USE OF POLYMERS AND A SURFACTANT IN THE TREATMENT OF KRAFT PROCESS WASTEWATER

by

Hans J. Seyffert

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APPROVED:

Gregory D. Boardman, Chairman

Clifford W. Randall

John T. Novak

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(ABSTRACT)

This study investigated the use of cationic polymers, and a surfactant, EHDABr, in the color removal treatment of Kraft pulp and paper wastewater. Four polymers were evaluated for their color removal performance by jar test procedures. The polymers removed between 77 and 87% of the wastewater color. The affect of pH upon polymer performance varied with the polymer tested. Powdered activated carbon addition improved the performance of the polymers.

The color removal ability of EHDABr was evaluated by jar test, and by continuous-flow, foam flotation. EHDABr removed 77% of the wastewater color by jar test and was relatively unaffected by pH variation. The addition of powdered activated carbon improved EHDABr performance in jar tests.

EHDABr removed 90% of the wastewater color by continuous-flow, foam flotation. Color bodies were precipitated in the foaming system before being removed by flotation. Total suspended solids removal improved with increasing column detention time.

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INTRODUCTION

The pulp and paper industry is the third greatest user of fresh water of all United States industries, after primary metals and chemicals. The current use rate of over two trillion gallons annually is expected to increase as the demand for paper products continues to rise. The continued growth of this industry depends, however, upon better management of water resources as procurement costs increase and public concern for environmental protection influences the enactment of more comprehensive pollution control laws.

Of the various methods of producing paper from wood, the Kraft process is the most widely used. The quality of pulp produced by this method provides the basis of production of quality writing paper, strong wrapping and board paper and other products in high demand. Thus, the Kraft process comprises over 50% of the number of paper processes carried out in the United States. The quality of paper produced by this process, however, requires large amounts of fresh water and results in production of high pollutional strength wastewater.

Color, dissolved and suspended organic matter, and dissolved inorganic solids are major pollutants in Kraft production wastewater. Current federal regulations limit the amount of solids and organic matter that a Kraft Production facility may dispose into public waters and most plants have some form of treatment of wastewater to meet these limitations. These treatment methods are generally limited to the removal of suspended materials by settling and the reduction of organic components by aeration before discharge into the environment.

Kraft process and other paper making facilities are facing upheavals in the paper market. The increase of foreign competition and the rising cost of procurement and treatment of large quantities of water and wastewater, coupled with more strict impending pollution control laws have caused the domestic paper industry to reevaluate production methods. Water wasting procedures of the past are being replaced by more observant in plant controls and modern, more streamlined production methods are being incorporated in many operations. In addition, the possibility of reusing some of the large amount of wastewater generated has led the industry to focus on improving wastewater treatment facilities. Existing methods of advanced wastewater treatment are being tested as pilot plants in some facilities and the discovery of new technology is being supported to increase the efficiency of existing treatment processes. By this focus upon modernizing production and treatment practices, the paper industry may function better in the increasingly complex world paper market and federal environmental protection plan.

Interest in securing long term water needs led a Virginia pulp and paper company to initiate a study of treatment methods of process wastewater for recycle use. The Facility produces 1800 tons of bleached and unbleached Kraft paper per day with a wastewater discharge rate of 30 million gallons per day. Treatment of this flow consists of primary settling and aeration in a stabilization basin. The company already practices some in-plant recycle and is interested in evaluating advanced treatment methods of the aerated wastewater to produce water for recycle in production.

In this study the ability of two methods to remove color from the wastewater produced at the plant was investigated. The performance of organic polyelectrolytes was evaluated by jar test procedures in the first method. The nature of reaction of the wastewater and the polyelectrolytes and the resulting color change of the wastewater was established. The roles of pH variation and powdered activated carbon (PAC) addition in the alteration of polyelectrolyte color removing ability were also observed.

