

COLOR REMOVAL FROM PULP AND PAPER WASTES BY COAGULATION

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(ABSTRACT)

Coagulation studies were conducted to determine an appropriate treatment approach to remove color and organic carbon from the pulp and paper wastes from the Union Camp Corporation, Franklin, Va.

Based on a preliminary analysis of the data collected during this research, either alum or ferric chloride may be used to remove color from pulp and paper wastes. An effluent with final residual color less than 5 color units can be generated using PAC treatment after flocculating certain waste streams with alum or ferric chloride. Higher molecular weight organics (above 5K mass units) showed a near complete removal by coagulation.

It is expected that alum coagulation would involve a lesser cost in pH adjustment as compared to ferric chloride coagulation. Alum sludge dewatered and thickened more rapidly than the iron sludge; however, after mechanical dewatering, the alum cake had a slightly greater moisture content than the sludge produced after ferric chloride coagulation.

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CHAPTER I

INTRODUCTION

One of the major pollutants in the pulp and paper industry is the color of the effluents to be finally discharged. Apart from aesthetic reasons, color in receiving streams has a considerable effect on the biological activity as it hinders light penetration. Due to these reasons, the United States Environmental Protection Agency has imposed certain specific criteria for color in discharging effluents.

A major problem in the pulp and paper industry is the immense amount of water required for the pulping and bleaching processes. A typical plant uses about 15,000 to 60,000 gallons per ton of bleached pulp (1). The alternative sought to cut down on this large water requirement is recycle and reuse of wastewater; however, the final treated effluent to be recycled may be required to have color levels as low as 5 Pt-Co units (2).

Conventional biological treatment processes remove very little color from pulp and paper wastes. At present, coagulation is considered to be a technically feasible method for color removal. The use of various chemical coagulants has been reported in the literature. The success of a particular

coagulant in removing color depends upon a number of factors such as wastewater characteristics, coagulant dosage and cost, pH conditions, sludge production and sludge characteristics, reuse and regeneration of coagulant, etc.

Alternatively, ion exchange, carbon adsorption, reverse osmosis, and ozonation have also been tested for color removal from pulp and paper wastes and have been shown to be quite successful in many cases. However, the economics of these processes often precludes total treatment and has application only for the removal of residual color after coagulation.

This research has been aimed at treating the effluents from a pulp and paper plant for color removal using coagulation techniques. The main objectives of this research could be broadly classified as to:

1. Determine the optimum dosage and pH conditions for removal of color and organic carbon from pulp and paper wastes using alum or iron;
2. Compare the effectiveness of polymers with metal ion coagulants for color removal;
3. Use ultrafiltration techniques to determine the molecular weight size of organics present in pulp and paper wastes during coagulation; and

4. Perform sludge testing to determine thickening and dewatering characteristics of sludge produced in metal ion coagulation.

CHAPTER II

LITERATURE REVIEW

A review of literature published in the recent past was conducted to look into the various coagulation techniques used in the pulp and paper industry to solve the problem of removing color from wastewaters. The following sections deal with the characteristics of color bodies, the numerous measurement techniques applicable for color analysis, and the various physico-chemical and biological color removal techniques used in practice.

CHARACTERISTICS OF ORGANICS AND COLOR BODIES IN PULP AND PAPER WASTES

In a study to investigate the origin of color in pulp and paper wastes, Nebel et al. (3) reported that color may be produced by both organic and inorganic constituents. In the pulp and paper industry, one is predominantly concerned with colors of organic origin. The naturally occurring organic colored materials were classified into an undefined category known as humus materials. Such humus materials are very water soluble and have intermediate molecular weights,

are colored and are not readily biodegraded. The second type of organic materials, discussed by Nebel et al. were the water soluble synthetic dyes employed in the production of colored papers. These were felt to be more bio-degradable than the humus materials.

The major sources of color from the pulp mill are the caustic extraction stage in bleaching, the unbleached screenings and the decker filtrates (4). The colored material was felt to originate from the lignin and the lignin derivatives which are washed out of the cooked pulp. Since lignin is highly resistant to biological degradation, it passes through the biological treatment processes and makes the effluent waters brownish-black in color.

Fuller et al. (5) reported that tannins reacting with iron, natural color bodies of the wood, and the biomass, particularly if it went anaerobic, also add to the color levels of wastewaters. The presence of all these substances tends to color the effluent black.

In addition to color, there are also many other pollutants in pulp mill wastes that can be a cause of major concern. Rapson et al. (6) indicated these to be the suspended solids consisting mainly of bark fines and wood fibers, soluble organics which lead to a high Biochemical Oxygen Demand (BOD), and various substances which were toxic to aquatic life.

Schimdt and Joyce (7) provided evidence to indicate that the functional groups which contribute the greatest amount of color to pulping and bleaching effluents are aromatic and quinonoid nuclei which may be conjugated with carbonyl and ethylenic groups. Also, color bodies were found to be polydisperse. A single effluent may contain species ranging in molecular weight from less than 400 up to 150,000 mass units, and have an average molecular weight of 6000 mass units.

The caustic extraction stage effluent from the Kraft Mill is a true solution of colored compounds. Nasr and MacDonald (8) classified these colored compounds as hydrophilic colloids as the solution containing these caused scattering of light. The compounds were found to have high molecular weights and contain weak acidic groups which were mainly carbonyl groups that could react with trivalent ions of aluminium and iron to form a precipitate.

A study by Dugal et al. (9) showed that the color bodies which are not removed by lime treatment have an average molecular weight of less than 400 mass units. These color bodies contain conjugated carboxyl groups, have some lignin like character, and are associated with colorless carbon compounds.

COLOR MEASUREMENT TECHNIQUES.

Different color measurement techniques have been reported in the literature. Most of these involve filtering the sample to be analysed for color through a particular size filter, with or without any pH adjustment before measuring absorbance at a particular wavelength. The color is then reported either as absorbance, or converted to Platinum Cobalt Color units from an appropriate calibration curve. Some of these techniques commonly used in pulp and paper research have been described in brief as below:

A wavelength of 420 nm was used by Olthof and Eckenfelder (10) to measure absorbance of their samples. The pH was adjusted to 7.0 ± 0.1 prior to measuring absorbance. The color was reported in absorbance units.

Lathia and Joyce (11) filtered all samples for color measurement through a 0.8 micron membrane filter and adjusted pH to 7.6 before measuring absorbance at 465 nm. This procedure is prescribed by the National Council of the Paper Industry for Air and Stream Improvement, Inc., (NCASI) (12). This procedure adjusts for the pH and turbidity to give the true color of the effluent. Standardization of the spectrophotometer is accomplished by using the commercially used Platinum Cobalt Standard which conforms to 500 APHA

color units. Care is taken not to increase the volume of the samples by more than 1% during pH adjustments.

Standard Methods (13) describes a visual comparison method and a spectrophotometric method for color measurements. The spectrophotometric method involves adjusting the pH of the samples for color measurement to 7.6, and measurement of the transmittance at various wavelengths. Averaging techniques are then used to estimate the sample color value. Also described is the Tristimulus Filter Method which uses the transmittance through three special tristimulus light filters as a measure of color.

A Whatman 42 filter paper was used by Smith and Christman (14) to filter the supernatant obtained after coagulation. Color was determined by measuring absorbance at a wavelength of 420 nm at pH 7.0.

The methodology recommended by the Pulp and Paper Research Institute of reporting color in mg/L of color was made by Melynk et al. (15) in their study on color removal from Pulp Bleachery wastes. A sample having 1 mg/L of color has the same absorbance as that of 1 mg/L of platinum in a standard chloroplatinate solution (Fisher Scientific Reagent No. SO-P-120) at a wavelength of 465 nm.

In order to reduce any interference on color measurement during adjustment of pH of samples, Dugal et al. (4) made a slight change from the NCASI method by using a non carbonate

buffer for pH adjustment to 7.6 before measuring color according to the standard methods of APHA.

A different type of NCASI procedure was used by Kisla and McKelvey (16) to estimate color. Color units were determined by multiplying the optical density of the samples at a wavelength of 450 nm by 4400. No pH adjustment was made prior to optical density determination.

Instead of filtering, Lee et al. (17) centrifuged the samples and then adjusted the pH to 7.5. The absorbance of the centrifuged samples was measured at 450 nm and converted to APHA units using a standard curve.

Sundman et al. (18) reported an absorbance of 1.0 cm^{-1} at 465 nm, at pH 7.6, to be equal to 3770 NCASI color units based on chloroplatinate.

COLOR REMOVAL BY COAGULATION

Various coagulants are used in pulp and paper mills to remove color from the wastewaters. Of these, alum, ferric chloride, lime, and magnesium, have found great use. The following sections review the optimum conditions under which these coagulants have effected best color removal. Some of the limitations are also discussed.

Color removal by alum coagulation : The results of pilot plant operations with four inplant effluents as reported by

Lang (19), showed that alum coagulation consistently removed 81-93% of color, 50-62% of TOC, 22-25% of BOD and 70-86% of tall oil, and gave a product almost free of suspended solids. The optimum coagulation pH was approximately 5.5. Alum treatment of secondary Kraft effluent gave about the same results. Anionic or neutral polymers were effective at a dosage of 1-2% of alum dosage in providing rapid floc settling rates. Lab and pilot plant tests indicated that the best method for the disposal of the sludge was to regenerate the alum from the settled sludge by addition of H_2SO_4 to a pH of 2.0-2.5 and heating to 80°C. The resulting sludge was found to filter rapidly to give a cake of >20% solids and a filtrate containing the removed alum for reuse. Further tests showed that >90% of the alum was recovered with the above method and that it was as effective as fresh alum through three cycles of regeneration.

Alum flocculation was found to remove 95% color from both the alkali extraction stage and the chlorination stage effluents (20). Only 40% removal of COD was observed in contrast to the high percent color removal.

A comparison of coagulation by lime, alum, and iron on bleached kraft wastewater was carried out by Olthof and Eckenfelder (10). The results of the study are summarized in Table 1. Lime sludge was found to be difficult to dewater, and high in pH with a significant amount of calcium in solution. Hence some additional treatment steps are necessary

Table 1. Comparison of coagulation by lime, alum and iron on Bleached Kraft wastewater. (10)

COAGULANT	OPTIMUM PH	OPTIMUM DOSE (mg/L)	SVI	COLOR REMOVAL (%)
Lime	-	1500	120-200	92
Alum	4.0-5.0	250	190-230	93
Iron	3.5-4.5	500	115-200	92

after lime coagulation. Iron and alum produced an acidic sludge, but no additional treatment step was felt necessary.

Smith and Christman (14) compared color removal by alum and ferric chloride on Kraft mill effluents:

Hardwood: The hardwood effluent had an initial color of 710 Pt-Co units. Alum readily coagulated with a broad optimum pH range. Color removal of 89% was effected at a dosage of 150 mg/L at an optimum pH of 5.3. The color to optimum dose ratio with alum coagulation was determined to be 4.7. Ferric chloride, on the other hand, showed a very narrow range of optimum pH. Color removal of 87% was observed at a dose of 286 mg/L at a pH of 3.9. The color to optimum ratio was the same as that for alum.

Softwood: The softwood effluent had an initial color of 1320 Pt-Co units. Alum coagulation achieved 92% color removal at 300 mg/L at a pH of 5.3, at a color to optimum dose ratio of 4.2.

Both iron and alum were found to be ineffective for color removal when treating sulfite wastes. Recycle of the sludge was found to be helpful. Bulking of the sludge was found to be a major problem with sludge handling.

Apolinarski et al. (21) attained substantial COD and color reductions at alum doses of about 450 mg/L added to an activated sludge aeration vessel to simultaneously coagulate lignin compounds. This method produced increased amounts of

sludge, but with better filtration properties. No effect on BOD reduction was observed.

In developing relationships between alum dose, alkalinity, acid for neutralization, and effluent color, to control chemical treatment of biologically treated kraft mill effluent, Alesina et al. (22) concluded that the alkalinity of the effluents was often higher than necessary for the hydrolysis of aluminium sulfate; hence, an extra amount of alum was required to achieve the optimum pH for coagulation. In such cases, the authors observed a reduction in the amount of alum required by partially neutralizing the effluent with sulfuric acid (the neutralization level being a function of the initial color). For practical purposes, the coagulant dose required was considered to be equal to the alkalinity of the wastewater.

Berov et al. (23) suggested that neutralization after alum coagulation of biologically treated kraft mill effluents was not necessary before discharge into the receiving stream. Although the optimum pH for the alum coagulation was 5.5 to 5.8, the reaction of the H^+ ions with the dissociated OH^- groups of lignin increased the pH to 6.2-7.1.

Addition of clay and polymers to paper mill process water along with alum can improve coagulation (24); however, there are some problems of fine alum floc carryover and the post-precipitation of aluminium after filtration.

The combined treatment involving aeration in the presence of powdered activated carbon (PAC), followed by alum coagulation, was proposed by Dorica and Wong (25) to be the most effective method for color and toxicity removal. An initial color of 175-870 color units was reduced by 90% with either 110 mg/L of alum or 500 mg/L of lime.

Fuller et al. (5) studied the use of silica skeleton as a slurry with aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3$) or aluminium chloride (AlCl_3) to act as a reaction surface, an agglomerating medium, a settling aid, and a filter aid. Best color removal was observed at pH 5.0 to 5.3. Coagulation after biological oxidation was recommended for best reduction of color and other parameters. Alum could be regenerated by treating the incineration ash with sulfuric acid (H_2SO_4).

The recovery and reuse of the alum sludge from treatment of kraft mill effluent for COD and color removal was investigated by Horikoshi et al. (26). The approach suggested involved first conditioning the sludge with lime and calcium carbonate (CaCO_3) to increase pH to 12.0, then dewatering, followed by incineration at 900°C with H_2SO_4 or hydrochloric acid (HCl).

In a study to determine if zeta potential could predict optimum conditions for color removal by coagulation, Jo et al. (27) observed that the minimum zeta potential occurred at the optimum pH in coagulation of lignin in pulp mill

effluents with alum. This correlation was not nearly as strong for small doses of alum.

Color removal using lime : Dugal et al. (4) reported lime treatment to remove an average of 86% color, 57% TOC and 17% reducing sugars. Color bodies having molecular weight <400 are not removed by lime treatment at all, while color bodies with molecular weight >5000 are completely removed. No removal of chlorides was achieved by lime coagulation.

In their study of iron coagulation in conjunction with lime on kraft bleached caustic extracts, Dugal et al. (9) observed that over 50% of the color left behind by the conventional lime treatment processes could be removed by incorporating Fe^{+3} ions with lime. Ferric chloride ($FeCl_3$) (100-300 ppm) with lime (300-500 ppm) resulted in 90% color removal, whereas 600 ppm lime alone could achieve only 72% removal.

No substantial reduction in the quantity of lime required to remove color by manipulation of the hydraulic residence time (HRT) or the mean cell residence time (MCRT) could be achieved by Joyce et al. (28). Best color removal for the effluent with initial color of 360 Pt-Co units was 94% at a lime dose of 3000 mg/L.

Lathia and Joyce (11) observed that the combination of lime treatment with magnesium oxide (MgO) was more effective than lime alone in both the Neutral Semi Sulfite Chemical

(NSSC) and the Bleached Kraft Mill Effluent (BKME). A dosage of 500 ppm of lime with 50-100 ppm of MgO resulted in 90% removal of color from BKME. Magnesium recovery from the sludge was possible; the recovered magnesium could be effectively recycled.

A tremendous improvement in color removal from pulp wastes was observed by adding a small amount of seawater (10-20%) to the effluents alongwith lime. Table 2 depicts the various combinations of seawater with lime that Rapson et al. (6) found to be successful in comparison to lime alone when treating various wastewaters.

Color removal using Iron: Nasr and MacDonald (8) observed very high color removals from Kraft pulp caustic extraction wastes using trivalent metal ions. Ferric addition resulted in 88.6% removal at a pH of 3.3; aluminium affected 99.6% removal at pH 5.0 at an equivalent dosage. Lime produced 97.8% color removal at a pH of 12.4-12.7. The use of acidified flyash as a source of aluminium and ferric was suggested.

Color removal using Magnesium: The use of magnesium (Mg) in conjunction with lime can be very effective in color removal from pulp and paper wastes. In a study on Total Kraft mill effluents by Oldham and Rush (40), a 90% color removal was possible using 300 mg/L of calcium oxide (CaO) with 60-90

Table 2. Addition of sea-water along with lime to improve color removal from pulp and paper wastes. (6)

LIME (mg/L)	SEA-WATER percent	INITIAL COLOR Pt-Co units	PERCENT COLOR REMOVAL
Alkaline Bleach Effluent			
1800	0	10000-12000	< 20
1600	20	10000-12000	80
Kraft Mill Acid Bleach Effluent			
1800	0	300	70
1800	10	300	88
Combined Effluent			
1800	0	2500-4000	84
350	10/20	2500-4000	84
1800	10/20	2500-4000	95

mg/L of Mg. The biologically treated Kraft mill effluents (BTKME) required a dosage of 1000 mg/L of CaO for a 90% removal of color and a 80% reduction in the chemical oxygen demand (COD). However, with 30-60 mg/L of Mg, only 500 mg/L of CaO was necessary to achieve the same color and COD removals from the BTKME.

In dealing with reuse of magnesium from color sludge, Rush and Oldham (29) reported that the magnesium recovery by recarbonation was very efficient. An 80% recycled magnesium was found to be equally efficient in removing color as 100% fresh magnesium.

Color removal using Polymers : Polymers have been used in the pulp and paper industry alone or in conjunction with chemical coagulants for color removal as well as sludge conditioning.

Kisla and McKelvey (16) tested several polyamines for color removal from softwood kraft bleach pulp effluents. Low molecular weight polyamines were less effective, while larger branched polyamines containing more cationic sites per molecule (Polyethyleneimine, MW 1800, 1200, and 600) showed about 85-90% removal at pH 7.0-8.5 at concentrations of 550-800 ppm. Results showed color removal to involve interaction between anionic color bodies and the cationic polyamines.

Polyacrylamide in conjunction with alum can reduce color from 1500-2000 Pt-Co color units to 6-100. Tipsev (30) found this method of removing color to be more effective than lime,

although sediment processing with the polymer presented considerable difficulty.

BIOLOGICAL METHODS FOR COLOR REMOVAL

Since the present study involved removing color from a biologically treated effluent, literature dealing with biological methods used with moderate success in removing color from pulp and paper wastes was also reviewed.

Bacteria and fungi are thought to be the principal organisms involved in the destruction of lignin in nature. Lee et al. (17) suggested that algae could also decolorize dilute BKME. Pure and mixed algal cultures reduced color of dilute BKME (50-150 APHA) by up to 50% within 20 days. Transformation of the color bodies to non-colored bodies was found to be the principal mechanism instead of adsorption. The authors further concluded that decolorization by algae is of significance in alleviating any effects of BKME on light transmission and primary productivity in colored receiving waters.

Color removals up to 80% could be achieved using a white rot fungus (*Phanerochete chrysosporium*) on a Kraft Bleach Plant Effluent. Sundman et al. (18) suggested that the mechanism affecting this color removal involved destruction of the chromophores in the wastes to low molecular weight colorless soluble/volatile products.

Lois et al. (31) concluded that adsorption played a major role in biological decolorization of black liquor wastewater in a bio tower, but that enzymatic degradation also occurred to a significant degree. Color reductions in the range of 33-54% were achieved with initial color levels ranging from 590-4000 NCASI units with a detention time of 50 hours.

GENERAL REFERENCES

A study by Akamatsu et al. (32) revealed that stannous chloride (SnCl_2) is a most effective chemical agent in flocculating lignin from a kraft pulp scrubbing wastewater. A dosage of 200 ppm reduced lignin content from about 300 ppm to <60 ppm; other coagulants had to be added in dosages >500 ppm for the same removal.

An EPA study (33) concluded that granular activated carbon (GAC) could be used as a polishing step for caustic bleach plant effluent. Color removal by GAC was found to be comparable with lime. A combined process of massive lime treatment (15000 ppm CaO), biological treatment and activated carbon treatment can result in an effluent practically free of color.

Giampetri and Voysey (34) recommended the use of GAC for the final color polishing step. Color removal from 50 color

units to 5.0 is possible; the exhausted carbon can also be regenerated.

CHAPTER III

METHODS AND MATERIALS

SAMPLE COLLECTION

Raw water for this research was obtained from the Pulp and Paper Plant, Union Camp Corporation, Franklin, Va., from three different locations in the plant. The Bleach Plant Effluent was collected from the bleaching units; the Main Mill or pulp mill effluent collected following clarification. The biologically treated effluent was collected at the #2 Pump Station after the Bleach Plant and the Main Mill effluents had been combined and stabilized using aerobic biological treatment. A characterization of the three wastes used in this study is presented in Table 3.

Nalgene carboys were used for sample collection, transport and storage. Samples were collected and transported by Union Camp employees and graduate students from Virginia Tech every two to three weeks.

Table 3. Waste characteristics of the biologically treated, the Main Mill and the Bleach Plant wastes.

PARAMETER	W A S T E		
	BIOTREATED	MAIN MILL	BLEACH PLANT
pH	6.9	7.5	2.9
Color, Pt-Co units	2400	1100	2100
Cl ⁻ , mg/L	594.0	49.2	598.0
SO ₄ ⁼ , mg/L	157.2	108.2	598.0
TSS, mg/L	80	40 ¹	15
TOC, mg/L	180	225	370

Note: Cl⁻ - Chloride
 SO₄⁼ - Sulfate
 TSS - Total Suspended Solids
 TOC - Total Organic Carbon
 *** - No analysis done.
 1 - Main Mill effluent after clarification.

COAGULATION

All coagulation/flocculation tests were performed using a standard six-place Phipps and Bird (Richmond, Va) laboratory stirrer and square glass coagulation jars. Usually 1-liter waste samples were used, but in some cases 500 mL or 1500 mL volume samples were used. Standard stock solutions of alum ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$), ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), lime ($\text{Ca}(\text{OH})_2$), and ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) were prepared prior to performing the tests. The appropriate amount of stock solution was added to the wastewater sample to produce the desired coagulant concentration. Coagulant was added to the sample jars with the stirrer operating at full speed [in excess of 100 revolutions per minute (rpm)]. After two minutes of rapid mixing, the sample was slow mixed at 20 rpm for 30 minutes. Adjustment of sample pH was done immediately after the rapid mix period. Desired pH adjustments were made by addition of either sulfuric acid or sodium hydroxide. The flocculated samples were then allowed to settle for at least 30 minutes. The supernatant was collected for color, TOC and other analyses. Sometimes the samples had to be refrigerated several days before the TOC could be measured because of the non-availability of the TOC analysing machine.

Although the Bleach Plant and the Main Mill wastewaters originate at temperatures higher than room temperature, all coagulation tests were conducted at room temperature. A

higher temperature was found to enhance color removal during coagulation at alum dosages above 500 mg/L, as depicted in Figure 1. Hence, in carrying out these coagulation tests at room temperature, a conservative approach has been taken, when in actuality, the same dosages under identical pH conditions would be expected to result in a lower residual color level.

Another similar study to check if the slow mix time for flocculation affected color removal from the biotreated effluent was carried out using three polymer solutions (CP41B, CP42B, and CP43B) containing ferric sulfate. In general, no difference in residual color was noted when considering flocculation times of thirty versus sixty minutes (Figure 2). The only exceptions to this related to low coagulant doses. In such cases longer coagulation times result in lower residual color values.

