is that hog fuel ash is highly permeable to water and could also serve to remove solid materials suspended in the wastewater.

An alternate scheme would be split treatment. A small portion of the wastewater could be treated to a particular standard by hog fuel ash sorption. Discharge water and various reuse waters have different quality requirements. A small flow of hog fuel ash sorbed wastewater may meet one of these requirements.

Another possibility is the use of hog fuel ash in place of activated carbon. This would require regeneration and recycling of the hog fuel ash, since it is not produced in sufficient quantities to use only once. This scheme has advantages. First, the hog fuel ash is essentially free. Second, the hog fuel ash passes the wastewater freely without clogging.

This alternative also would have disadvantages. Hog fuel ash does not sorb as well as activated carbon. It was about ninety percent as efficient as carbon at color sorption, but only about seventy percent as efficient at A_{265} removal and sixty percent as efficient at TOC removal. Therefore, hog fuel ash sorption would require larger quantities of sorbent and correspondingly larger treatment equipment.

Further research is needed before the feasibility of hog fuel sorption can be determined. A continuous flow process must be evaluated and regeneration techniques must be tested. The batch tests performed during this research indicate promise.

The gel permeation chromatography of raw and treated Kraft bleach wastewater showed the molecules in the solution are of a molecular size less than 500 MW. If the wastewater prior to massive lime precipitation contains molecules of size greater than 500 MW as claimed by NCASI (58, 61), then this result confirms the claims of NCASI (58, 61) that lime precipitation removes the larger molecules.

It is evident the wastewater is composed of three distinct molecular size fractions. One of these fractions coincides with the peak for inorganic carbon, so it represents a molecular size of about sixty. Within the accuracy of this technique, this peak could represent a single aromatic ring. There is no clue to the identities of the other two peaks.

As pointed out in the previous section, the gel behaved somewhat differently for each sample. For two samples, the gel appeared to sorb a portion of the molecules. For other samples, the TOC of the sample and the eluate were closely matched. For still other samples, the gel appeared to release previously sorbed molecules so the eluate TOC was higher than the sample TOC. Apparently, some quality of the wastewater samples affected the behavior of the gel.

One possible parameter which could affect the gel is sample pH. The wastewaters with the highest yield from GPC were the two with pH's in excess of 12. Beyond that, there is no apparent relationship between pH of sample and yield.

Aromaticity of the sample is another consideration. It may be predicted that the wastewaters with the largest concentrations of aromatic compounds will have the lowest yields on Sephadex GPC because of aromatic adsorption (see Section II. D. 1. a.). But the activated carbon treated wastewater had little aromaticity as evidenced by its low A_{265}, yet it shows the poorest yield.

Another variable to be considered is sample ionic strength. Weber (100) warned that not only pH, but also ionic strength can profoundly affect the behavior of Sephadex gels. No ionic strength measurements were made in this research.

For lack of an explanation for the variable GPC yields, it would be presumptuous to attempt to analyze the chromatograms with respect to sorption of the specific fractions by the various sorbents. Further research utilizing pH and ionic strength adjustment of the treated wastewaters and GPC on Bio-Gel gels may yield insight into this aspect of the problem.

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