The second method of color removal treatment consisted of the treatment of the wastewater by a lab-scale, continuous-flow, foam flotation system. The nature of the reaction of the wastewater and the foaming agent, ethylhexadecyldimethylammoniumbromide (EHDABr), and resulting color alteration were evaluated by jar test. The wastewater treatment performance of the foam flotation system was evaluated by the analysis of samples obtained from the operating flotation system. Changes in color intensity, total organic carbon (TOC) content, total suspended solids (TSS) content and effluent EHDA-Br concentration of the wastewater were found as the wastewater underwent treatment. The effects of wastewater pH variation and PAC addition in changing the color removal performance of the flotation system was also established.

LITERATURE REVIEW

The Kraft Process

The Kraft process produces paper pulp by employing heat, pressure, and an alkaline solution of sodium hydroxide and sodium sulfide. The pulp produced is then made into paper or first bleached when finer quality is desired. Chemicals used in the pulping process are regularly recycled in the process to economize on raw materials and reduce disposal problems. The entire process may be carried out as a continuous flow or batch method, the latter of which is considered the least economical method and is thus being replaced by the former.

The process is carried out as follows: After preparation by debarking and chipping, the wood is digested under high and pressure with an alkaline solution (NaOH and $NaCO_3$) of $NaSO_2$ and $NaSO_4$. The mixture is cooked at 340^{O} F and 100 psi for two to four hours. The grade of pulp produced increases with reaction time, up to a certain point, as the alkaline reaction mixture progressively dissolves the lignin of the wood, resulting in separation of the fibers. The pulped chips are then washed to remove the cooking liquor, dissolved lignin, and carbohydrates. The cooking liquor and dissolved materials is known at this point as black liquor. This mixture is concentrated by evaporation, burned in an oven to reduce carbohydrate concentration and further concentrate the mixture, then dissolved in water and slaked with lime and causticized. The resulting white liquor is then reintroduced into the digesting process.(1)

Kraft pulp may be made into paper directly after washing or may first undergo a bleaching process. The most economical and often used method of bleaching is staged bleaching with chlorine solutions. Pulp is generally bleached in three or more steps.(2)

The pulp brown stock is first reacted with an acidic chlorine solution that results in chlorination of the lignin in the pulp. The chlorinated lignin is then dissolved in a caustic extraction. Various combinations of peroxide, hypochlorite and $ClCO_2$ are used in the bleaching stages to regulate the degree of pulp brightness. The pulp is washed with clean water after the last bleaching stage and is then ready to be made into paper.

Wastewater Production

Wastewater streams from Kraft pulp and paper mills contain high amounts of suspended and dissolved materials(1). Because up to 95% of all pulping chemicals are recovered, the pollutional character of the wastewater is due almost entirely to the decomposition of wood. The waste streams of pulping, bleaching and papermaking are often combined before treatment and the character of the wastewater stream is influenced by the components of the wasteflow of each process.

Wood Preparation - Before undergoing pulping, raw wood is debarked and chipped into suitably sized pieces for chemical degradation (1). The debarking is often carried out by subjecting wood to high pressure water flow. Bits of bark, wood chips and dirt are then carried away by the water stream. More modern practices debark wood by mechanical means and any water used to clean raw wood is reused instead of being added to the combined wastewater stream.

Chemical Pulping - The chemical pulping of wood produces suspended and dissolved wood components by the reaction of oxidizing agents with the chemical matrix of the wood (3). The cementing compounds of the wood and the polysaccharide structure of the fibers are degraded into soluble and suspended lignin, carbohydrates and sugars. Pulp washing before further production introduces these compounds into the wastewater stream.

Pulp Bleaching - Work by Singh (2) showed bleaching of pulp results in further oxidation of the lignin of the wood and, to a lesser extent, the carbohydrate portion of the pulp. Large amounts of chlorinated lignin compounds are introduced into the pulp wash water as the dissolved materials are extracted and the pulp is washed in preparation for paper making. Chloride compounds resulting from bleaching are also introduced into the wastewater stream.