PHYSICAL AND CHEMICAL ANALYSES

pH : Samples were analysed for pH using a Fisher Accumet pH meter Model 610, which uses the glass electrode method as described in Standard Methods (13), Method 424.

Color : Color measurements were done in accordance with the NCASI method (12). This procedure requires all samples for color measurements to be filtered through a 0.8 micron mem-

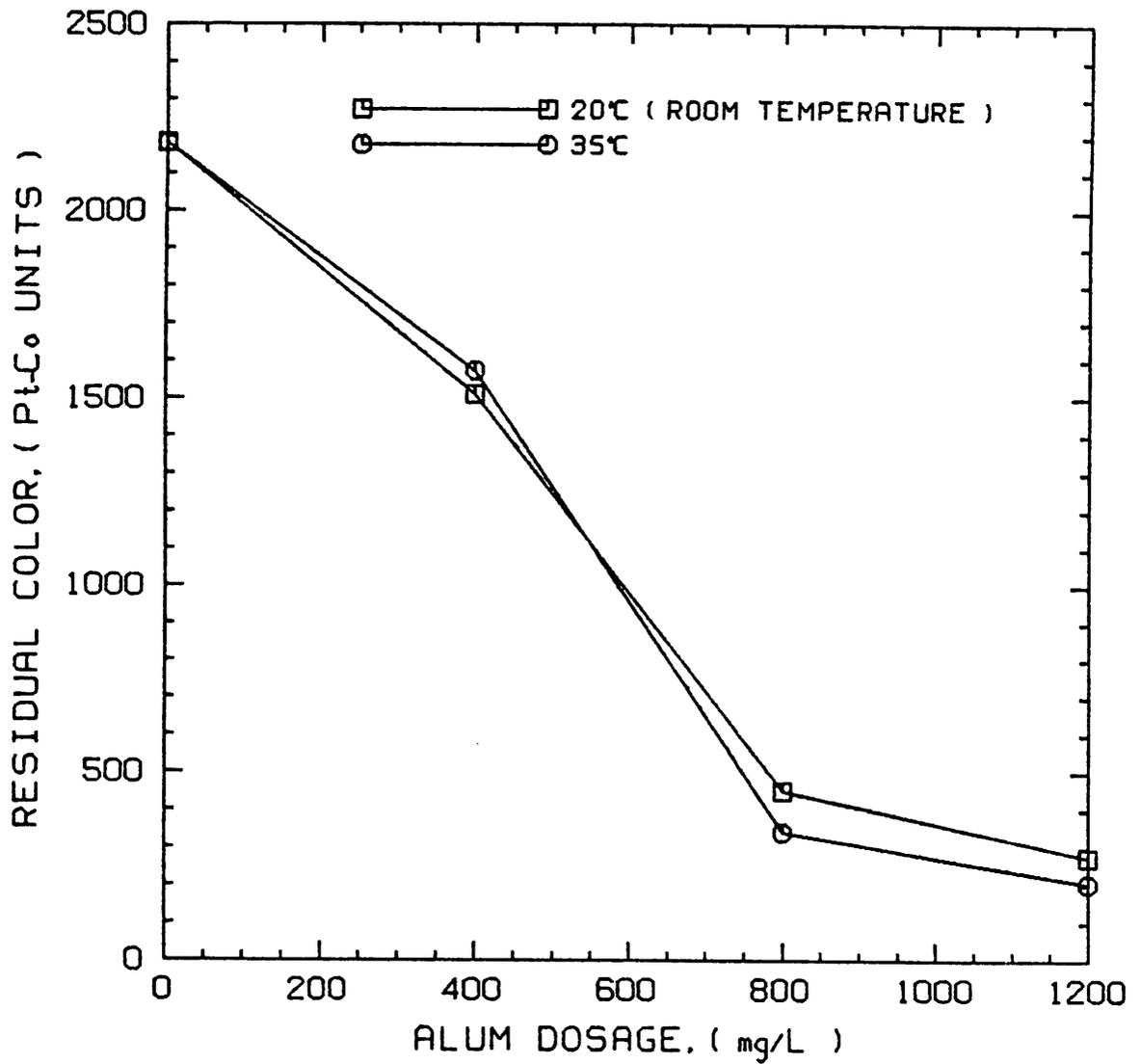


Figure 1. Effect of temperature on color removal by alum coagulation from the Bleach Plant waste.

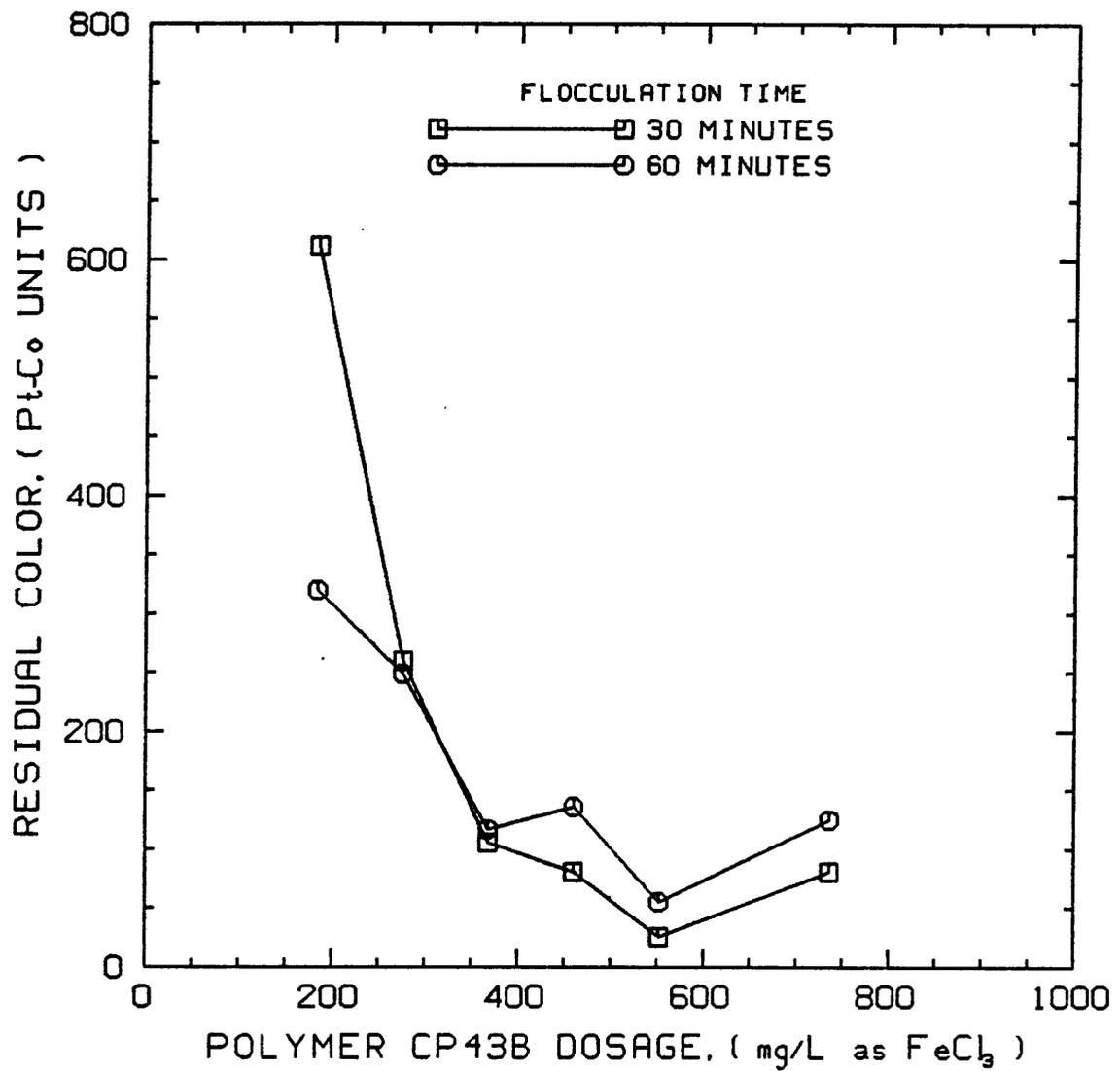


Figure 2. Residual color of Biotreated waste as a function of polymer (CP43B) dose at 30 min and 60 min flocculation times at pH 4.0. Initial raw color : 2350 color units.

brane filter (MSI Magna Nylon 66) and pH adjusted to 7.6 before measuring absorbance at 465 nm. The absorbance was measured using a Beckman DU-6 Spectrophotometer. The standard curve for absorbance against color was plotted using dilutions of the Platinum Cobalt Color Standard (500 color units). Standard curves were plotted once every month, to account for any instrument changes. Figure 3 shows a typical standard curve which was used to determine the color of test samples.

Total Organic Carbon (TOC) : Total Organic Carbon (TOC) of raw and treated samples was measured on the Dohrmann Envirotech instrument. The DC-54 Ultra Low Level Total Organic Carbon Analyser system was used to measure the samples with TOC concentrations below 10 mg/L, while the samples with TOC concentrations above 40 mg/L were analyzed using the DC-52D High TOC Unit. Samples with intermediate TOC levels were diluted to fall into the desired range. The methods of TOC analysis used for each of the above instruments can be described in brief as below:

Low Unit : Approximately 50 mL of sample was added into the sparger along with a reagent containing phosphoric acid and potassium persulfate. Helium purged the purgeable carbon dioxide (CO₂) and the Purgeable Organic Carbon (POC). The Non-Purgeable Organic Carbon (NPOC) was then exposed to intense ultra violet radiation which, aided by the persulfate

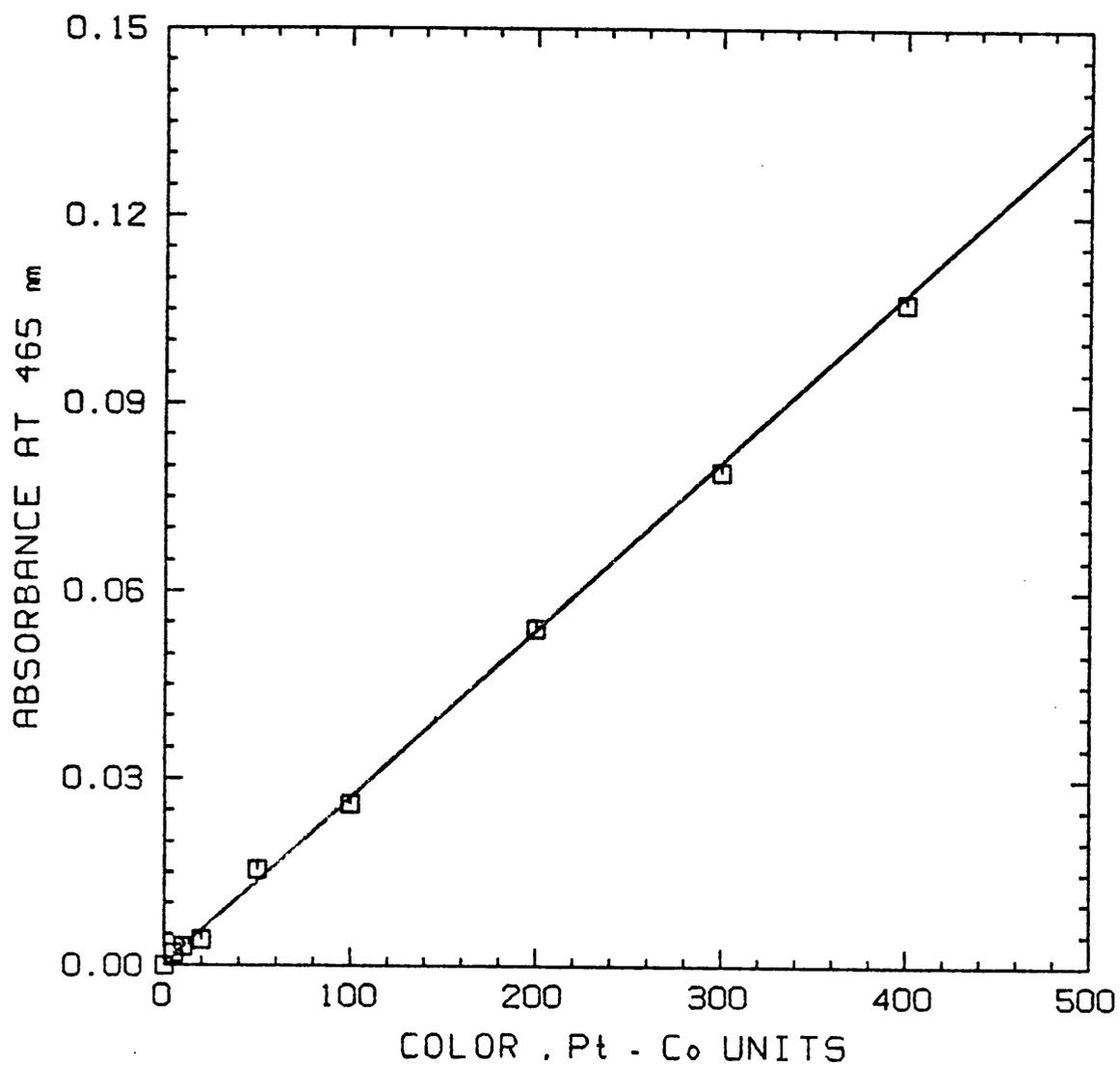


Figure 3. A typical standard curve showing color as a function of absorbance at a wavelength of 465 nm.

reagent added, oxidized all the remaining organic carbon to CO_2 . Both the POC and the CO_2 from the NPOC were converted to methane (CH_4) by passing them over a nickel catalyst at 350°C with hydrogen. The methane was detected by a Flame Ionization Detector (FID) and read from a digital display in mg/L.

High Unit : The sample to be analysed was deposited on a bed of granular manganese dioxide (MnO_2) in a platinum sample boat. The MnO_2 oxidizer eliminated coke formation by giving off oxygen (O_2) to the carbonaceous sample residue on demand during a pyrolyze step at 850°C . The boat then moved into a vaporization zone, where water, CO_2 and the volatile organic carbon (VOC) were swept out. Only the VOC was retained in a bypass column, from where it was backflushed. The backflushed VOC and the residual organic carbon (ROC) left in the boat were then pyrolyzed at 850°C to produce CO_2 , which then reduced to CH_4 . The resulting methane was then measured by the FID as in the low unit.

Total Suspended Solids (TSS) : Total Suspended Solids (TSS) were measured in accordance with Standard Methods(13), using 934AH filters.

SLUDGE THICKENING/DEWATERING METHODS

Column Studies: The column used for the flocculant settling studies was 6 feet in height, 2.6 inches in internal diameter, with 8 ports 8 inches apart for sampling. The flocculated sample was pumped through the bottommost port. This was preferred to directly pouring into the top of the column, as the latter would have resulted in greater shearing of the floc. About 75 mL of sample was collected from selected ports at selected intervals of time. The samples were then analysed for total suspended solids which, when compared to the initial TSS, gave the percent removal of solids. Settling curves were generated from these data.

Zone Settling: Zone settling studies were conducted on the iron and alum sludges in 40 cm high, 1000 mL graduated cylinders. Several dilutions of the thickened sludge were used to give various initial suspended solids concentrations. In each case, the sludge-water interface height was noted at different time intervals. Settling curves, showing variation of settling velocity (V) as a function of initial solids concentration on a semi-logarithmic scale, were drawn for each sludge.

Vacuum Filtration: The thickened sludge from the gravity thickening tests was used for vacuum filtration studies to

determine the sludge resistances of the iron and the alum sludges. The sludge specific resistance is a measure of the dewatering rate of the sludge. A Fisher Scientific Doerr pump was used to create the desired vacuum pressures between 17 in Hg to 20 in Hg. A 100 mL sludge sample was poured in a Buchner funnel containing a wetted filter paper (Whatman 40, 9.0 cm in diameter, ashless). Filtrate volume, collected in the graduated cylinder below the Buchner funnel, was measured as a function of dewatering time. The sludge resistance was then calculated from these data by first plotting filtrate time (T) versus T/V (time/filtrate volume) to obtain the dewatering rate constant b.

MOLECULAR WEIGHT DISTRIBUTION OF ORGANICS

The Molecular Weight Distribution (MWD) for the raw and the treated wastes was conducted using an AMICON 8200 apparatus on Corning stirrers (PC 353) using different pore size filter membranes. Table 4 presents the pore sizes and the molecular weight cut-off for the filters used. Appropriate dilutions of the sample to be analysed for MWD were done to insure that the TOC of the diluted sample was below 10 mg/L. About 50 mL of the diluted samples were added into the AMICON containers havin 500, 5K, 10K or 30K filter membranes. The TOC of the filtrate in each case was then compared with the

Table 4. Pore size and nominal molecular-weight exclusion limit of ultra filters.

(Data from Amicon Co., Lexington, MA.)

Membrane	Approximate pore size (nm)	Nominal molecular-weight exclusion limit (daltons)
YC05	1.1	500
YM5	1.5	5,000
YM10	1.6	10,000
YM30	2.1	30,000

initial diluted TOC to give the MWD of the organics present in the sample.

CHAPTER IV

RESULTS

This research was aimed at optimizing the removal of color from pulp and paper wastes generated at the Union Camp Corporation Mill at Franklin, Virginia. Several coagulants were tested to determine which could achieve an effluent within the color standards for discharge or for internal recycle. This research study attempted to answer the following questions:

1. Which coagulant is most effective for color removal?
2. What is the optimum dosage and the optimum coagulation pH for each coagulant?
3. Under what conditions can powdered activated carbon be used in conjunction with chemical coagulants to remove residual color?
4. Can polymers be used in conjunction with chemical coagulants to improve color removal efficiency?
5. What molecular weight fractions of organics are removed from the raw waste during coagulation?
6. How much TOC removal can be achieved when color removal is optimized?

7. What are the dewatering and thickening characteristics of the chemical sludges produced during the coagulation treatment?

Most of the research was carried out on the biologically treated effluent as it was considered the most likely waste for recycle or reuse. Another alternative is removal of color from the Main Mill effluent and the Bleach Plant effluent before they are combined for biological treatment. Hence, a limited number of studies were also conducted using Main Mill and Bleach Plant waste samples.

It should be noted that coagulation studies were conducted using a wide range of pH conditions; however, all color analyses were performed on samples adjusted to a pH of 7.6. Thus, all values reported represent the equivalent color concentration at pH 7.6.

OPTIMIZATION OF METAL ION COAGULATION DOSE AND PH FOR COLOR REMOVAL

Preliminary coagulation tests were performed using each of the coagulants for color removal from the waste streams. Based on these preliminary data, a dosage was selected to determine the optimum pH. At this optimum pH, the optimum dose for color removal was then determined. In certain cases even very high coagulant dosages did not yield effective

color removal, and, hence, further tests to determine the optimum dose conditions in these situations were not pursued.

Figure 4 and Figure 5 present data related to color removal from the biotreated effluent using alum and ferric chloride respectively. Figure 4 reflects the efficiency of alum coagulation on waste samples collected on two separate days. A dosage of 300-400 mg/L can be taken as the optimum dose for both the coagulants. The final color after coagulation in each case is around 50-80 color units, representing an optimum color removal of 96.4% for alum and 98.6% for ferric chloride.

High lime dosages produced pH conditions in the range of 10.0 to 12.2 in the lime coagulation of the three wastes. Residual color as a function of lime dosage for the three wastes has been plotted in Figure 6. Even with very high dosages (>2000 mg/L), color removal was not efficient. In fact, dosages around 500-800 mg/L resulted in an increase of color.

The efficiency of alum, ferric chloride and ferric sulfate for removing color from Main Mill wastewaters is presented in Figure 7. The optimum dosages as seen from the figure is 200 mg/L for alum at pH 5.5, 300 mg/L for ferric chloride at pH 4.0, and about 300 to 500 mg/L for ferric sulfate at pH 4.0. Ferric sulfate showed maximum color removal with a final effluent color of only 13 color units corresponding to a color removal efficiency of 99.99% .

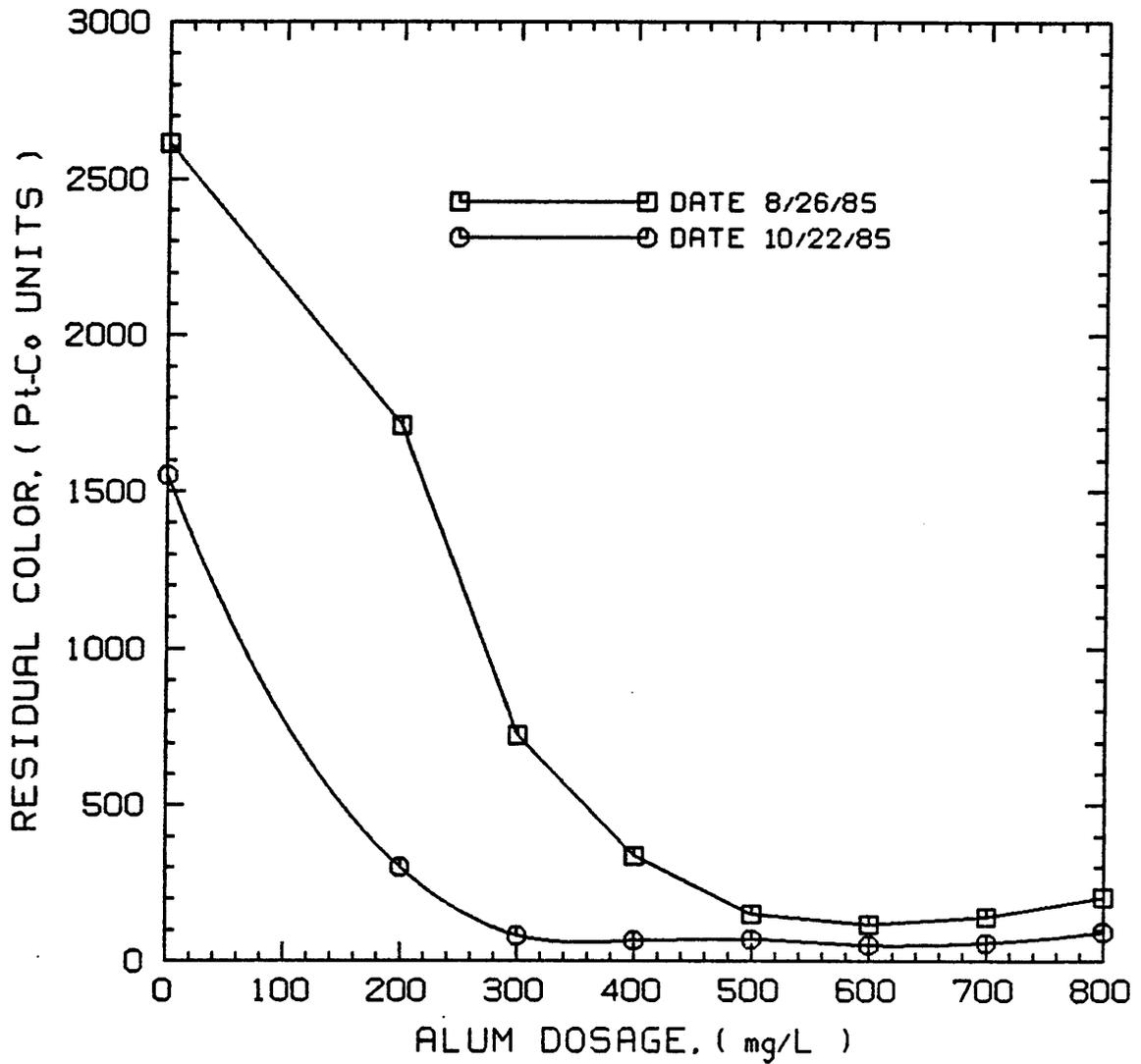


Figure 4. Determination of optimum alum dosage for color removal from biotreated waste at optimum pH of 5.3.

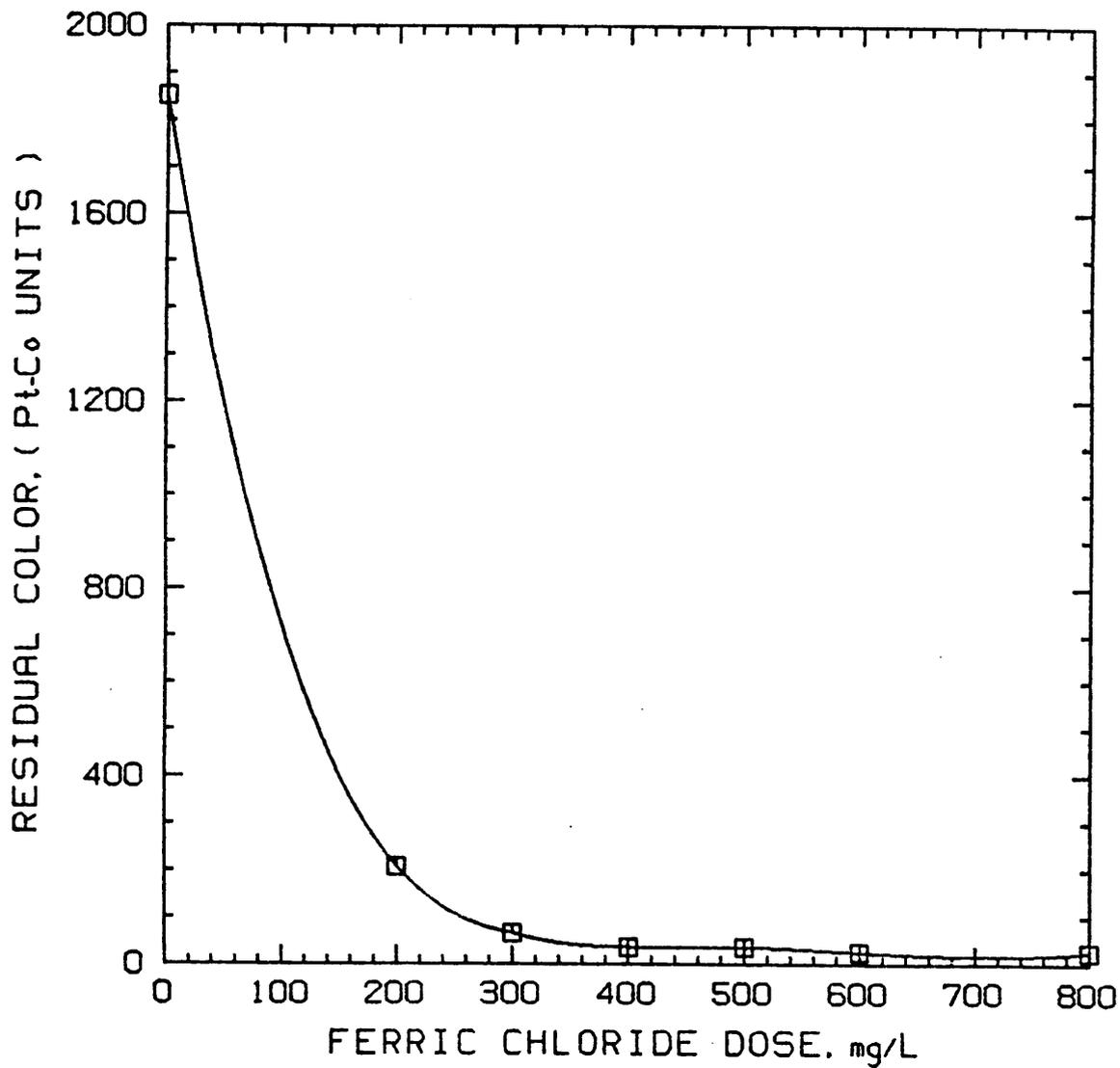


Figure 5. Determination of optimum ferric chloride dosage for color removal from biotreated waste at optimum pH of 4.0.

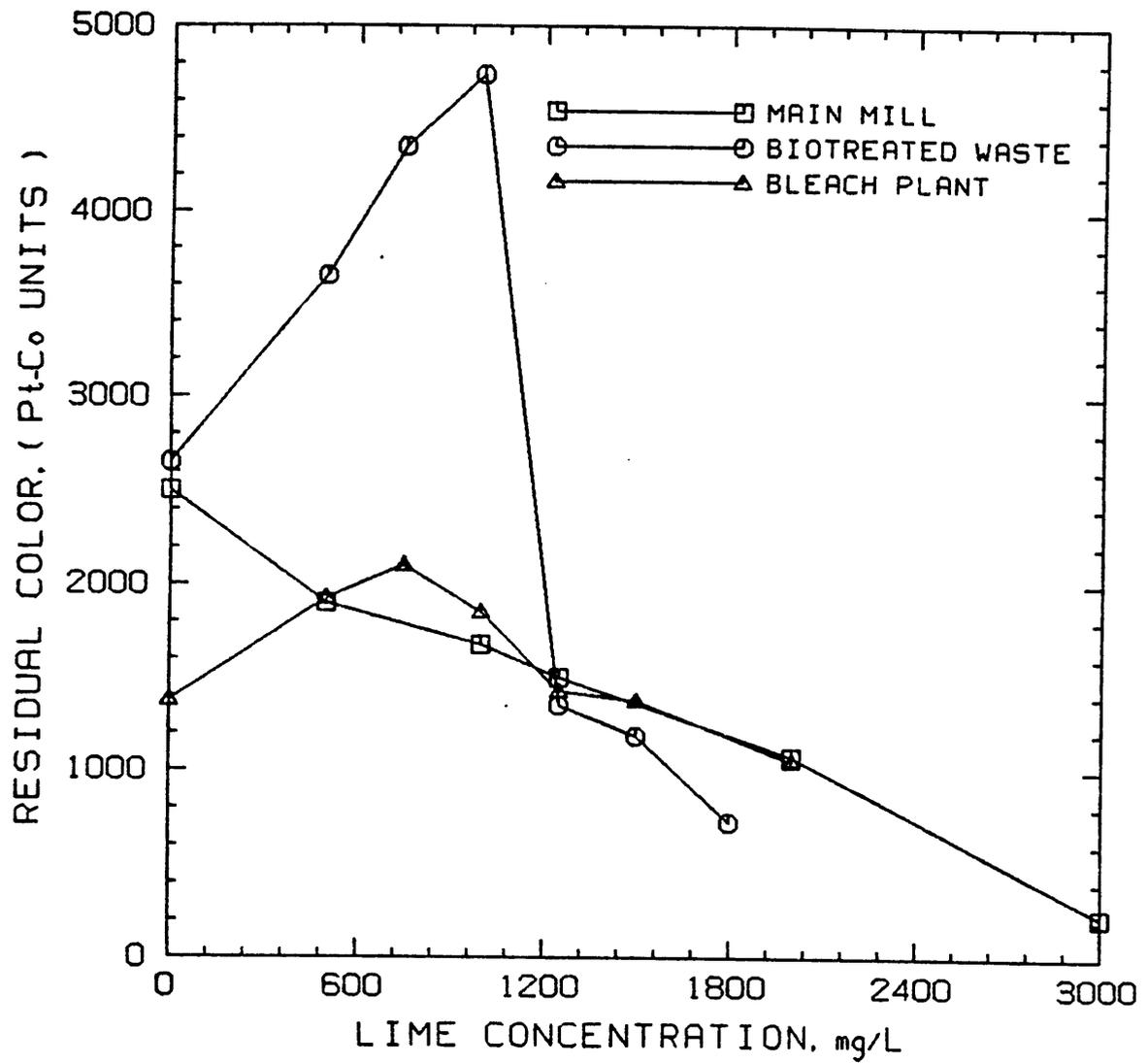


Figure 6. Variation of residual color with lime dosage when treating Main Mill, biotreated and Bleach Plant wastes, without any pH adjustment.

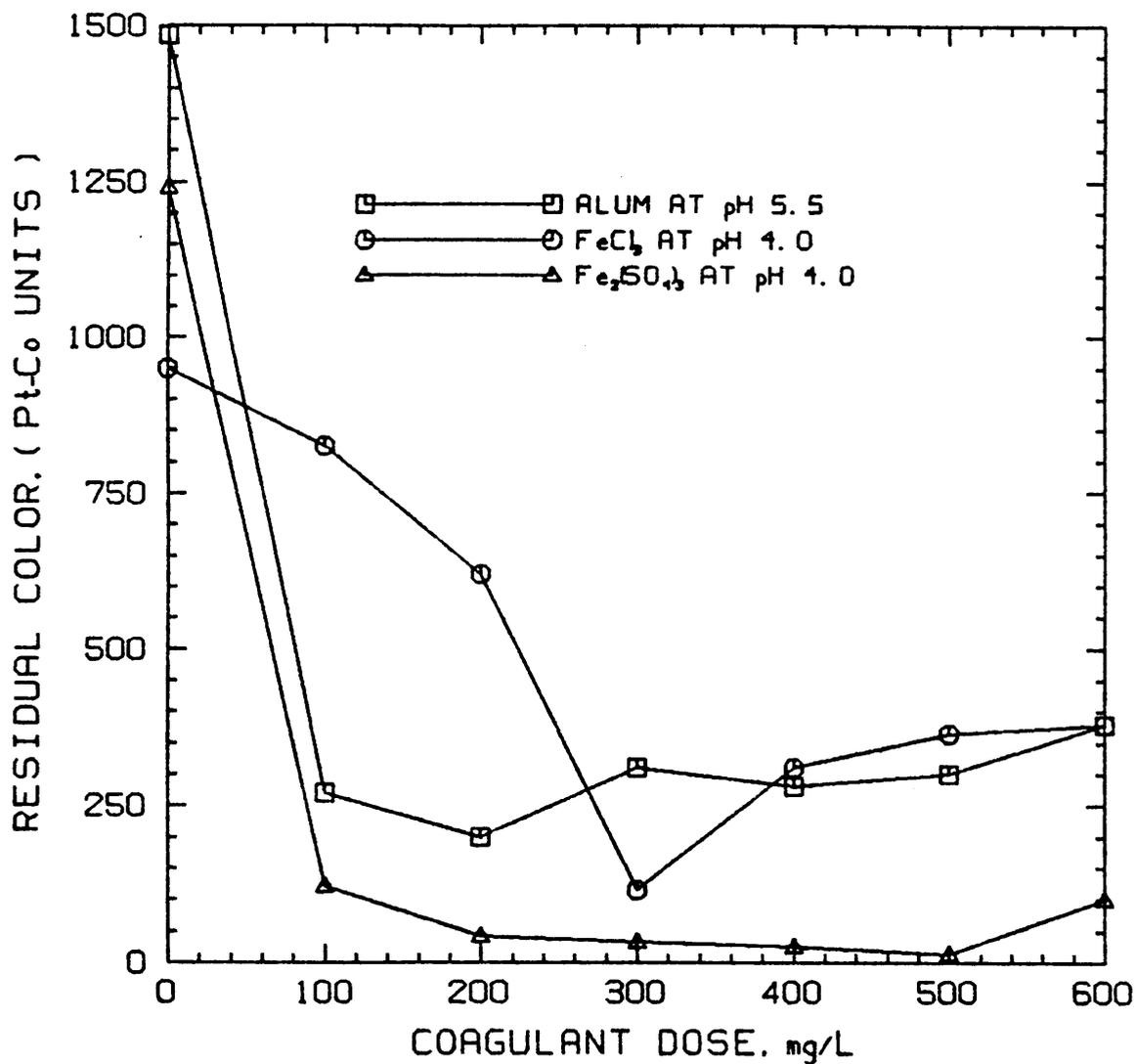


Figure 7. Determination of optimum dosage for color removal using alum, ferric chloride and ferric sulfate when treating Main Mill waste (pH 5.5 for alum and 4.0 for ferric chloride and ferric sulfate).

Ferric chloride coagulation on the Main Mill waste showed a very narrow optimum dose range as compared to alum and ferric sulfate.

Figure 8 shows how residual color varies as a function of initial color level for alum treated samples of the Main Mill wastewater, indicating a relatively constant percent removal of color at a constant alum dose.

Coagulation studies using Bleach Plant wastewater samples resulted in comparatively poor color removal even at very high coagulant dosages. Optimum alum dosing yielded a final color of about 350 color units at 1500 mg/L as can be seen in Figure 9.

An attempt was made to determine the optimum pH for color removal for alum and lime coagulation in treating the biologically treated effluent. The results, presented in Figure 10, show that pH 5.0 was the optimum pH for color removal using alum; a pH of 12.0 gave the best color removal for lime. Maximum removal efficiency for color removal was 96% for alum and 73% for lime at dosages of 540 mg/L for alum and 1250 mg/L for lime.

Experiments were conducted on the Main Mill waste samples to determine the optimum pH for color removal by coagulation. Figure 11 indicates that a pH of 5.5 is the optimum pH for alum coagulation, and that for ferric chloride is 4.0. Both coagulants exhibited a defined optimum pH range for color removal.

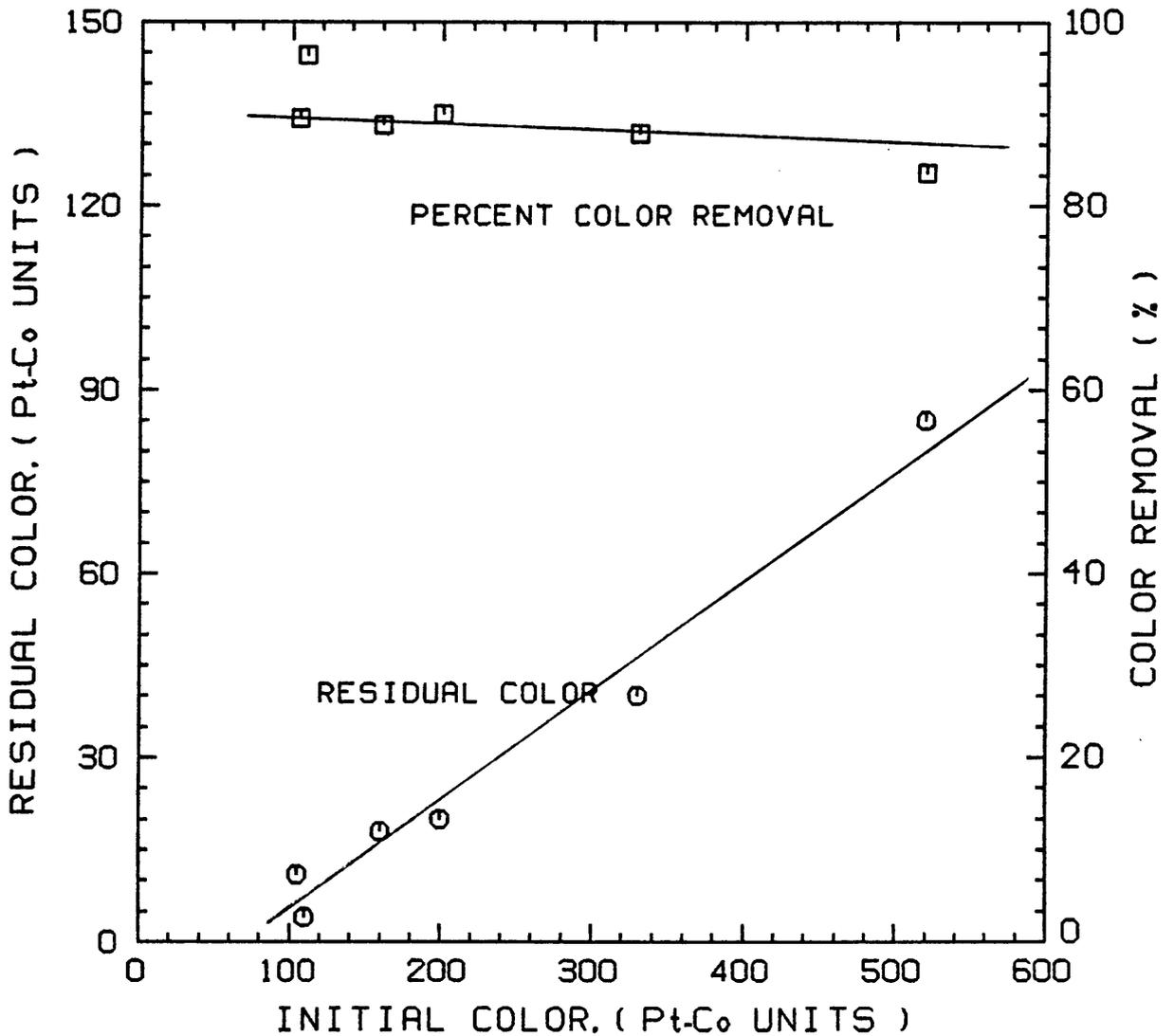


Figure 8. Relationship between initial and residual color concentrations in the Main Mill wastewaters treated with a constant alum dose of 200 mg/L at a pH of 5.5.

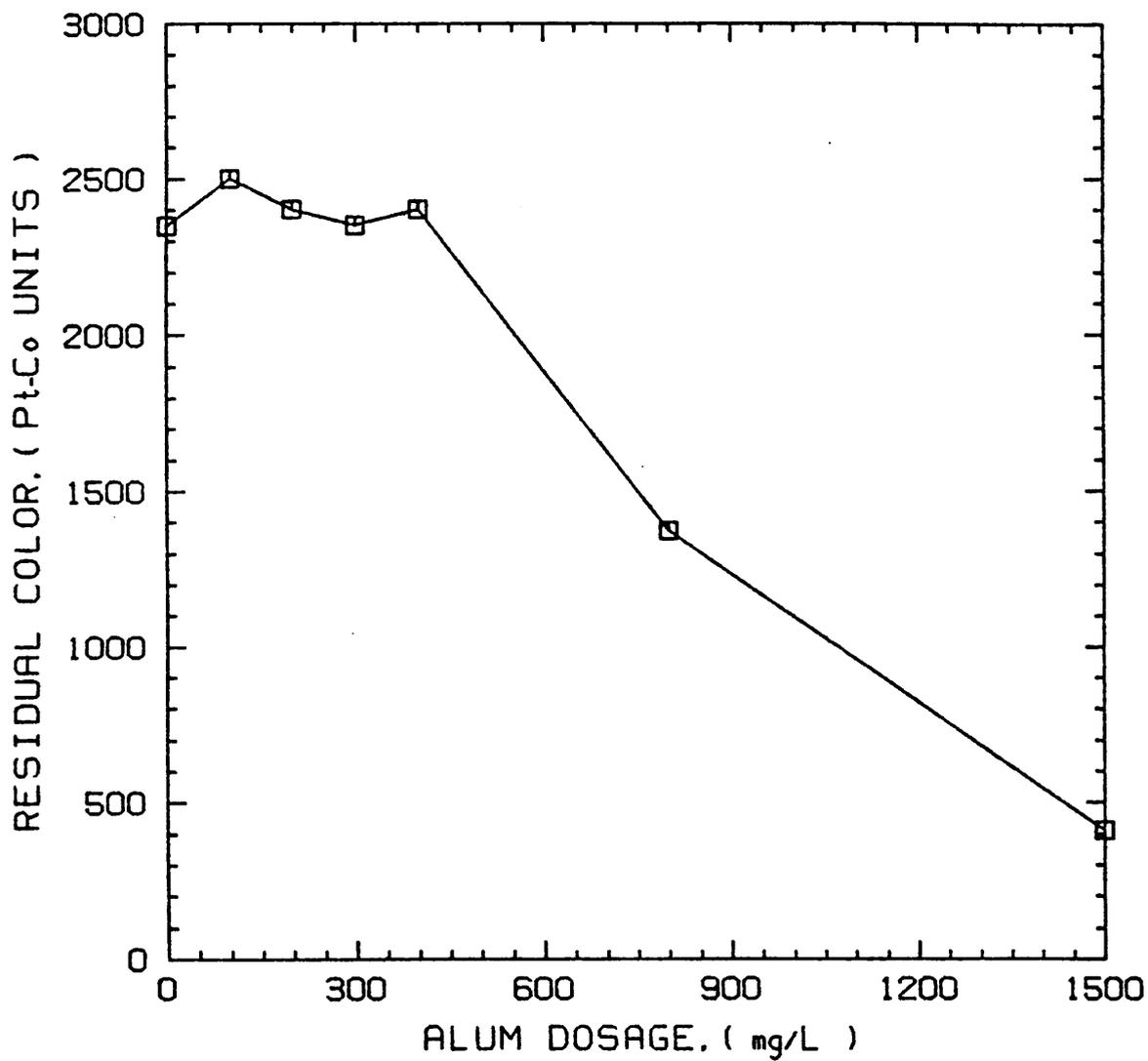


Figure 9. Variation of residual color with alum dosage on Bleach Plant waste at a pH of 6.0.