Condensate Collection and Paper Making - Condensed gases from pulping and bleaching processes are often added to the wastewater stream and introduce low concentrations of hydrogen sulfide, mercaptans and other sulfur compounds to the wastewater (1). Paper production of both bleached and unbleached pulp imparts suspended materials into the water used to float the pulp onto presses. During final preparation of the pulp, binders and coatings are added to the pulp slurry. The water pressed from the conditioned pulp may then contain suspended wood fibers, clay, and sizing residue.(4)

Wastewater Obtained for Study - The composition of the wastewater used in this study is described in Table 1. This information was obtained from reports from the pulp and paper wastewater treatment plant. The wastewater stream described as main mill was subjected to primary clarification before combination with the bleach plant stream. The combined flow was treated in an aerated stabilization basin and is known as biotreated flow in the table. Actual samples obtained for this study were taken from the stabilization basin.

Table 1. Kraft Pulp and Paper Facility 1984 Effluent Characterisitics

Parameter	Biotreated Average	Biotreated Range	Bleach Plant Average	Bleach Plant Range	Main Mill Average	Main Mill Range
BOD_5 (mg/L)	73	34-168	312	110-640	552	120-1479
TSS (mg/L)	66	38- 123	130	12-198	775	135-3468
Temp. °F	72	50-94	117	104-126	101	93-116
Conductivity (umhos/cm)	2547	1380-3500	3710	1600-6300	1675	800-3100
pH	7.2	6.6-7.6	3.4	2.1-4.9	11.0	9.6-12.3
Color (Pt-Co units)	2280	1710-4600	2505	1250-5200	1400	390-1960
Chlorides (mg/L)	633	500-720	1035	875-1210	32	20-50

The table shows high amounts of solids, organic material and color originating in the pulping mill flows. Bleach plant effluent contributes 36% of organic materials, 14% of suspended materials, 64% of color, and 97% of chlorides to the wastewater stream. Chemical oxygen demand and chlorides are reduced after biotreatment. Color of the biotreated flow remained in high concentration, however, and high conductivity values for this wastewater stream indicated continued presence of dissolved solids. The information in the table also suggests that suspended materials were reduced by 92% in the stabilization basin.

Color Production

Singh (2) found that much of the color present in Kraft process wastewater originates from the bleaching of pulp. Some amounts of color also originate from the pulping process (3). While a fraction of this color develops from the degradation of the structural carbohydrates of wood, the major contributor to color in Kraft process wastewater is lignin which has been dissolved by pulping and bleaching chemicals.

Sarkanen (5) described Lignin as a high molecular weight, partly aromatic polymer composed of amorphously arranged aliphatic and phenolic groups. Lignin in its natural state is insoluble in water and many solvents, and is essentially the cementing substance holding together the cells of wood. Lignin is slightly soluble in alkaline solution, is readily attacked by oxidizing agents and self condenses in acid solution.

Nolan (3) determined that under conditions of Kraft pulping, the reaction of aqueous alkali and sulfides under pressure and high temperature with lignin results in the hydrolysis of polymeric bonds in the lignin molecule. The resulting formation of acidic groups in the molecule contributes to lignin's solubility. Some of the lignin is then rendered soluble in the reaction solution as a sodium salt and is removed during cooking liquor recovery and pulp washing. Lignin present in the cooking liquor is incinerated during purification and the lignin present in the wash water contributes to coloration of the effluent (1).

Nolan (3) also found complete delignification cannot be carried out under conditions of Kraft pulping without reducing the strength of the pulp. Kraft pulping chemicals will readily solubilize wood fibers and uncontrolled, prolonged pulping will result in high wastewater organic concentration and reduced strength of the final paper product. Chlorine has been found to react readily with the noncarbohydrate component of chemically produced pulp. Its economic availability has made it the major constituent of pulp bleaching processes (1). The desired whiteness of the final paper product results from control of the forms of chlorine in the bleaching process. Lignin remaining in the pulp is removed in a controlled way, and the degree of brightness is established by the extend of its removal (3). Thus the bleaching process is thought to be a controlled extension of the pulping process.

Britt (4) showed that in its reaction with chlorine, the residual lignin in the chemical pulp undergoes reactions which lead to its degradation into water and alkali soluble entities. The highly amorphous nature of the lignin molecule makes it difficult to establish the exact nature of the lignin products, but results from Nolan's work suggest that oxidation produces soluble acidic lignin fragments that are removed by washing. In addition, the substitution of chlorine upon other lignin molecules occurs, producing heterogeneous alkali soluble chlorinated lignin fragments. The high coloration of the bleaching effluent thus occurs as the soluble lignin fragments are washed from the pulp.