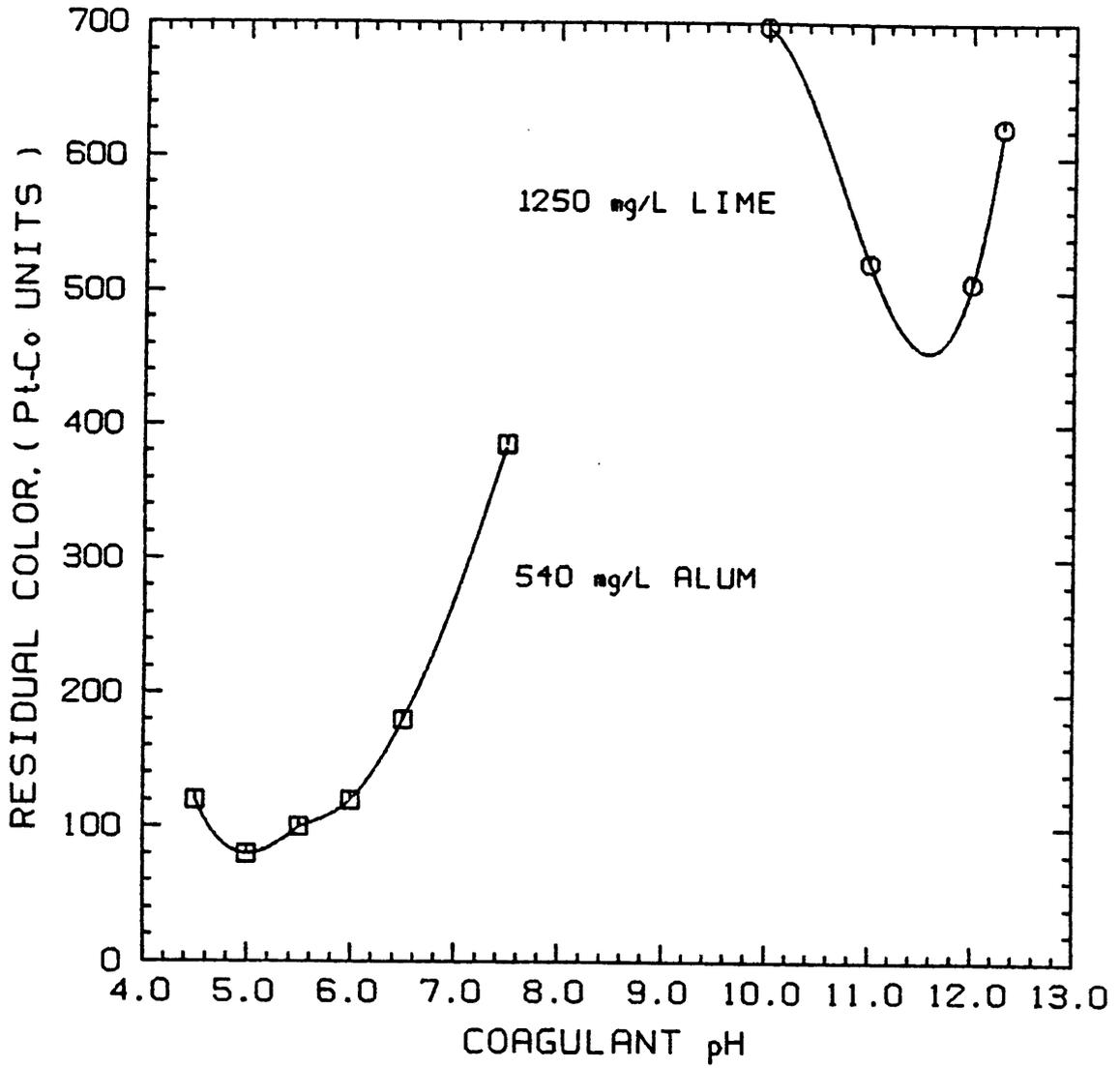


Figure 10. Effect of solution pH on color removal efficiency from the biologically treated wastewater using 540 mg/L alum and 1250 mg/L lime.

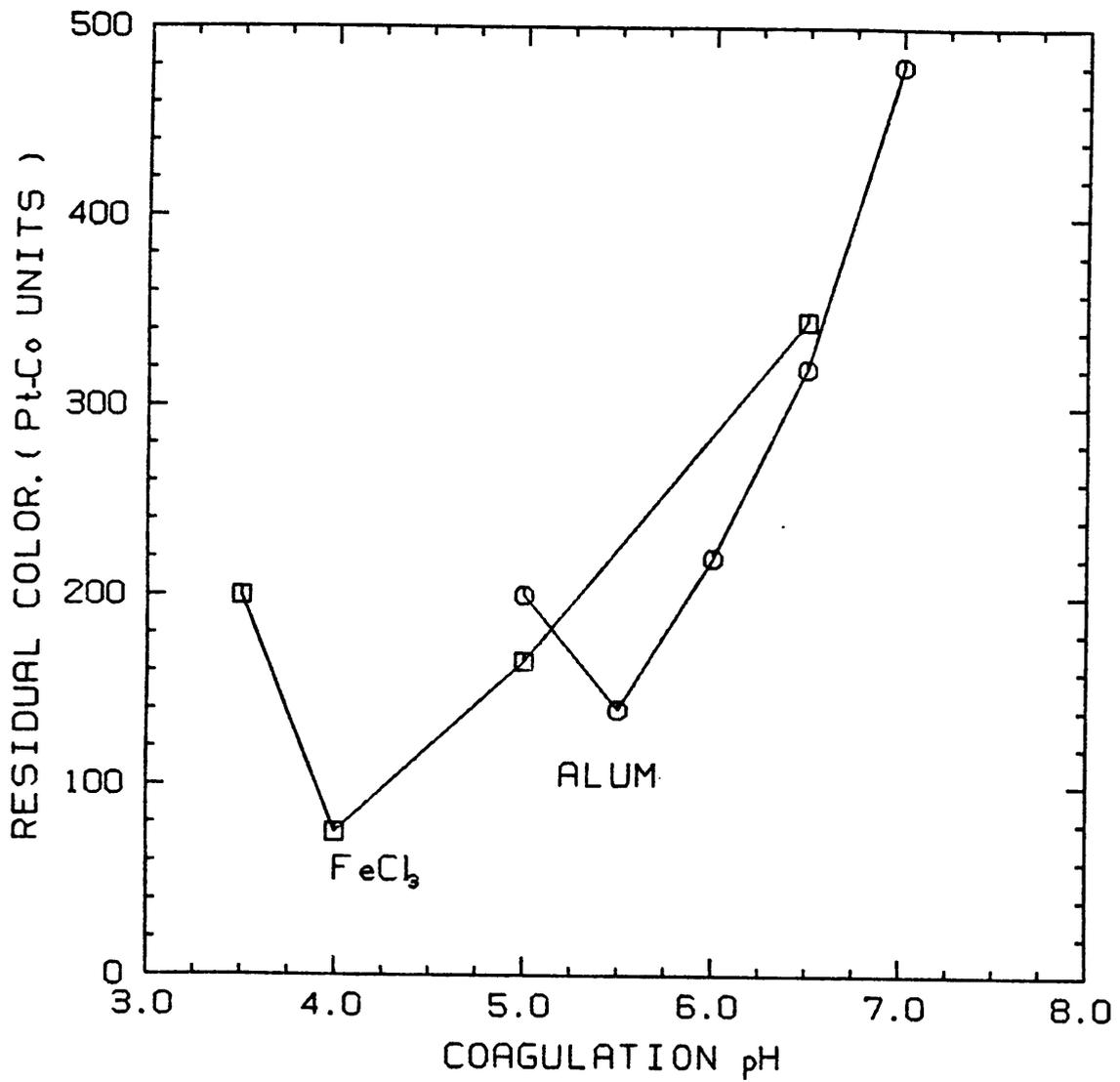


Figure 11. Effect of solution pH on color removal efficiency from Main Mill waste samples using 300 mg/L alum or 300 mg/L ferric chloride.

A summary of coagulant dosages and pH conditions resulting in maximum percent color removal from the three pulp and paper wastes treated using the various coagulants is provided in Table 5.

USE OF POWDERED ACTIVATED CARBON TO ENHANCE COLOR REMOVAL.

Studies using powdered activated carbon (PAC) in conjunction with coagulants were conducted to determine whether the residual color after coagulation could be further removed by PAC addition. Two approaches were explored in this study. The first was by adding PAC along with the coagulant during the rapid mix phase. The second approach involved adding PAC to the non-filtered supernatant after the coagulation step. The first is referred to as "simultaneous treatment" while the latter is referred as "separate treatment".

PAC used in conjunction with ferric chloride on the biologically treated effluent achieved no significant color removal even at very high doses of PAC. In fact, as seen from Figure 12, PAC showed an increase in the color at doses below 1000 mg/L.

PAC added separately to the biologically treated waste after alum coagulation resulted in the best color removal (Figure 13) with essentially zero residual color at a dosage of 500 mg/L of PAC. Simultaneous treatment with PAC also yielded significant additional color removal.

Table 5. Summary of chemical coagulation results achieving maximum percent color removal from the biotreated, Main Mill and Bleach Plant wastes using alum, lime, ferric chloride and ferric sulfate.

COAGULANT	OPTIMUM PH	OPTIMUM DOSE (mg/L)	FINAL COLOR Pt-Co Units	OPTIMUM Removal (%)
1. BIOTREATED EFFLUENT				
Alum	5.5	400	80	96
FeCl ₃	4.0	300	26	99
Lime	12.0	1800	750	73
2. MAIN MILL SOURCE				
Alum	5.0	200	200	92
FeCl ₃	4.0	300	115	95
Fe ₂ (SO ₄) ₃	4.0	500	20	100
Lime	-	3000	225	91
3. BLEACH PLANT EFFLUENT				
Alum	-	1500	400	83
Lime	-	2000	1000	24

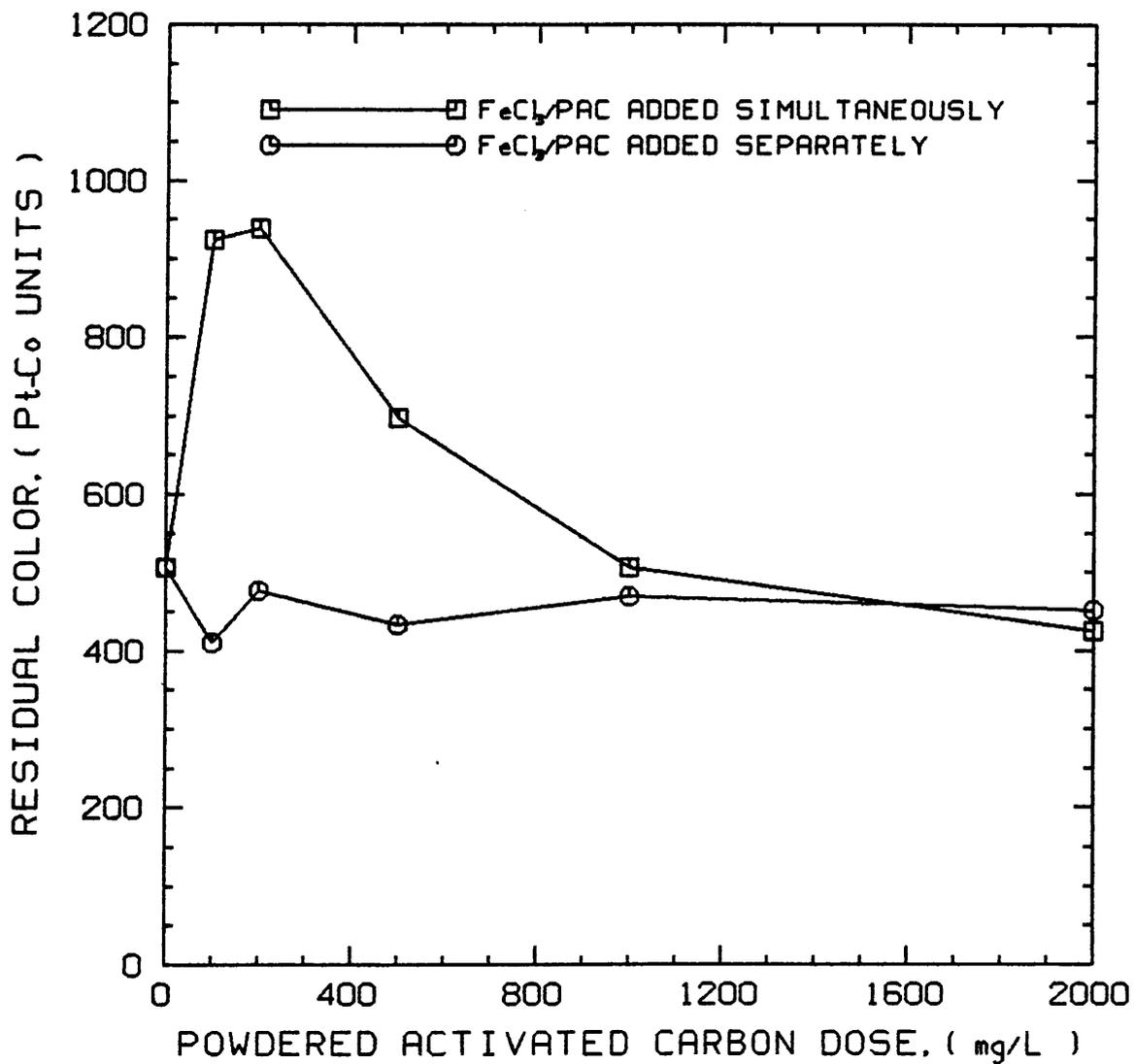


Figure 12. Variation of residual color with powdered activated carbon dose when used in conjunction with 200 mg/L ferric chloride to treat biotreated wastewater at pH 4.0.

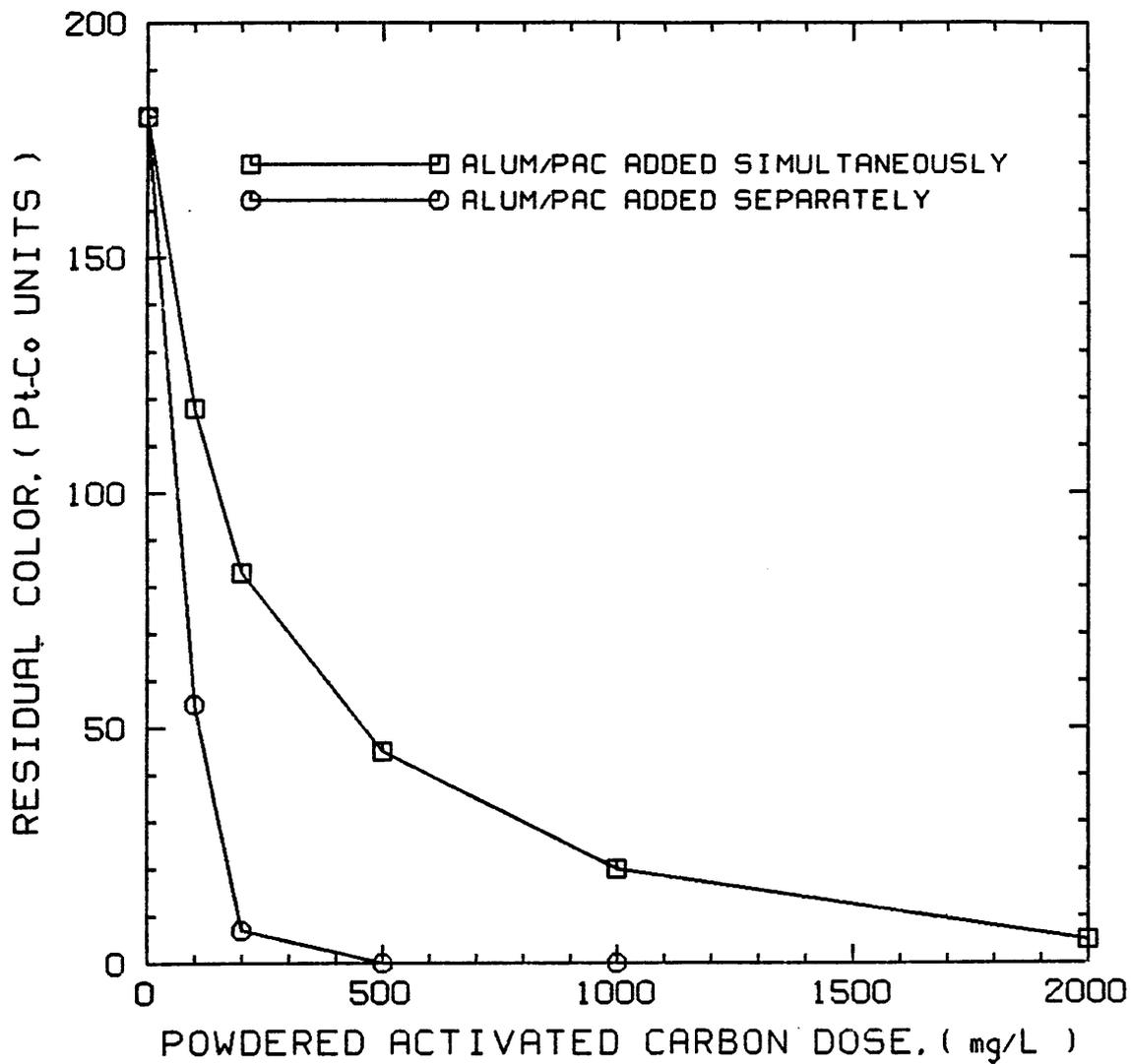


Figure 13. Variation of residual color with powdered activated carbon dose in conjunction with 400 mg/L alum on biotreated waste samples at pH 5.3.

Figure 14 shows the effect of adding PAC along with alum or ferric chloride in treating the Main Mill effluent. An effluent with almost no color could be produced in each treatment situation with PAC dosages less than 500 mg/L.

POLYMERS USED WITH METAL ION COAGULANTS FOR REMOVING COLOR

Polymers have been found to be quite successful in removing color from pulp and paper wastes, when used either as the primary coagulant or in conjunction with chemical coagulants. In this study, a preliminary study was done on a large number of polymers, both anionic and cationic, and the ones which showed good color removal were considered for further testing. Four polymers (BETZ 1190, MAGNIFLOC 581C, TRETOLITE J118, and NALCO 7107) were found to be effective in removing color from the wastes. The various characteristics of these polymers have been highlighted in Table 6. As in the case of the chemical coagulants, an optimum pH was first determined using a selected dosage based on the preliminary test; then, the optimum dosage for color removal was determined for each polymer at its respective optimum pH.

The effect of varying the solution pH on color removal by the polymers from the biotreated waste is presented in Figure 15. BETZ 1190 was found to be relatively independent of pH, while a pH range of 5.0-8.0 was favorable for

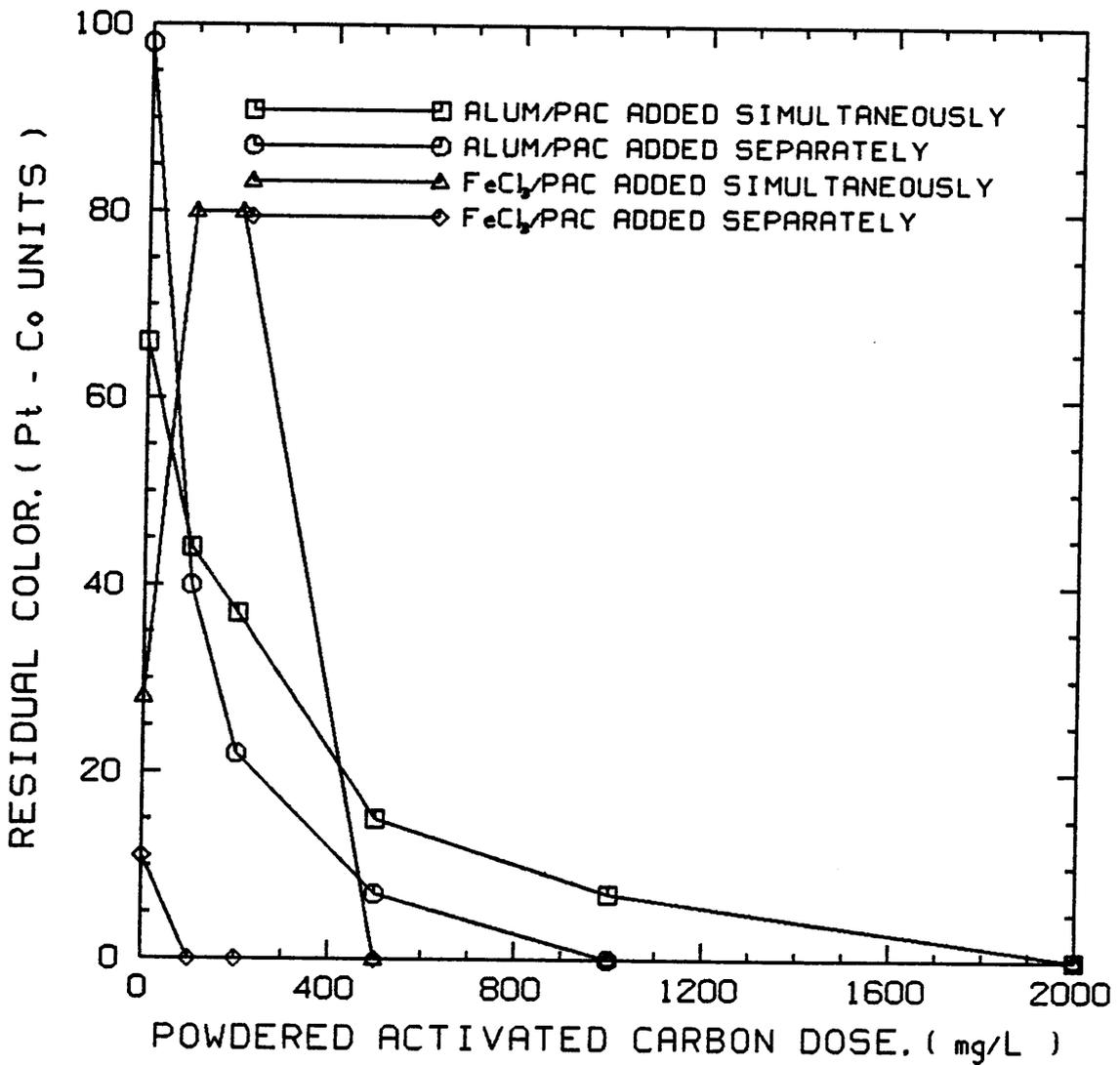


Figure 14. Variation of residual color with powdered activated carbon dose added along with 300 mg/L alum at pH 5.5 or 300 mg/L ferric chloride at pH 4.0 to treat the Main Mill wastewater.

Table 6. Characteristics of polymers (BETZ 1190, MAGNIFLOC 581C, TRETOLITE J118 and NALCO 7107) tested for color removal from the biologically treated and the Bleach Plant wastes.

POLYMER	CHARACTERISTICS
1. <u>BETZ 1195</u>	<ul style="list-style-type: none"> -Strongly cationic. -Low molecular weight. -Liquid coagulant.
2. <u>TRETOLITE J118</u>	<ul style="list-style-type: none"> -Cationic polyelectrolyte. -Solution of polyalkanol-amines and oil-in-water demulsifier.
3. <u>MAGNIFLOC 581C</u>	<ul style="list-style-type: none"> -Cationic Flocculant.
4. <u>NALCO 7107</u>	<ul style="list-style-type: none"> -Cationic. -Liquid. -Oil-in-water emulsion breaker.

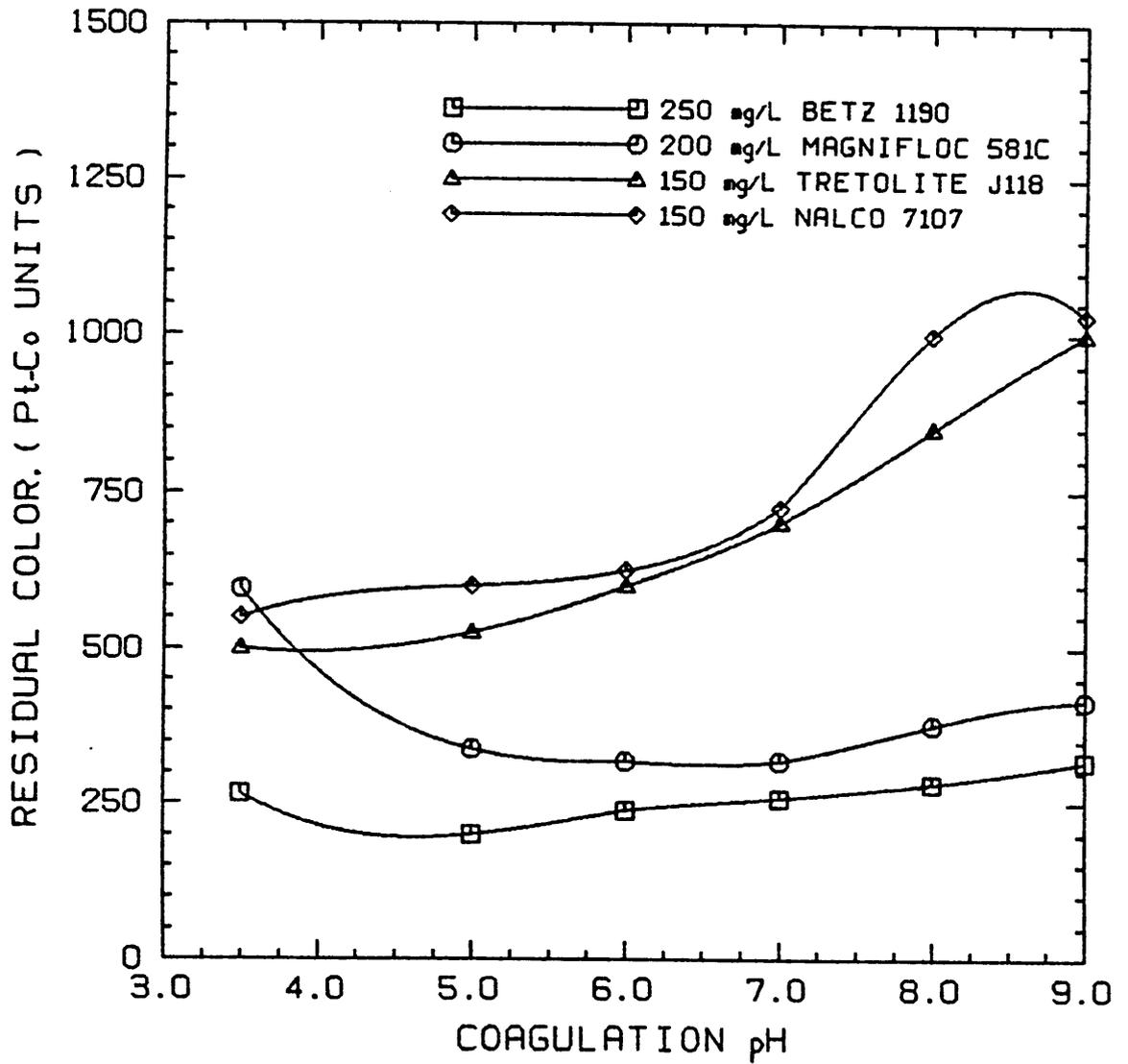


Figure 15. Determination of optimum pH for color removal from the biotreated waste using polymers (BETZ 1190, MAGNIFLOC 581C, TRETOLITE J118 and NALCO 7107).

MAGNIFLOC 581C. Both TRETOLITE J118 and NALCO 7107 showed best removal at the pH 3.5, the lowest pH considered.

Data on color removal from the biotreated waste using varying polymer dosage for the four polymers at their respective optimum pH are presented in Figure 16. BETZ 1190 and MAGNIFLOC 581C show the best color removal, with a residual color of 200 color units at dosages of 200 mg/L and 250 mg/L respectively.

The optimum pH for color removal from the Bleach Plant waste using the polymers was not determined, as very high polymer dosages were required to achieve any significant color removal. As seen in Figure 17, MAGNIFLOC 581C is the most efficient for color removal, with a final residual color of 150 color units at a dose of 500 mg/L.

The use of BETZ 1190 along with alum for the removal of color from the biotreated effluent is illustrated in Figure 18. The optimum pH for alum coagulation (pH 5.0-5.5) was used for this study. Addition of alum followed by polymer addition, both during the rapid mix phase, gave better results than with the polymer added before the alum. The least residual color obtained was about 80 color units when using 400 mg/L alum and 150 mg/L BETZ 1190.

The effect of PAC in conjunction with polymer on the Bleach Plant effluent is depicted in Figure 19. In the case of BETZ 1190, 1000 mg/L of PAC reduced the concentration of color from 850 to 325 color units. The same PAC dosage used

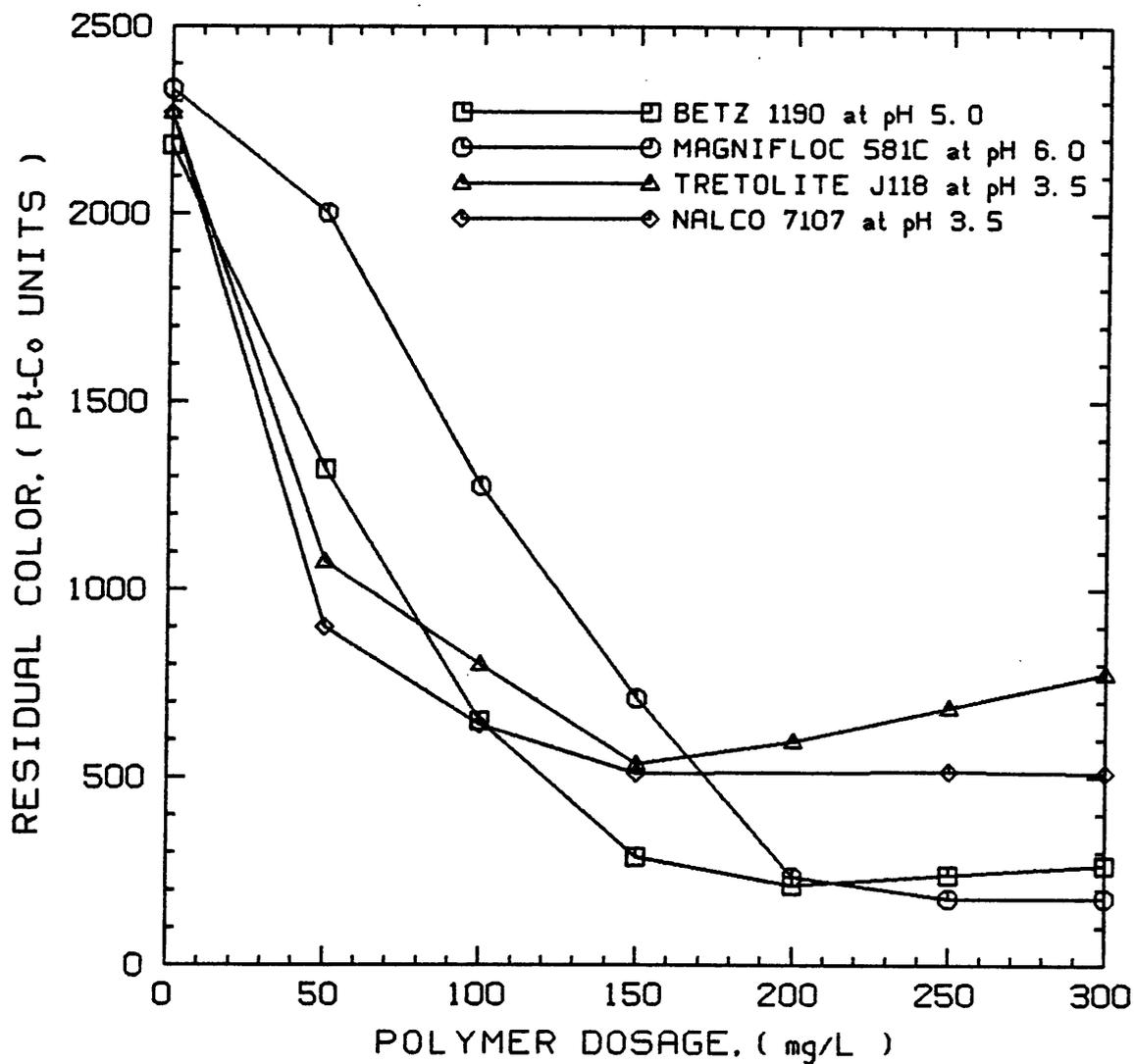


Figure 16. Determination of optimum polymer dosage for color removal from the biotreated waste at optimum pH for BETZ 1190, MAGNIFLOC 581C, TRETOLITE J118 and NALCO 7107.

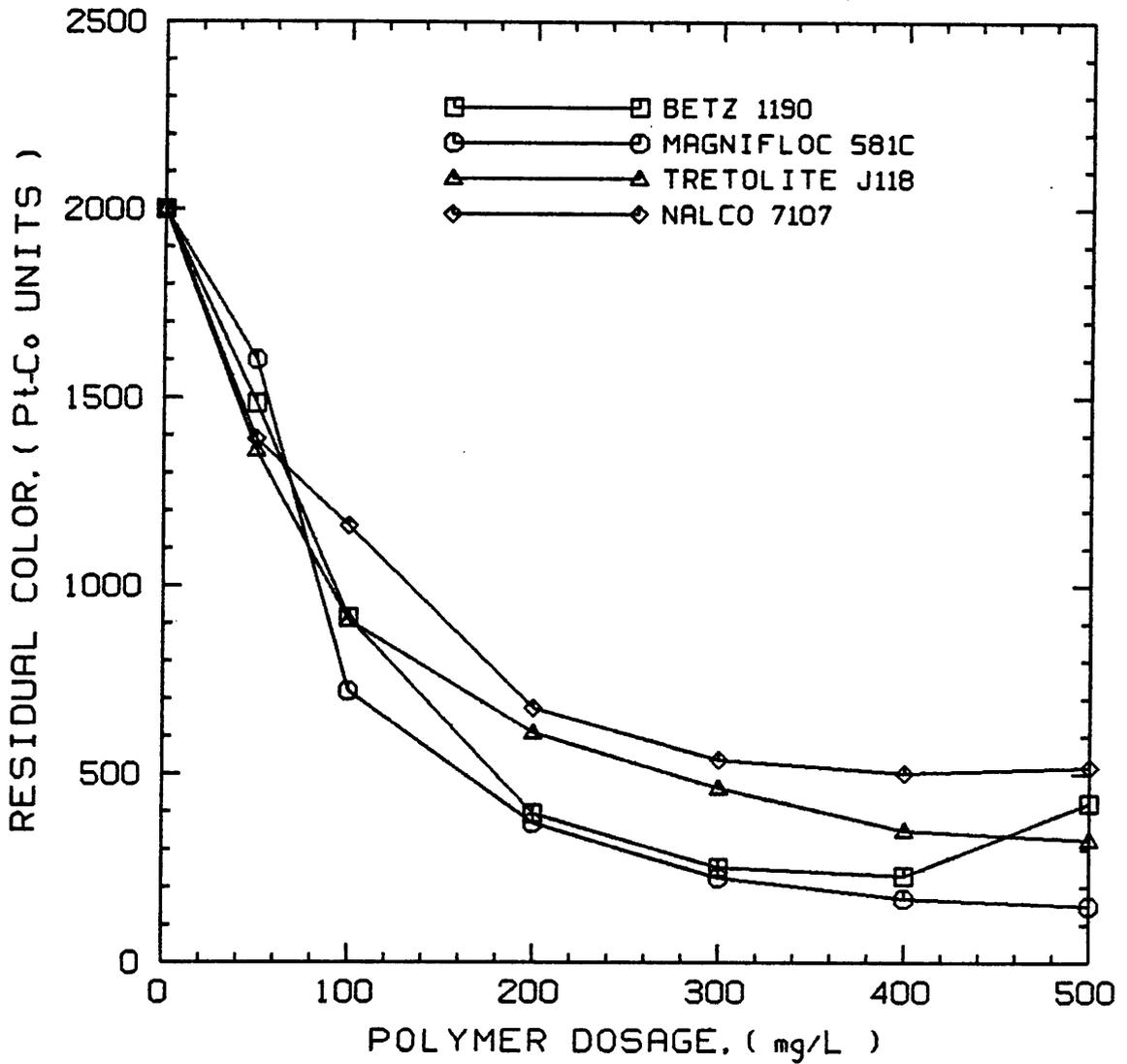


Figure 17. Residual color as a function of polymer dosage on the Bleach Plant waste with no pH adjustment for BETZ 1190, MAGNIFLOC 581C, TRETOLITE J118 and NALCO 7107.

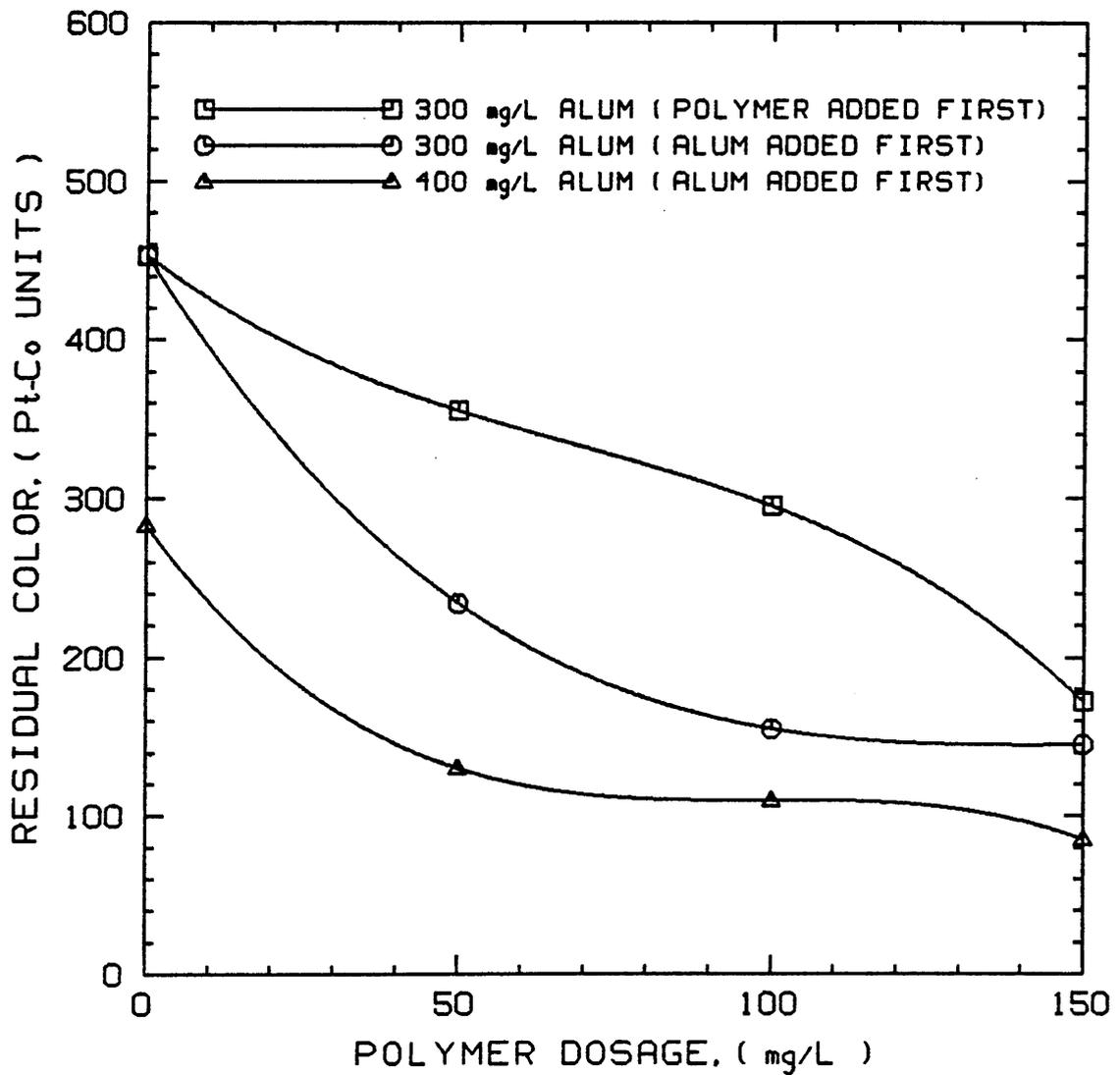


Figure 18. Residual color of biotreated waste as a function of polymer dosage (BETZ 1190) in conjunction with 300 mg/L or 400 mg/L alum at pH 5.3.
Initial raw color : 2250 color units.

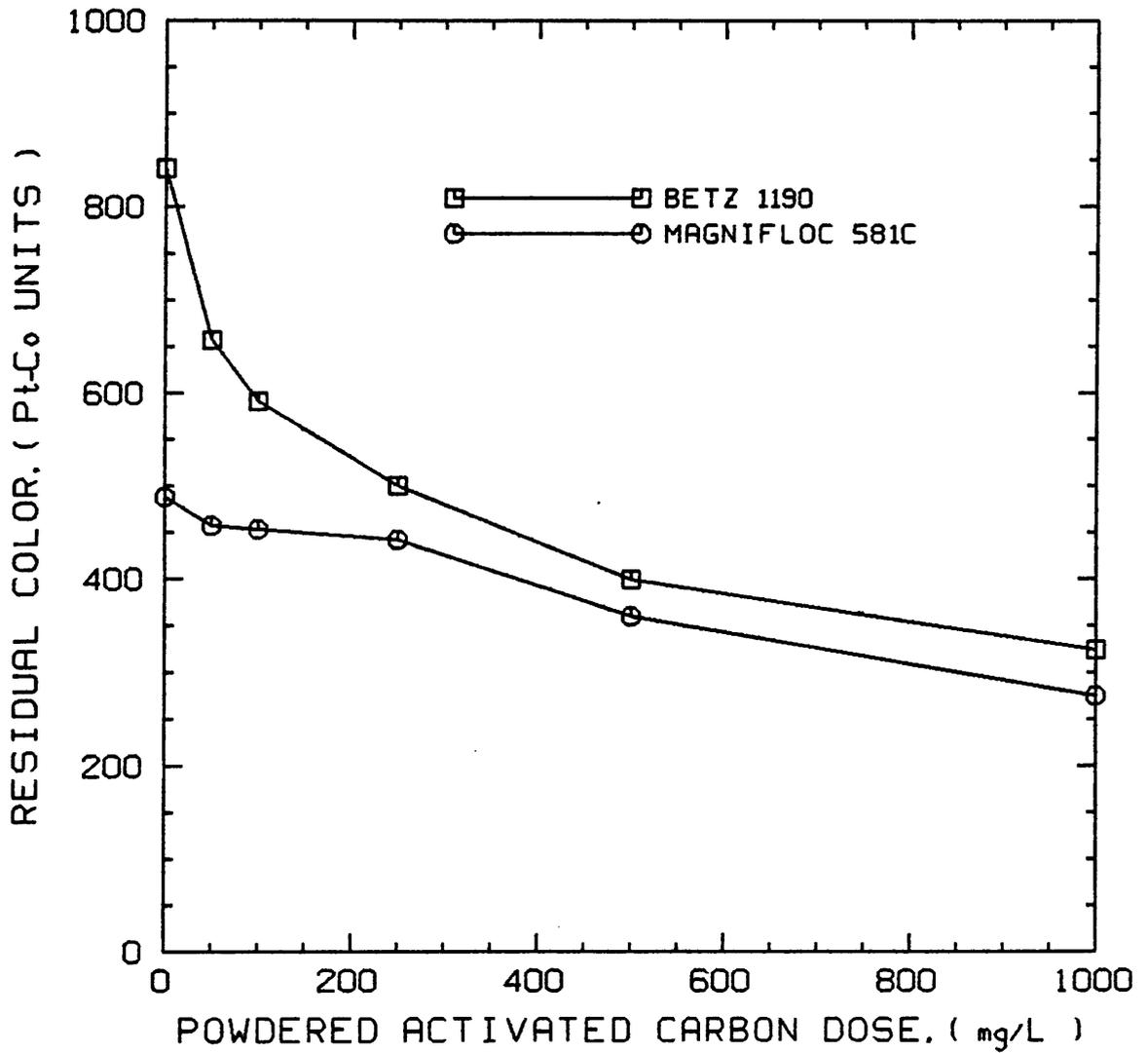


Figure 19. Residual color of Bleach Plant waste as a function of powdered activated carbon dose in conjunction with 200 mg/L polymer (BETZ 1190 and MAGNIFLOC 581C) at pH 6.3. Initial raw color : 2215 color units.

along with MAGNIFLOC 581C removed about 220 color units more than the case with the polymer alone.

In a study on color removal from the biotreated effluent using three solutions, CP41B, CP42B, and CP43B, containing ferric sulfate with three different polymers, ferric chloride alone showed better color removal from the wastewater in comparison to any of the polymers, as can be seen from Figure 20.

REMOVAL OF TOTAL ORGANIC CARBON USING METAL ION COAGULANTS

Along with removal of color, samples were also analysed for removal of TOC. Alum and ferric chloride showed almost identical TOC removal from the biotreated effluent, with about 85% TOC removal at 800 mg/L, as shown in Figure 21 and Figure 22, respectively. Adding PAC separately to a ferric chloride treated biotreated effluent removed more TOC as compared to PAC added simultaneously with the coagulant for similar doses (illustrated in Figure 23).

Only about 30-50% TOC removal could be achieved by coagulation with alum, ferric chloride or ferric sulfate from the Main Mill effluent. Addition of PAC simultaneously along with FeCl_3 or alum removed very little additional TOC, as shown in Figure 24.

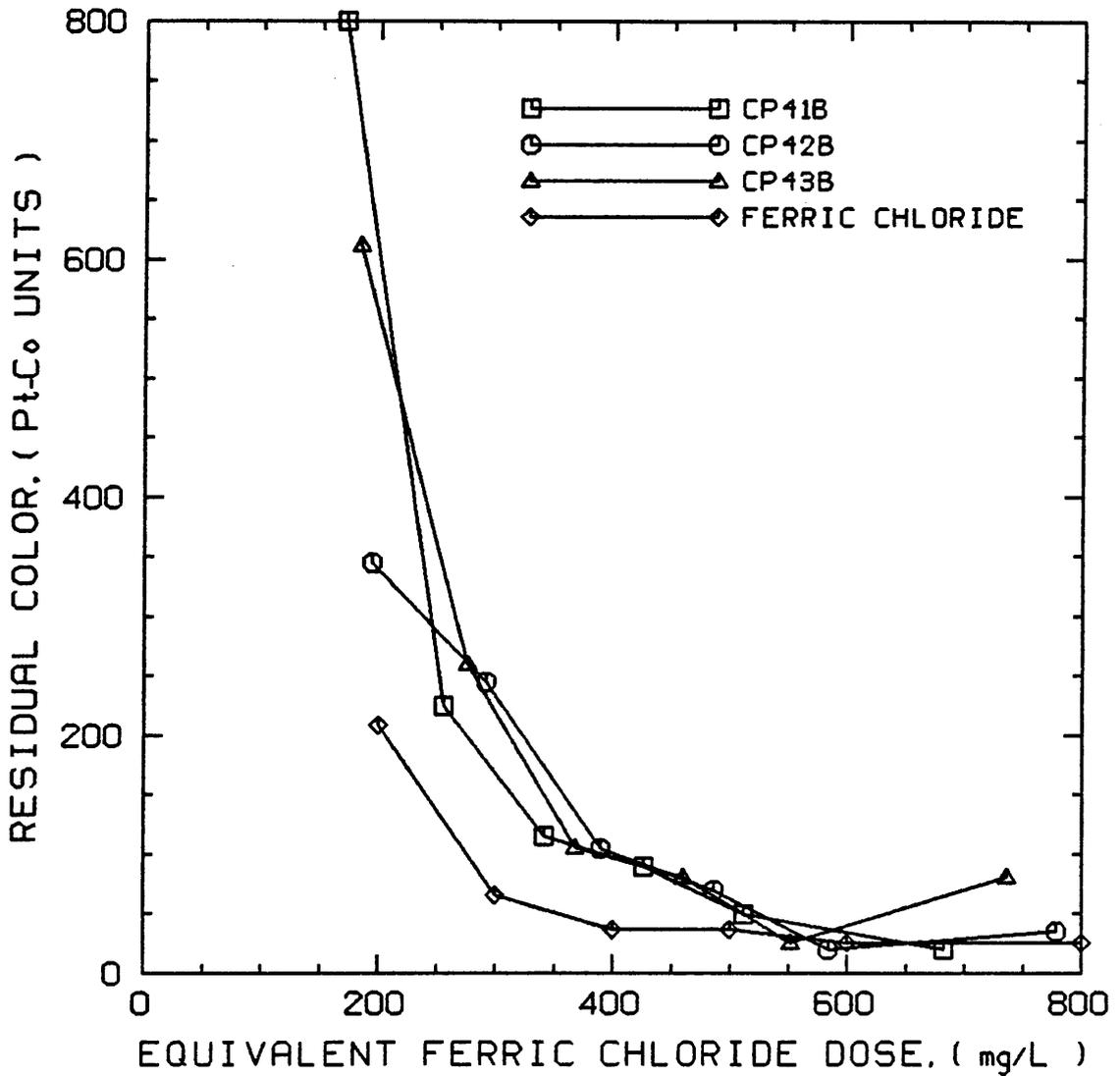


Figure 20. Residual color of biotreated waste as a function of dosage for coagulation using FeCl_3 , polymers CP41B, CP42B and CP43B (pH 4.0 and 30 min flocculation time). Initial raw color : 2215 color units.