Degraded Lignin Character - The degradation of the dense, amorphous lignin molecule by pulping and bleaching processes results in a diversity of acidic lignin and chlorinated lignin fragments. The density and relatively high molecular weight of these entities and the chemical stability of those carrying considerable chlorine substitutions contribute to the resistance of lignin fragments to biological degradation (3). Characterization studies of lignin color bodies resulting from pulping and bleaching has found them to range in molecular weight from around 50,000 to the millions (6, 7, 8). These lignin fragments are readily fractionated into acid soluble and acid insoluble groups (6, 7). The acid soluble fragments consist of aromatic compounds carrying short chained organic groups and are of relatively low molecular weight. Acid insoluble lignin fragments are made up of high molecular weight aliphatic entities and comprise the bulk of color producing lignin present in Kraft wastewater (6).

Both fractions carry a high density negative charge in aqueous solution. This charge and the molecular size of the lignin fragments cause them to exist in solution as colloidal particles (1). The extent that color removal methods function in reducing lignin concentration may thus depend upon the ability of the method to destabilize the charge of the molecule or the ability to drive the lignin from solution as a precipitate.

Wastewater Treatment and Pollution Control - Most Kraft mills operate some form of wastewater treatment to reduce the concentration of biodegradable material and suspended solids of effluents applied to public waters. The most common treatment methods consist of primary settling of suspended solids and activated sludge systems or aerated lagoons to reduce substances exerting a biological oxygen demand. (1) While this treatment scheme may remove up to 90% of settlable solids and 90% of the biological oxygen demand of the wastewater, color and dissolved solids reduction does not occur to any useful degree (1). The pulp and paper industry must currently consider improvements of this treatment practice as Federal regulations and the interest in recycle of production wastewater alter treatment quality requirements.

Hazen and Sawyer (1) proposed that to meet proposed effluent guidelines for reduction of suspended solids and biological oxygen demand of pulp and paper effluents, biotreatment by activated sludge or aeration will require additional organic and suspended solids removal before discharge. Depending upon the nature of the effluent from biotreatment, post aeration treatment may require the use of coagulants, filtration, or microstraining.

In addition, reduction of color and dissolved solids of biotreated effluent must also be considered if recycle of wastewater is to be carried out. Table 2 illustrates the guidelines established by the Technical Association of the Pulp and Paper Industry (TAPPI) for water quality of production water for pulp and paper production (1, 9). When compared to the characteristics of paper production wastewater used in this study, the need for specialized

Table 2. Water Quality Requirements for Recycle (1,9)

Parameter	TAPPI E603 Specifications (mg/L)
Turbidity	25
True Color (Pt-Co units)	5
TDS	250
Total Hardness	100
Free CO_2	10
Fe	0.1
Mn	0.05
Cl	75
Alkalinity	75
Silica as SiO_2	20

treatment of biotreated wastewater is evident. While many Kraft production facilities can produce good products using water of poorer quality than recommended, absence of color in the water used to make high quality white paper is recommended. The concentration of chlorides in production water should also be limited to reduce in-plant corrosion. The treatment methods applied to these problems are generally considered to be advanced methods and will probably best benefit the pulp and paper industry by being fitted into existing treatment facilities.

In addition to improving existing wastewater treatment operations and employing advanced treatment methods, the industry may improve the quality of wastewater discharges and optimize water reuse plans by improving production practices. Control of overflow and spillage, for example, reduces water waste and separation of wastewater flow from different operations and may help reduce or eliminate treatment for some flows. Improved production methods such as continuous flow digestion, countercurrent washing and combined mechanical and chemical pulping methods may be implemented to modernize paper making and reduce water needs. Study of bleaching chemistry has produced newer methods of bleaching such as oxygen bleaching and controlled bleaching methods with combinations of chlorine compounds. (10)

Color Removal

The pulp and paper industry has addressed the problem of effluent color as adversely effecting the environment for over 50 years. Complaints of wastewater color clouding local waterways led the industry to find methods of reducing the color in paper production wastewater. A number of color reduction methods exist today and the industry is currently evaluating some of them for use in treatment and recycle of colored wastewater. These methods rely upon physical or chemical means to remove color producing lignin fragments from solution and include coagulation with metal salts or lime, adsorption with activated carbon or resins, ultrafiltration, evaporation, and reverse osmosis. (1) Recent work has also been carried out in modifying coagulation methods by addition of polyelectrolyte compounds (11).