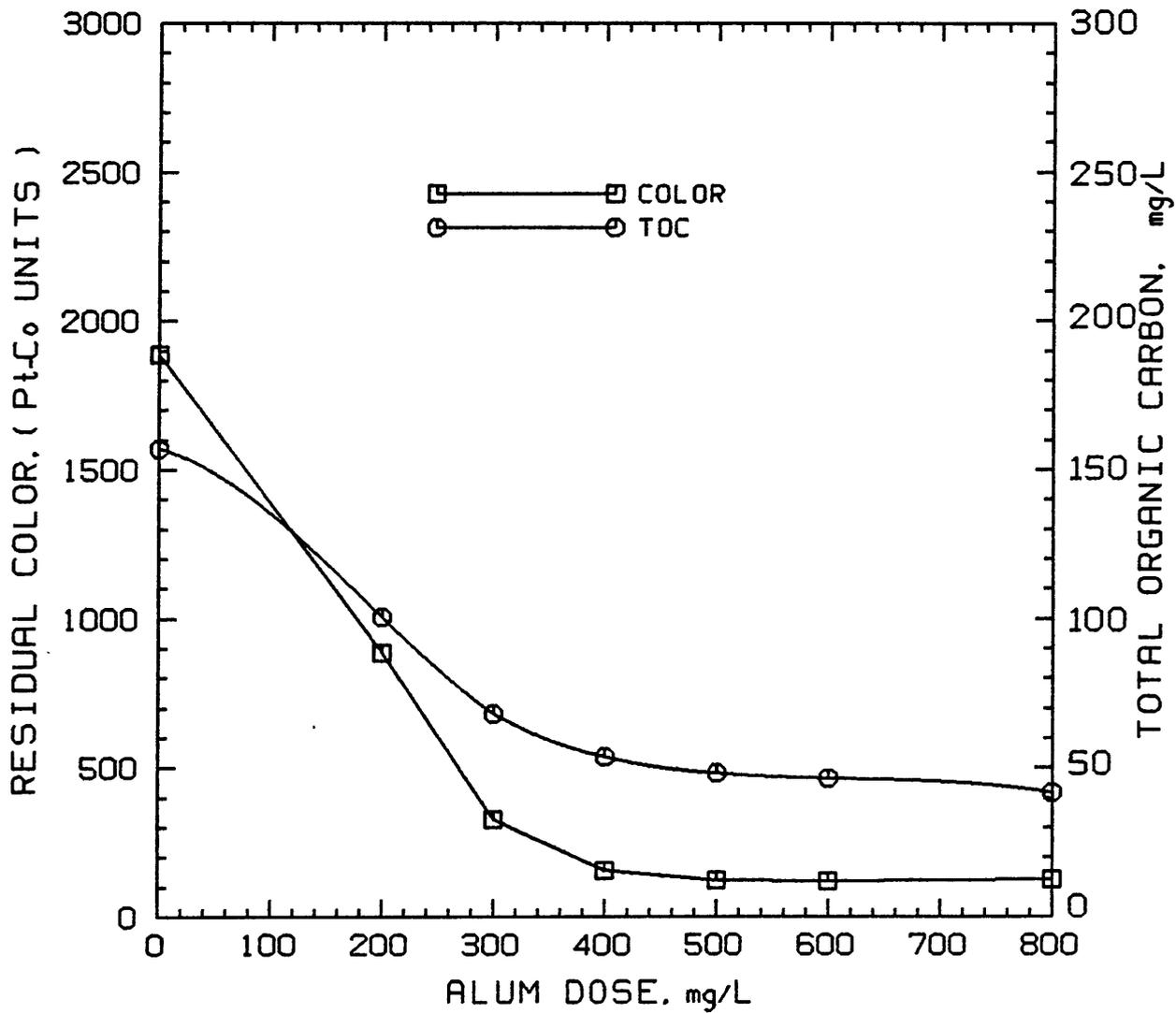


Figure 21. Relationship between color and TOC removal by alum coagulation when treating the biotreated waste at pH 5.3.

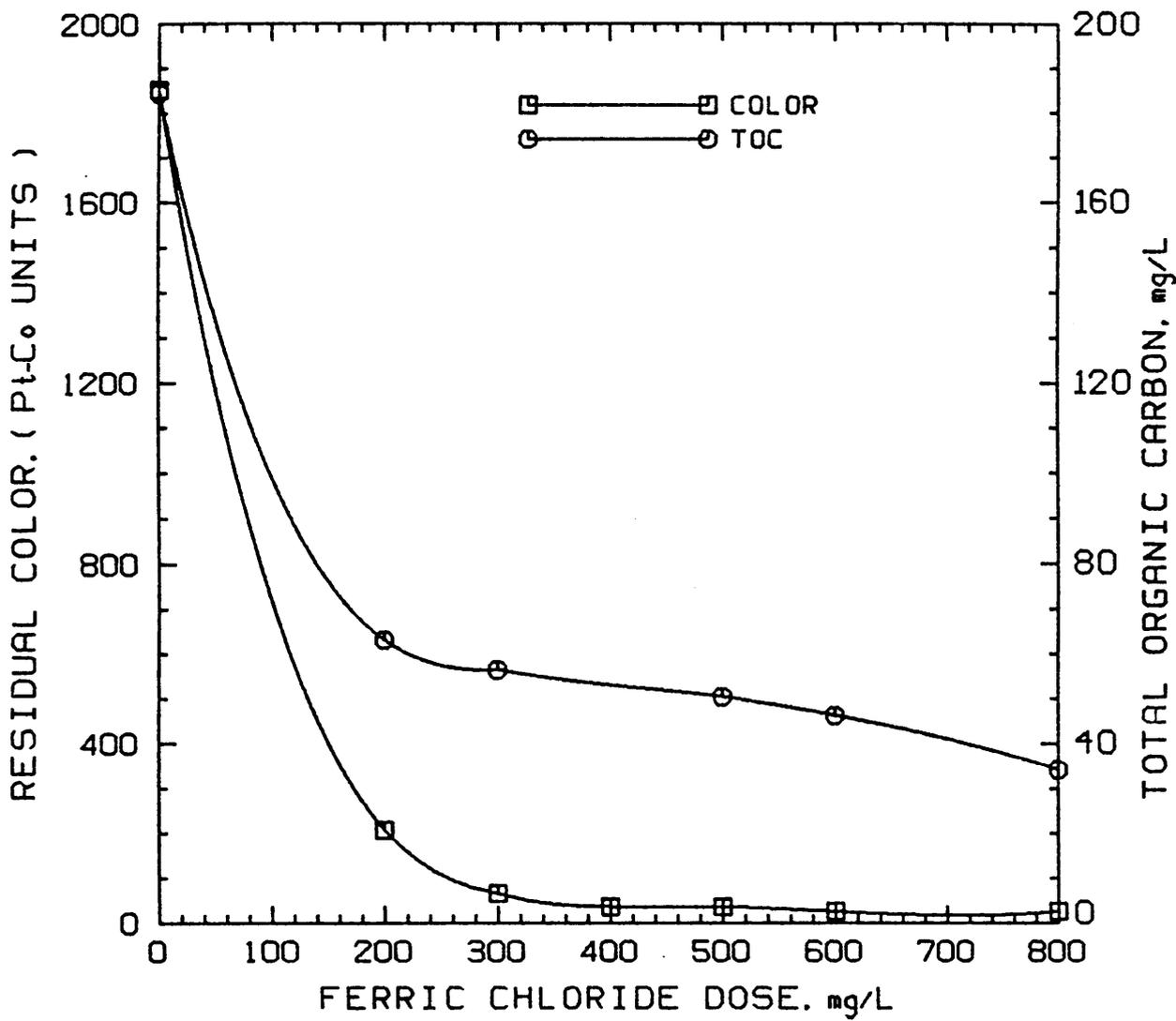


Figure 22. Relationship between color and TOC removal when using ferric chloride at pH 4.0 to coagulate the biotreated wastewater.

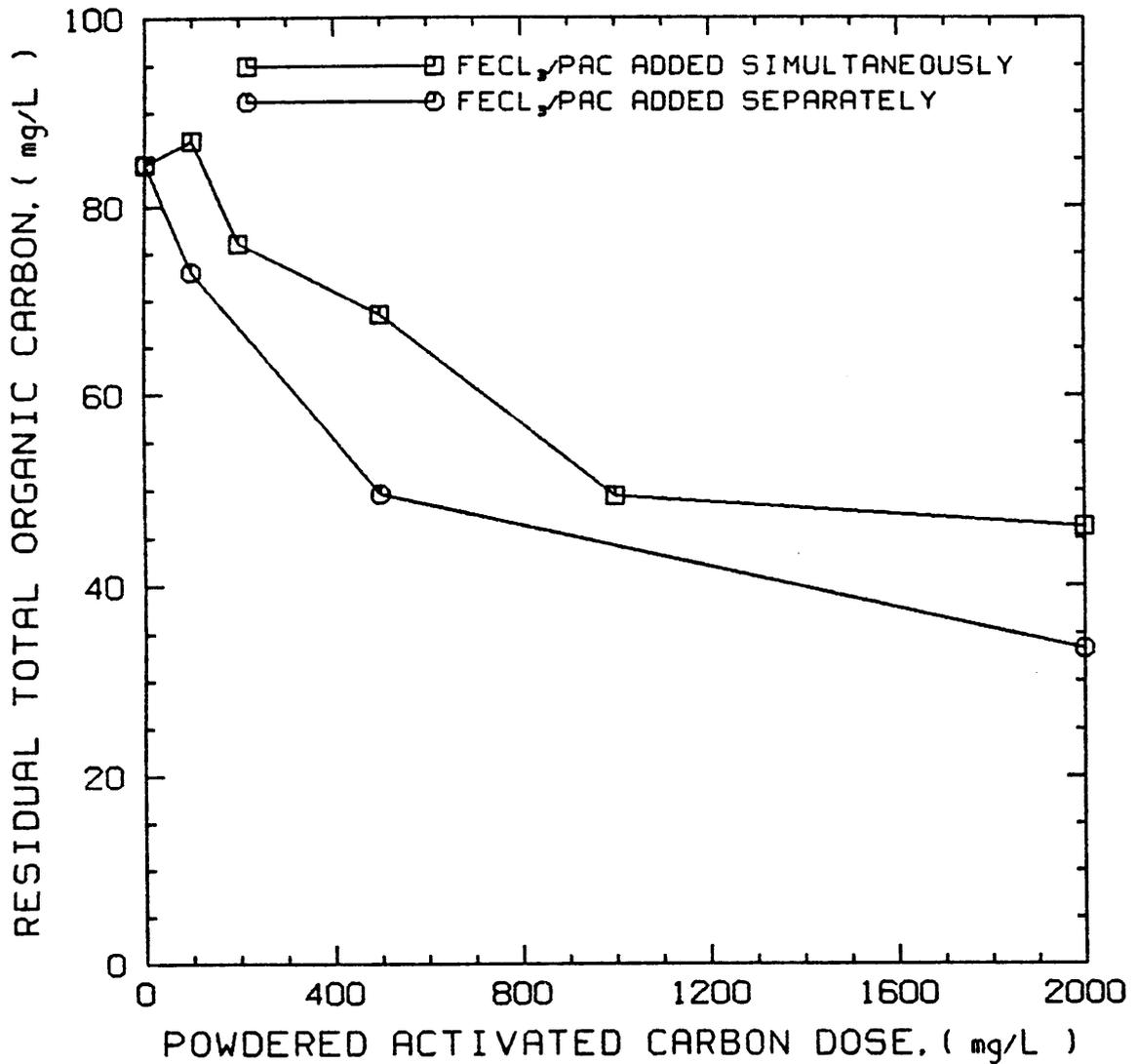


Figure 23. Residual TOC of biotreated waste as a function of powdered activated carbon dose in conjunction with 200 mg/L ferric chloride at pH 4.0.
Initial Raw TOC : 208.0 mg/L.

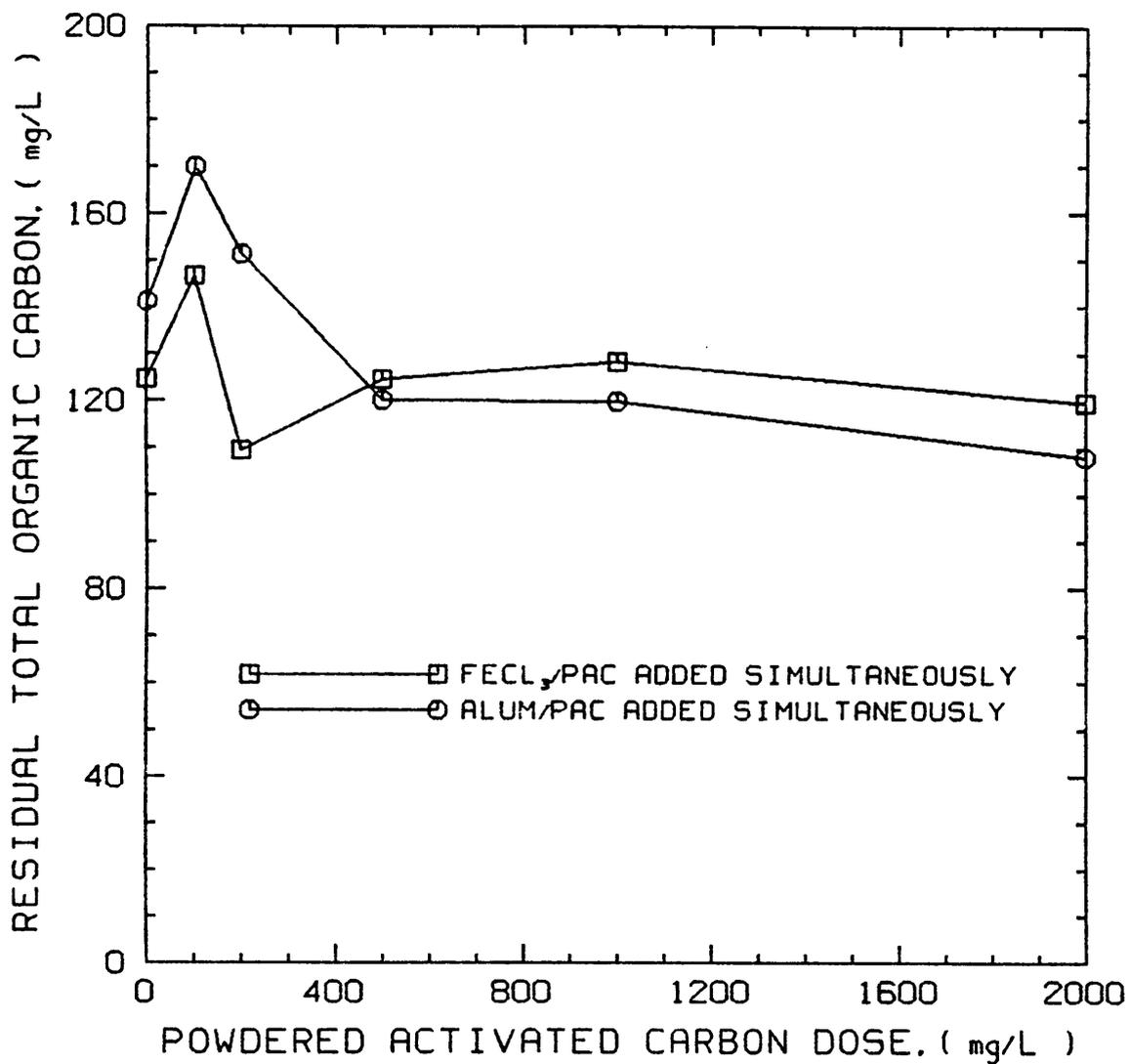


Figure 24. Residual TOC of the Main Mill waste as a function of powdered activated carbon dose in conjunction with 300 mg/L alum at pH 5.3 or 300 mg/L FeCl₃ at pH 4.0. Initial raw TOC : 251.6 mg/L.

SOLIDS SEPARATION AND DEWATERING CHARACTERISTICS OF SLUDGES PRODUCED DURING COAGULATION TREATMENT

Column studies were conducted to quantify the flocculant settling characteristics of the particles produced during alum and ferric chloride coagulation. Figure 25 shows typical settling data for particles produced by adding 500 mg/L alum on the biotreated wastewater. Using data from several tests, settling curves for percent suspended solids removal versus clarifier overflow rate were developed. Figure 26 presents these relationships for alum and ferric chloride treatment of the biotreated wastewater. It should be noted that settling characteristics are acceptable for overflow rates up to approximately 1000 gal/day/feet²

Zone settling studies on the two sludges yielded plots of sludge-water interface height versus time for a variety of initial solids concentrations. Figure 27 shows a typical plot for the alum and iron sludges at similar initial solids concentrations, while Figure 28 illustrates the variation of the settling velocity of the two sludges with initial suspended solids concentration. Alum sludge produced by treating biotreated waste with 500 mg/L alum at pH 5.3 showed better settling properties than the sludge produced by using the same dose of ferric chloride on the biotreated waste at pH 4.0. The settling velocity for the iron sludge was observed to remain fairly constant in the range of initial

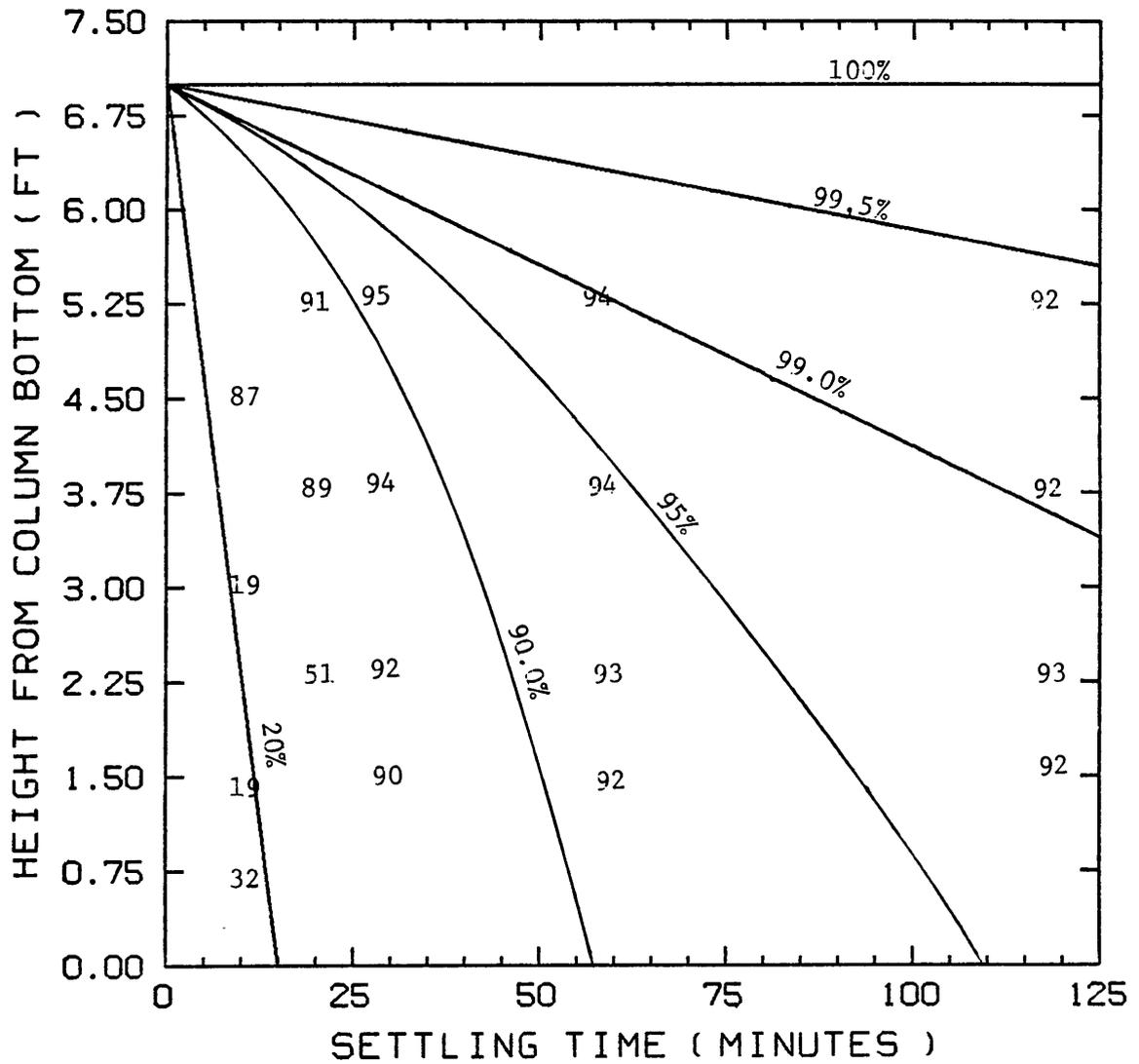


Figure 25. Settling curves showing percent suspended solids removal data as a function of height and settling time for the column studies on the biotreated waste treated with 500 mg/L alum at pH 5.3.

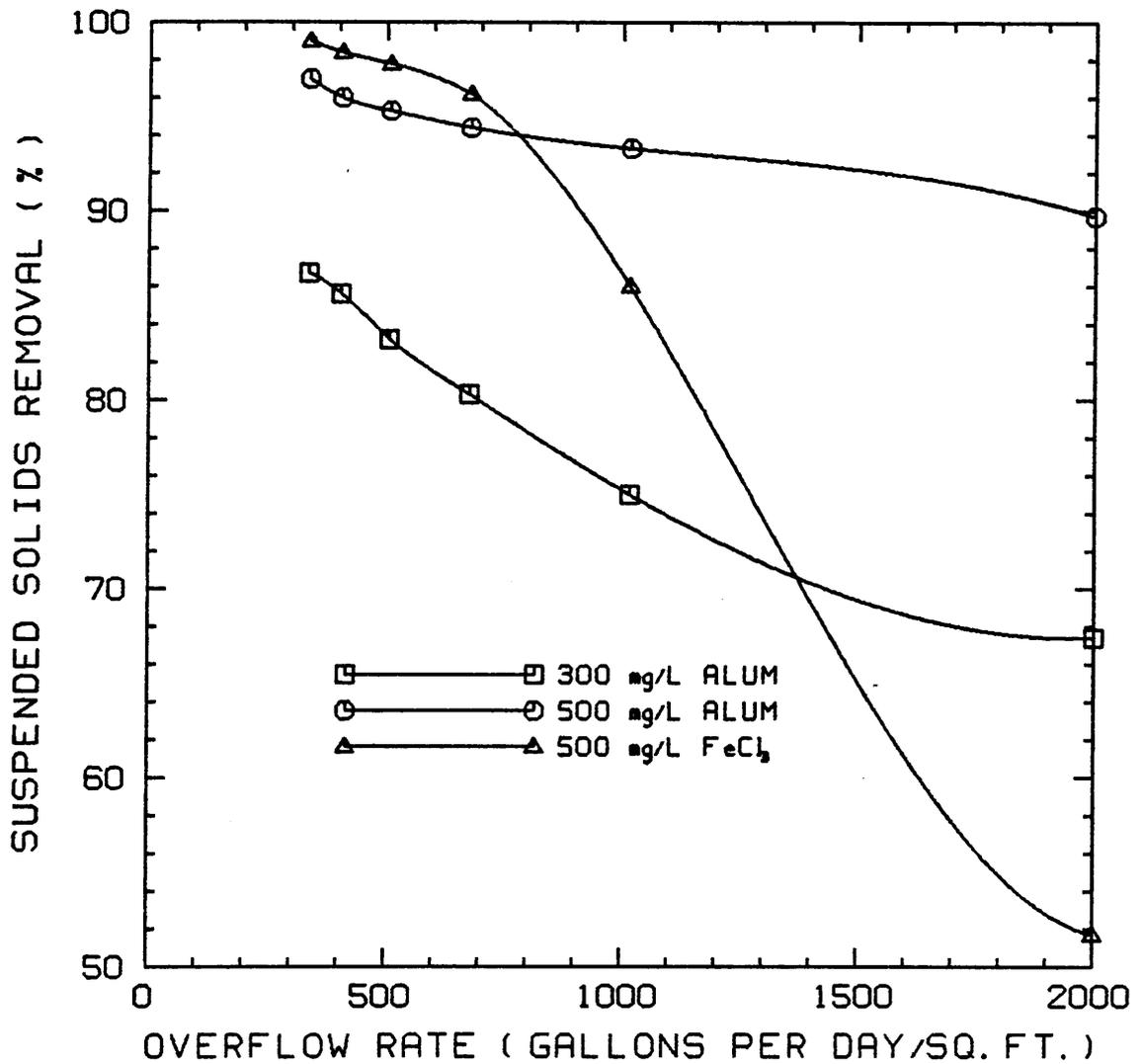


Figure 26. Settling curves showing variation of percent suspended solids removal with clarifier overflow rate for biotreated waste after treatment with alum or with ferric chloride.

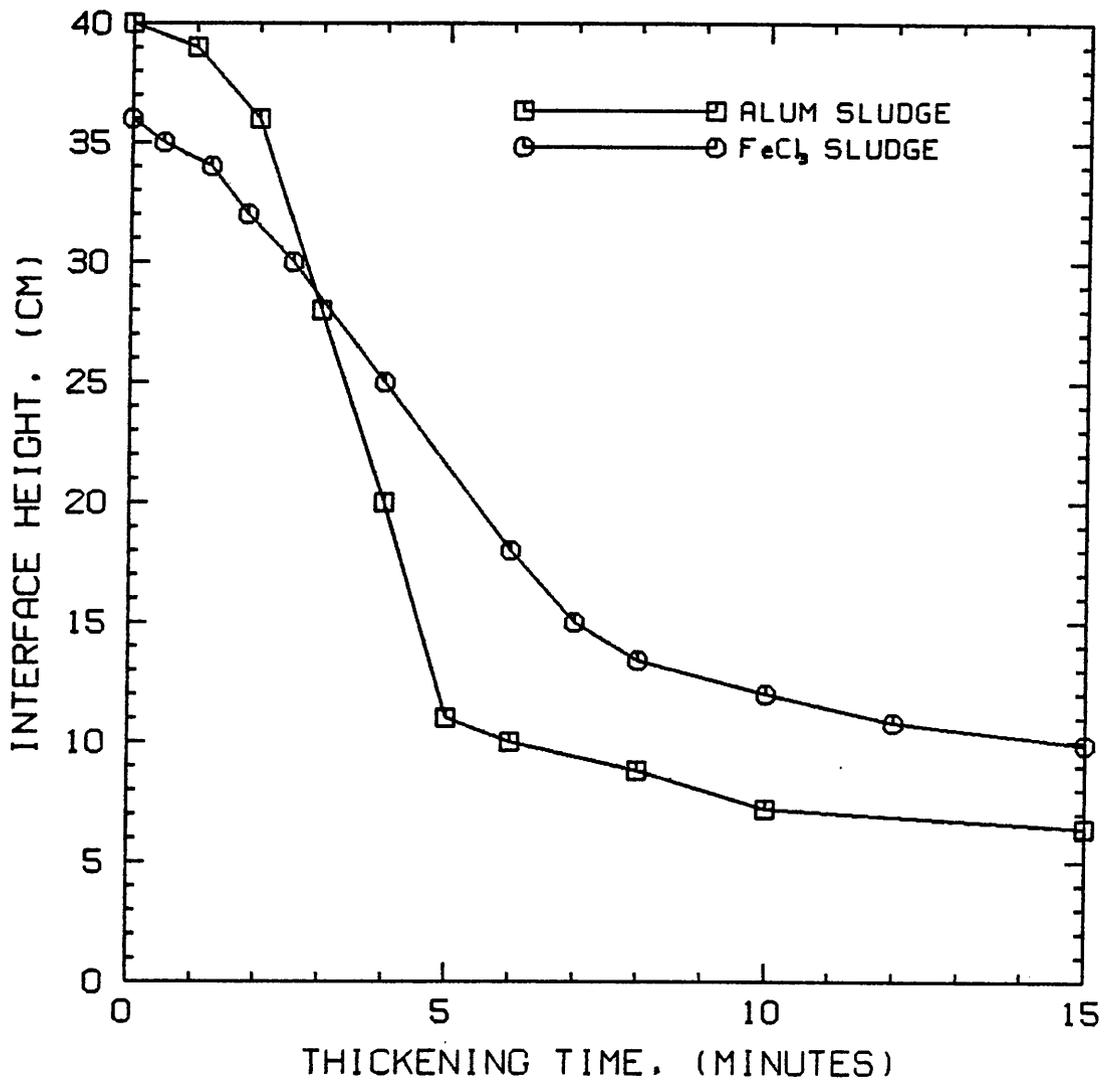


Figure 27. Interface height versus thickening time for alum and iron sludges produced by coagulation with 500 mg/L alum at pH 5.3 and 500 mg/L ferric chloride at pH 4.0 respectively, for the biotreated waste. Initial suspended solids concentration : 0.11%.

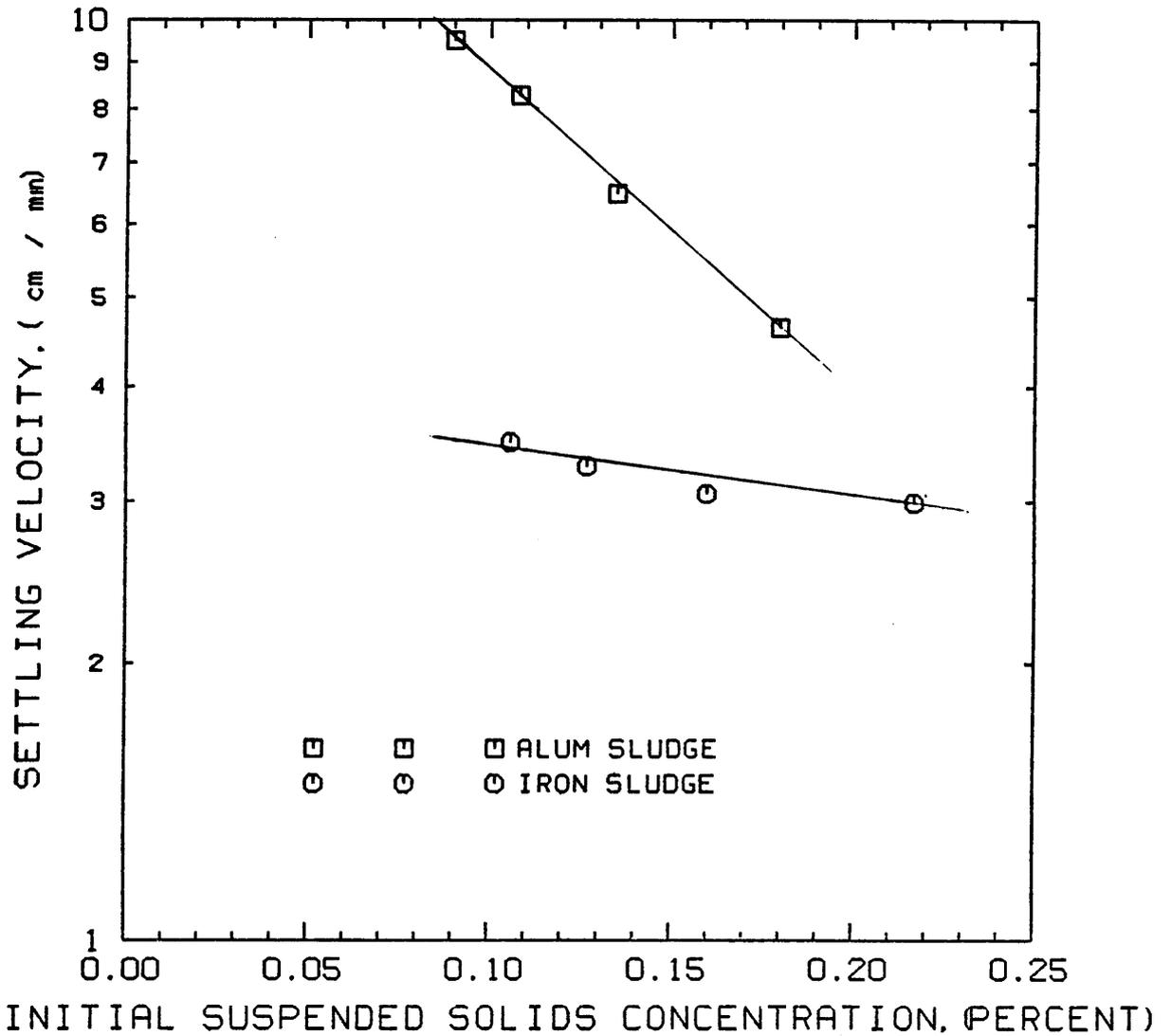


Figure 28. Settling curves showing variation of settling velocity versus initial suspended solids concentration for alum and ferric chloride sludges obtained by coagulation treatment on biotreated waste. Sludges obtained by treating biotreated waste with coagulant dose of 500 mg/L at optimum pH (5.3 for alum and 4.0 for ferric chloride).

suspended solids concentration used in the study. In comparison, the alum sludge showed a considerable drop in its settling velocity with increasing initial suspended solids concentration.

Vacuum filtration testing of the two sludges was completed to determine their sludge resistance values. Table 7 presents the sludge resistance values for each sludge type along with typical solids concentrations obtained after gravity thickening and vacuum dewatering.

MOLECULAR WEIGHT DISTRIBUTION OF ORGANICS

Ultrafiltration studies were performed on the wastewaters to determine the molecular weight distribution of organics initially present in the raw wastewater and the organics left behind after coagulation treatment. From these data, an attempt was made to determine the fractions of organics preferentially removed during coagulation.

Figure 29 through Figure 31 present the molecular weight distribution of the organics in the three wastewater sources. Raw biotreated effluent had little organics present at molecular weight of less than 500 daltons. The Main Mill wastewater had negligible organics in the 5K-30K range; also, in contrast to the biotreated effluent, it had about 60% of its organics in the molecular weight range <500 daltons. The Bleach Plant effluent exhibited a near uniform distribution,

Table 7. Sludge resistance values for alum and iron sludges along with final solids concentration after gravity thickening and vacuum dewatering.

Parameter	S L U D G E	
	Alum	Ferric Chloride
Specific Resistance (m/kg)	1.845 X 10 ¹²	1.88 X 10 ¹³
Solids Concentration after Gravity Thickening (percent solids)	1.35	1.34
Cake Solids Concentration after Vacuum Dewatering (percent solids) at vacuum pressures of		
17.0 inches of Hg	-	15.3
17.5 inches of Hg	14.51	-
20.0 inches of Hg	15.65	18.10

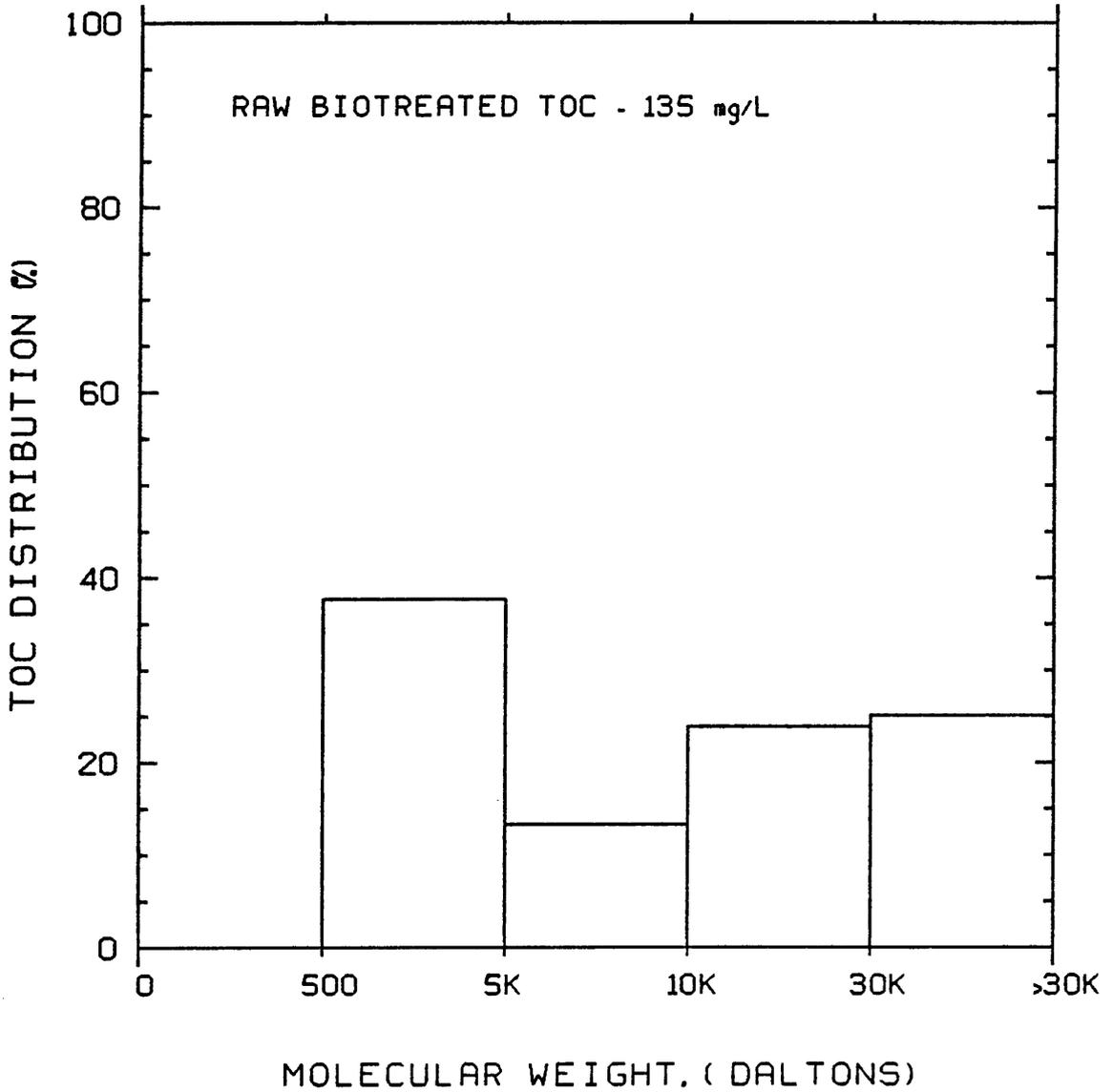


Figure 29. Molecular weight size distribution of the organics present in the raw Biotreated wastewater.

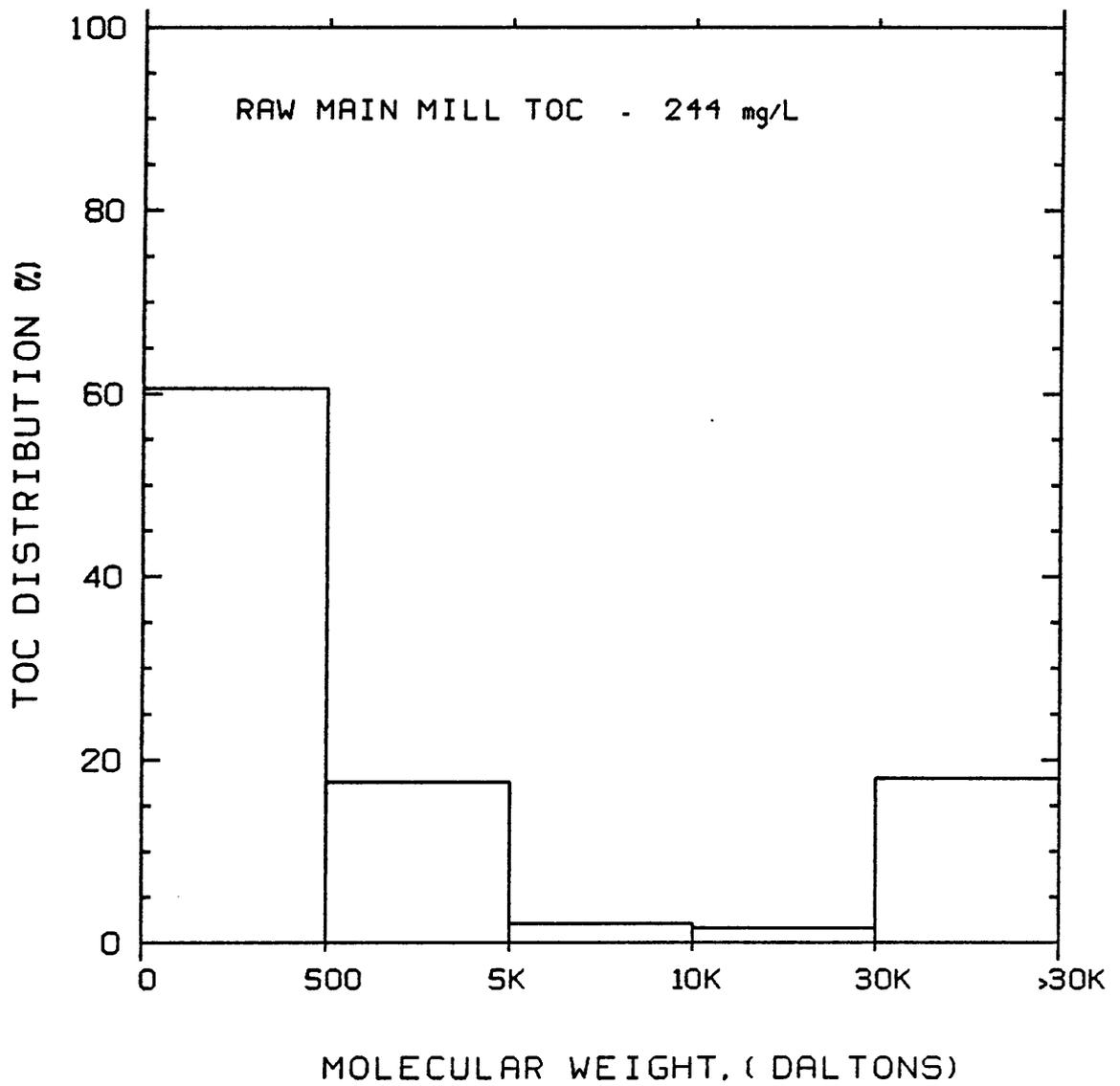


Figure 30. Molecular weight size distribution of the organics present in the raw Main Mill wastewater.

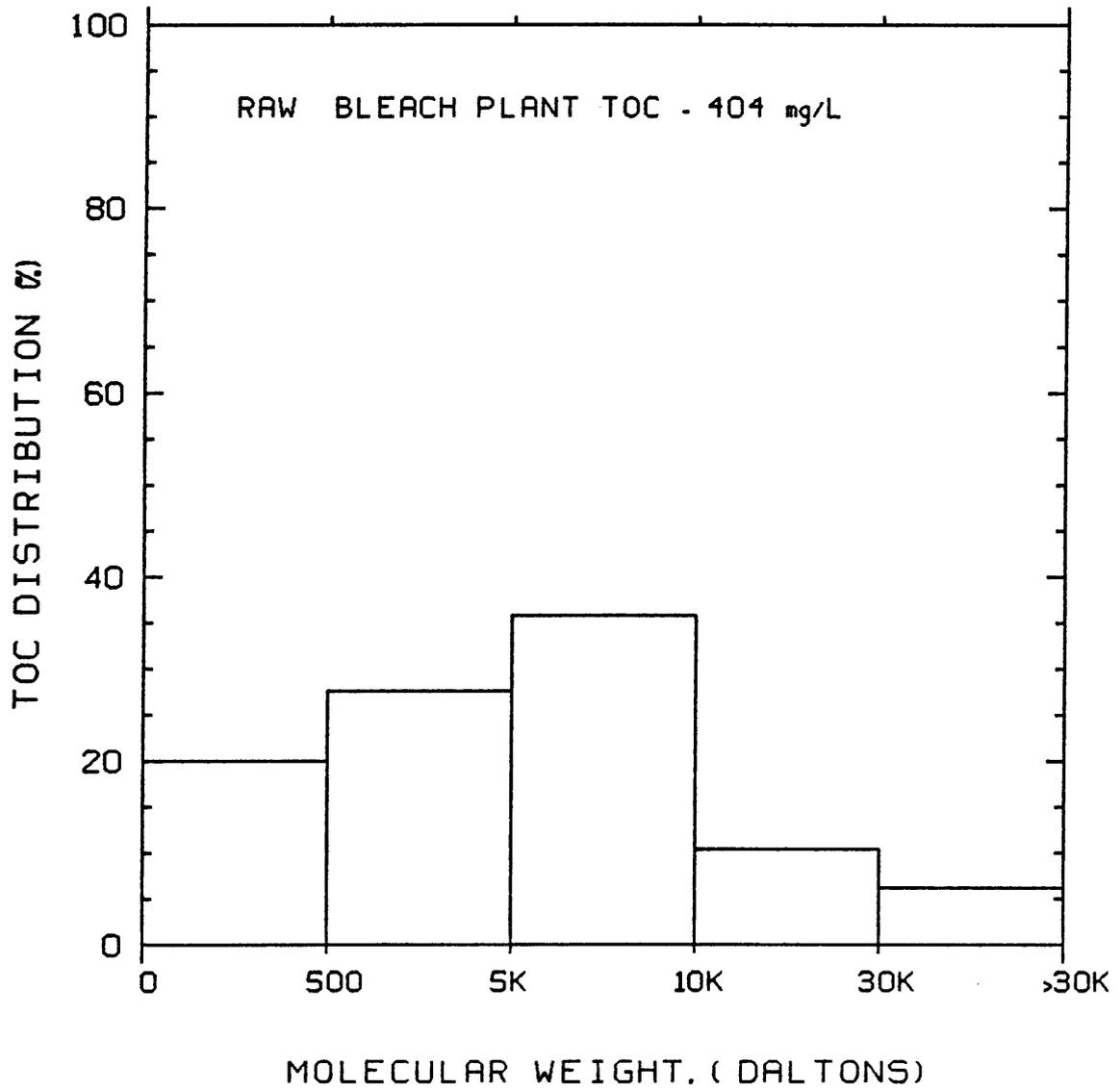


Figure 31. Molecular weight size distribution of the organics present in the raw Bleach Plant wastewater.

with about 36% of the organics present in the 5K-10K range. About 6% of the organics present in the Bleach Plant wastewater had a molecular weight above 30K daltons.

The molecular weight size distributions for the biotreated waste treated with 600 mg/L ferric chloride and 600 mg/L alum, respectively, are presented in Figure 32 and Figure 33. Both ferric chloride and alum showed essentially a 100% removal of organics in the 10K-30K range; Ferric chloride coagulation resulted in almost complete removal of the organics having molecular weights more than 5000 daltons. In both cases, no removal of TOC was observed in the <500 mass unit range.

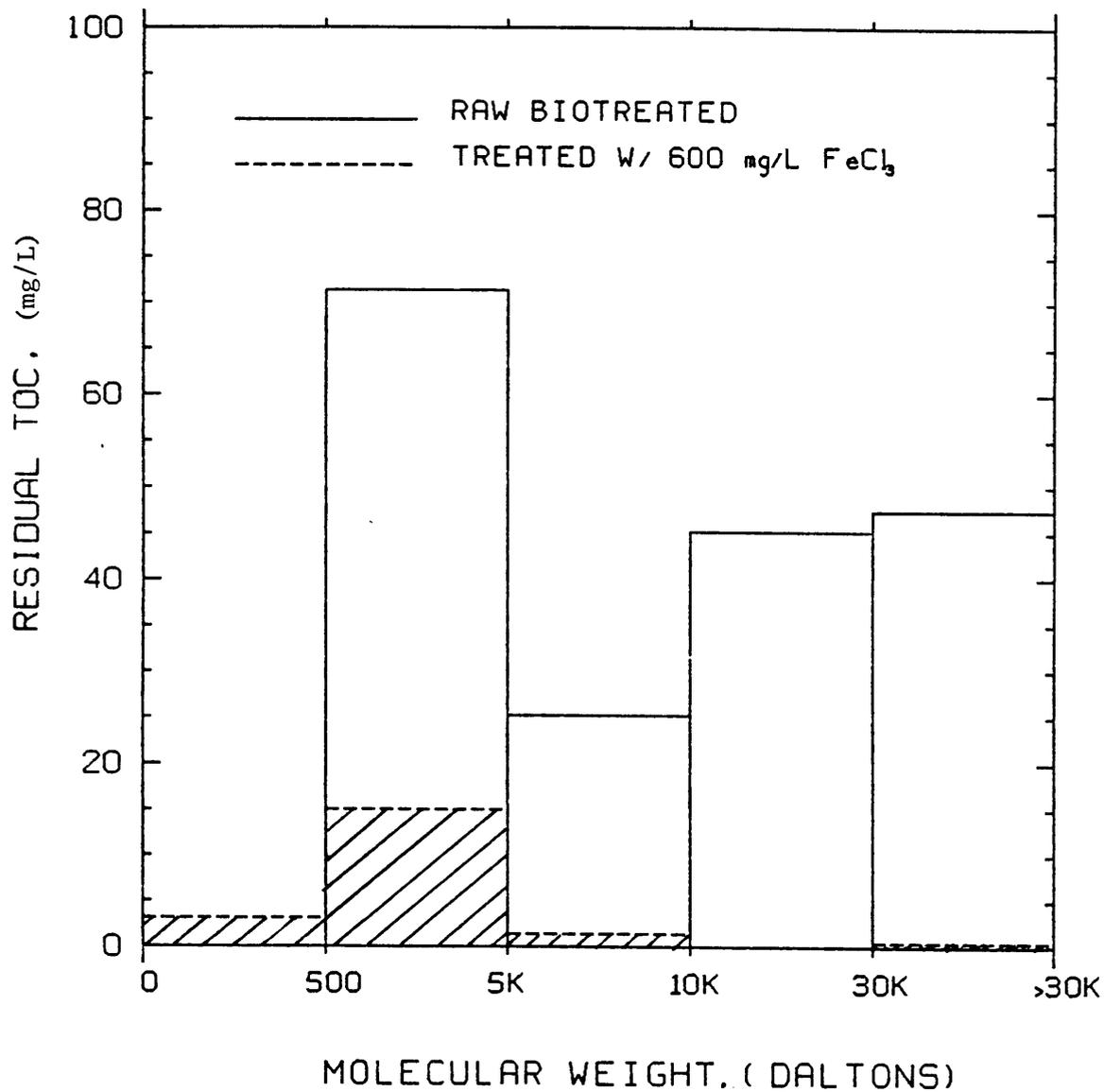


Figure 32. Molecular weight size distribution of residual organics present in the biotreated waste after coagulation treatment with 600 mg/L ferric chloride at pH 4.0.

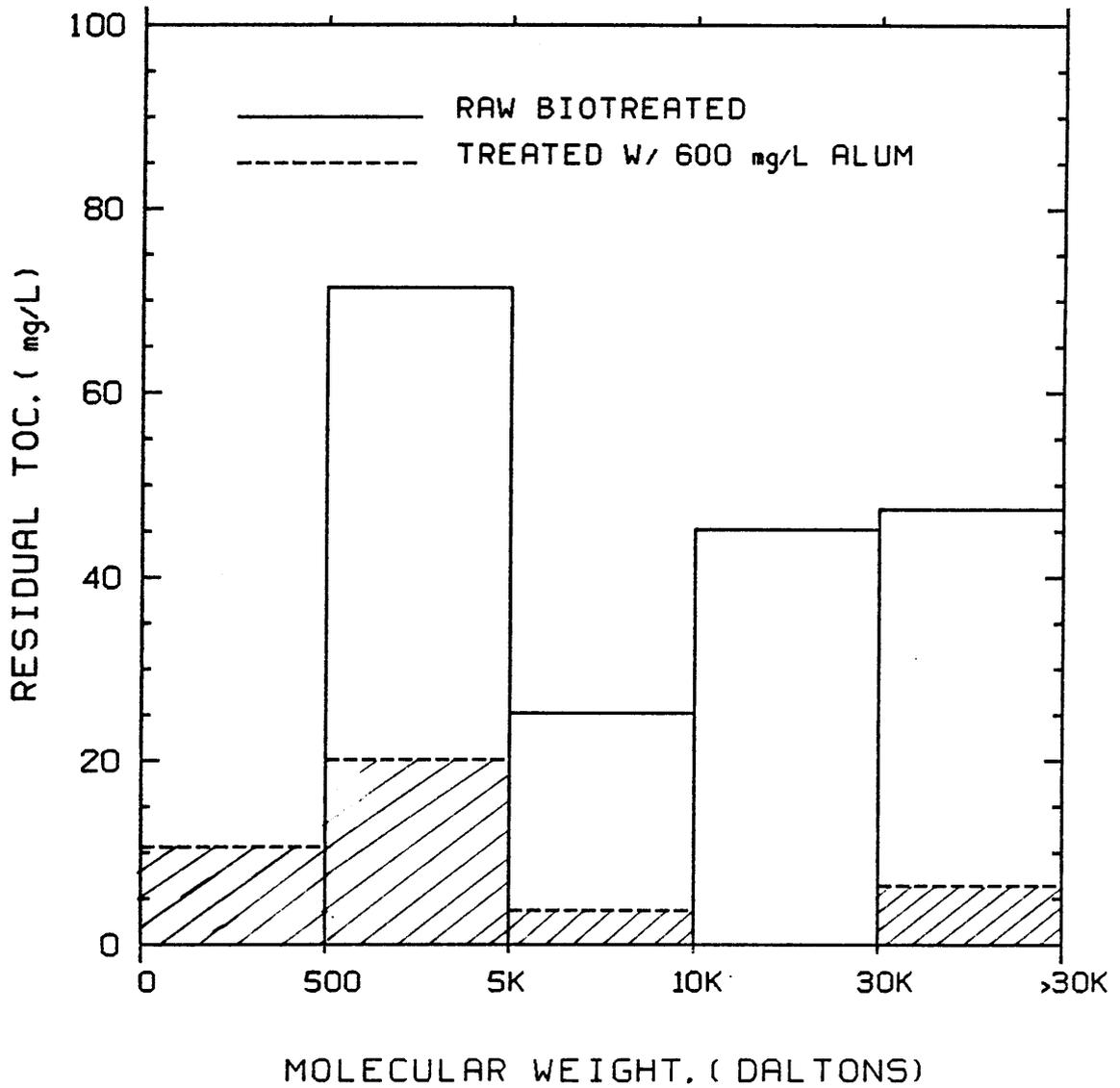


Figure 33. Molecular weight size distribution of residual organics present in the biotreated waste after coagulation treatment with 600 mg/L alum at pH 5.3.

CHAPTER V

DISCUSSION

The primary purpose of this research was to examine several coagulants to determine their effectiveness for removal of color from three pulp and paper waste streams using coagulation methods. Various chemical coagulants were tested. Preliminary tests indicated that lime was not effective in removing color from these wastes. Even with very high lime dosages (about 3000 mg/L), the residual color remained high (more than 200 Pt-Co color units). Ferric sulfate and ferric chloride showed similar behaviour with respect to color removal and optimum dose requirements. Hence, most of the work in this research was conducted using alum and ferric chloride. The use of powdered activated carbon (PAC) or polymers in conjunction with alum or ferric chloride enhanced removal of residual color.

OPTIMIZATION OF METAL ION COAGULATION DOSE AND PH FOR COLOR REMOVAL

The optimum pH values of 5.0-5.5 for alum and 4.0 for iron (Figure 10 and 11) as determined in this study are con-

sistent with values reported in literature for pulp and paper waste treatment (5, 6, 8, 9, 10, 14, 19, 23). Alum and iron coagulation in water treatment also yielded the same results (35, 36). Since pH is critical in defining the coagulation mechanisms, the coagulation mechanisms applicable to the removal of color from these three pulp and paper wastes can be assumed to be identical to those reported in the literature for water and wastewater treatment.

The percent color removal affected from the three wastes by alum and ferric chloride at optimum conditions compares favorably with the values reported by previous authors (8, 10, 14, 19, 20).

The widely accepted mechanism of color removal from pulp and paper wastes is charge neutralization. Color bodies in these wastes are present as negatively charged colloids. Addition of metal ions like Al^{+3} and Fe^{+3} causes charge neutralization by the charged hydrolysis species of these trivalent metal ions resulting in coagulation. Since the optimum pH conditions for coagulation observed in this research work are identical to those reported in literature, one can conclude that the same charge neutralization mechanism applies for color removal from the three wastes used in this research.

Most of the color and turbidity removal by coagulation/flocculation in water treatment plants takes place in the "sweep floc" range, because it is very difficult

to vary the coagulant dose to correspond to the influent conditions as required to operate in the range of complete particle destabilization (37). However, in this study, based on the trend of color removal as a function of coagulant dosage, it is unlikely that any color removal takes place due to enmeshment in the "sweep floc" range.

The amount of color removed per mg/L of coagulant dose of alum or ferric chloride at optimum conditions, when treating the biotreated or the Main Mill wastes, were calculated. Values in the range of 4.9 to 5.0 were obtained for this study. These ratios of initial color to optimum dose are close to the value of 4.7:1 for hardwood wastes as reported by Smith and Christman (14) for both alum and ferric chloride coagulation. This is consistent with the approach that the optimum dose required for color removal is a linear function of the initial color of the sample wastewater.

A corollary to the above approach would be to investigate whether the final residual color obtained using a constant coagulant dose varies linearly with the initial color, yielding a constant percent color removal. The linear dependency of the coagulant dose with the initial color level is confirmed by increasing residual color levels obtained when coagulating diluted samples of the Main Mill waste with a fixed alum dosage of 200 mg/L (Figure 8).

Massive lime dosages were required to remove significant amounts of color from the pulp and paper wastes. Dugal et al.

(4) reported color removal using lime to be largely dependent on the molecular weight size of the organics present in the samples. Organics having molecular weight <400 are not removed by lime, while those between 400 to 5000 are partially removed. Ultrafiltration studies on the three wastes indicate that the Main Mill contains about 60% of its organics below the molecular size of 500, and about 20% between 500 and 5K. Even the biotreated and the Bleach Plant wastes have about 50% of the total organics present below 5K. This could partly account for the low removal of color from these wastes using lime as the primary coagulant.

The Bleach Plant effluent was found to be the least amenable to color removal. Molecular weight size distribution data on the Bleach Plant wastewater show a production of lower molecular weight organics following the bleaching operations. It is a characteristic of chemical coagulation systems that the removal efficiency is a direct function of the molecular weight of the organics present.

Dugal et al. (9), in conducting experiments with various salts for color removal from pulp wastes made the observation that trivalent ions are more effective as color removing agents than bivalent ions. This is again in agreement with the proposed charge neutralization mechanism for color removal, in which one should expect higher dosages for divalent ions like lime in comparison to trivalent ions like alum and ferric chloride.

USE OF POWDERED ACTIVATED CARBON TO ENHANCE COLOR REMOVAL

Color removal by powdered activated carbon (PAC) is largely due to adsorption. Since this mechanism of color removal is different from the charge neutralization mechanism proposed for color removal by coagulation, studies involving PAC in conjunction with alum or ferric chloride were conducted to determine whether lower levels of residual color could be obtained by coagulation followed by PAC treatment.

Both ways of PAC addition, simultaneously as well as separately after coagulation, resulted in a lower residual color (Figure 12). The latter showed better results as compared to the simultaneous PAC addition under similar conditions (Figure 13). The ability of PAC to result in lower residual color levels after coagulation pretreatment could be explained by solubility considerations as proposed by Sullivan (38). Flocculation can be expected to reduce the solubility of the remaining organic molecules. This reduced solubility enhances the extent of adsorption, resulting in lower residual color levels.

POLYMERS USED WITH METAL ION COAGULANTS FOR REMOVING COLOR

The polymers that exhibited significant color removal from the three pulp and paper wastes were all cationic in nature. The mechanism proposed by Kisla and McKelvey (16) in

their study of the effects of polyamines on pulp wastes is relevant to this research. According to this mechanism, a complex formation occurs due to a coulombic attraction between the anionic color body sites and the cationic polymer sites. Addition of more polymer results in further aggregation and finally in neutralization of charge. Excess polymer results in an increase of color due to reversal of charge. Also, since the presence of anionic and cationic sites is pH dependent, color removal by polymers can be controlled by pH adjustment.

The polymers, BETZ 1190 and MAGNIFLOC 581C, both being strongly cationic, showed the best color removal (Figure 16). A greater understanding of the polymer characteristics and their dependency on pH is necessary to explain why the polymers TRETOLITE J118 and NALCO 7107 were more effective at lower pH while BETZ and MAGNIFLOC showed best color removal in the pH range 6.0-7.0 (Figure 15).

Since the mechanism of color removal for polymers is essentially similar to that proposed for chemical coagulants like alum and ferric chloride, no significant reduction in the final residual color could be achieved using polymers in conjunction with alum or ferric chloride.

REMOVAL OF TOTAL ORGANIC CARBON USING METAL ION COAGULANTS

A distinct correlation was observed between color removal and removal of total organic carbon (TOC) by coagulation using alum and ferric chloride on the pulp and paper wastes. (Figure 21 and Figure 22). Color matter in pulp wastes is organic in nature, and hence removal of color will be accompanied by removal of TOC as well. The goal of this study was to determine what fraction of the original TOC present is due to color bodies in the waste.

Results on the Main Mill waste (Figure 23) show that a large amount of organic carbon remained even after most of the color had been removed after coagulation, suggesting that more than 80% of the organics in the Main Mill waste are non color causing compounds. The biotreated waste, on the other hand, had most of its TOC removed along with color. Data relating to TOC removal from the biotreated waste indicate that less than 25% of the total organics present in it comes from non color-causing organics.

These results are consistent with the fact that the color causing compounds are mostly higher molecular weight humus substances which are not significantly removed by biological treatment. Hence, the biotreated waste consists of TOC mostly from color causing compounds. Most of the non color-causing organics, were apparently more readily biodegradable and were removed by the biological treatment. The

Main Mill effluent originating from the clarifiers has not undergone any biological treatment, and hence has a high fraction of TOC coming from non color-causing compounds.

SOLIDS SEPARATION AND DEWATERING CHARACTERISTICS OF SLUDGES PRODUCED DURING COAGULATION TREATMENT

Settling studies with sludges indicated that the sludge obtained by coagulation with alum settled better than the sludge obtained by coagulation using ferric chloride. The acceptable clarifier overflow rate of 500 gal/ft²/day (Figure 26), as obtained from the column studies using the alum and iron sludges, falls within the range of 300 to 600 gal/day/sq.ft. recommended for water plant design (39).

Zone settling studies on both the sludges yielded data conforming to the widely accepted relation $V = V_0 10^{-K C}$ for variation of sludge settling velocity (V) with the initial suspended solids concentration (C). The values of the constants V_0 and K obtained from this study are 19.9 cm/min and 3.5 (mg/L)^{-1} for alum sludge respectively, while those for iron sludge are 4.1 cm/min and 0.7 (mg/L)^{-1} .

The sludge specific resistance value obtained by vacuum filtration for the alum sludge was found to be lower than that for the iron sludge indicating that alum sludge dewateres better than iron sludge. Sludges having sludge resistance values around 1×10^{12} to 4×10^{12} have been found to exhibit

good dewatering characteristics. Based on these values, the iron sludge can be considered to be difficult to dewater.

MOLECULAR WEIGHT DISTRIBUTION OF ORGANICS

As presented earlier, based on the TOC removal data, more than 80% of the organics present in the biotreated waste comprised of color causing compounds. Hence, most of the molecular weight distribution (MWD) data applying to the organics present in the biotreated waste can be used in explaining the characteristics of the color bodies present. In contrast, since both the Main Mill and the Bleach Plant wastes have most of their organics of non-color causing nature, the MWD for these wastes cannot speak much for the color bodies present in them. Hence, no MWD studies were conducted on alum/ferric chloride treated samples of these two wastes.

The biotreated waste was found to have negligible organics present below molecular weight size of 500 daltons (Figure 29). This could be explained by the fact that the smaller sized organics are more readily oxidized by microorganisms, and are, hence, removed efficiently during the biological treatment. These data could also lead to the conclusion that color bodies present in these wastes have molecular weight size greater than 500 mass units.

A comparison of the MWD for the raw biotreated waste with that of the alum and ferric chloride treated samples points out that the organics in the range 10-30K are completely removed. Both alum and ferric chloride showed good removal of organics above 5K daltons.

An increase in TOC was observed in the <500 size range after coagulation treatment with alum/ferric chloride. A possible reasoning to explain this could be that the rapid mix phase during coagulation resulted in the breaking down of the larger size organics into smaller sizes causing an increase in the lower range TOC. But this reasoning does not seem strong when viewed in the light of the 30 minute slow mix flocculation that follows the rapid mix phase which should cause aggregation of the particles leading to larger sized particles.

CHAPTER VI

SUMMARY AND CONCLUSIONS

The objective of this study was to propose the best treatment approach for removing color from the pulp and paper wastes using coagulation techniques. Particular emphasis was placed on determining optimum pH conditions and corresponding coagulant dose requirements to achieve residual color levels acceptable for recycle of the wastewater as bleach process water. Characterization of the molecular weight organics present in the wastes was also accomplished and used to explain color removal from the wastewaters.

Based on the results obtained in this research, the following conclusions were formulated:

1. Both alum and ferric chloride gave good removal of color at dosages of 500 mg/L for the biotreated waste and 300 mg/L for the Main Mill waste. Color removal values ranging from 90-95% were achieved resulting in residual color levels less than 100 color units. However, treatment at these dosages would result in the production of significant quantities of waste sludge to be disposed. Optimum dose was found to be a function of the initial color and wastewater source.

2. The optimum pH for coagulation was found to be 5.0-5.5 for alum and 4.0 for ferric chloride. These pH conditions are the same as those observed in water treatment plants; hence, the same charge neutralization mechanism is expected to be responsible for color removal during coagulation.

3. Ultrafiltration studies on the raw and the treated samples for the biotreated wastes indicated that organics having molecular weight size more than 5K daltons underwent a near complete removal during coagulation. The molecular weight distribution of the organics present had a significant role in determining TOC removal efficiency. About 80% TOC removal could be achieved from the biotreated wastewater at optimum conditions for color removal. The Main Mill waste and the Bleach Plant, on the other hand, showed only about 20-30% TOC removal.

4. Coagulation studies using lime indicated that high dosages in the range of 1500-2000 mg/L were required to effect any significant color reduction. The residual color levels obtained after lime coagulation were not within acceptable limits for recycle.

5. Use of polymers along with alum or ferric chloride did not help in reducing the final residual color by any significant extent, even with dosages ranging from 300-500 mg/L of polymer.

6. Powdered activated carbon can be utilized in conjunction with metal ion coagulants to lower residual color levels to less than 10 color units for both the biotreated and the Main Mill wastes. The dosages required are high.

In view of the conclusive results obtained by this research work, a preliminary analysis can be made with respect to a particular treatment approach for removing color from the wastewater generated at the Union Camp Corporation, Franklin, Va.

Coagulation studies on the Main Mill and the Bleach Plant wastes do not show any advantage in treating either of these wastes for color before combining them for biological treatment. The Main Mill has a low initial color level (less than 1000 color units) and although, most of this color can be removed by coagulation, very little TOC removal is effected. The Bleach Plant required very high coagulant and polymer dosages to remove any considerable color. Hence, it is recommended that biotreated waste should be selected for treatment to remove color prior to reuse.

Both ferric chloride and alum showed similar color removal from the biotreated waste. In deciding which of these coagulants should be used, the pH is an important factor. The optimum pH required for ferric chloride coagulation is 4.0, about 1.5 units lower than that required for alum coagulation. Since the biotreated waste is nearly at neutral

conditions, and also since the pH desired after treatment for discharge or recycle is around 7.0, a lesser cost for pH adjustment would be incurred for alum coagulation.

A more detailed economic analysis of the cost of coagulants, sludge handling costs and the overall maintenance and operation costs, is necessary to make a final decision as regards to which particular coagulant should be used for color removal. Recycle of treated wastewater will probably require PAC treatment after pre-treatment with alum/ferric chloride. Finally, an in-depth study into the economics of recycle and incurred capital expenditures is necessary to decide what fraction portion of the effluent may be recycled.

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