Coagulation and Adsorption - With the exception of color removing methods relying purely upon physical means, the methods listed above tend to proceed by means of adsorption or coagulation. Lignin fragments removed by coagulation, for example, are found to coalesce into settlable groups by the enmeshing and charge altering character of metal salts precipitating in solution (6). Adsorption, on the other hand, proceeds from the attraction of colloidal color bodies to a substrate by physical, ionic or chemical means. Coagulation and adsorption methods tend to remove best those entities that are least soluble (12, 13). Thus these mechanisms of color removal depend upon the pH, ionic strength and temperature of solution, the nature of the substance removed, the type and concentration of removal aid employed and the nature and time of the contact of the reactants (12).

Color Removal and pH - The solubility of lignin, as mentioned previously, depends greatly upon pH. Metal salts used for coagulation are themselves subject to varying solubility as pH of the solution changes (12). Study of the coagulating effects of metal salts has shown coagulation efficiency to be most efficient under pH conditions providing minimum solubility of the salts (12, 13). Characterization studies of Kraft effluent color forms have shown optimal color removal performance of alum coagulation of lignin occurs at pH ranges of 5.5 to 5.6, a range within the pH realm of alum precipitation (6, 14). Similar results were reported with ferric sulfate coagulation of lignin with the exception of this salt operating efficiently over a slightly broader pH range (6). In addition, color removal methods employing lime are dependent upon optimal pH conditions (15, 16, 17). In this case the acidification of the colored effluent and lime mixture results in the precipitation of lime as calcium carbonate and the acid insoluble lignin fragments. Color removal efficiency by these methods was also thought to depend upon the quantity of lignin driven from solution at the pH ranges that produced precipitation of the metal salts (16).

Methods of color removal employing adsorption of the color bodies upon a substrate are also influenced by solution pH. In this case pH is thought to influence the adsorptive ability of the substrate by altering its surface character. The charge of the substrate surface, for example, may vary as pH changes in the solution determine the ionization of components of the substrate (12, 13). In addition, the variation of the solubility of lignin resulting from pH change will influence the concentration of insoluble entities readily available for adsorption (6, 7, 8).

Ionic Strength of Solution - Under conditions of coagulation, the concentration and nature of the ions present in solution may alter the pH range of optimal performance, the removal time, the coagulant dose, and the residual coagulant concentration (12). It has been found that anions tend to influence the solubility of metal salts and that this influence is enhanced as the anion charge increases. The net effect of the presence of anions appears to be a broadening of the optimal pH range for coagulation to the acidic side, with monovalent anions contributing least to this effect. Because pulp and paper effluents contain diverse mixtures of dissolved solids, the practical use of ion behavior information must be tempered with experimentation.

The effects of ions upon adsorption performance depends upon the solubility of the ions present and their relative adsorbable behavior (13). In solutions of mixtures of adsorbable compounds, those exhibiting the greatest affinity for the adsorbent are most easily removed from solution and will displace less adsorbable entities already present upon the adsorbent. Mutual reduction of absorbance of both entities may also occur. The effect of ionic forms present in solution upon the pH of the environment of adsorption may also influence the solubility of other components in solution and thus alter the way they are adsorbed (13). Again, the complexity of the ionic character of pulp and paper wastewater requires experimentation to arrive at best adsorption methods for a given adsorbent.

Temperature Effects - Under normal conditions temperature changes appear to have little effect upon the efficiency of coagulation reactions. Although the rate of coagulation by metal salts seems slightly depressed as solution temperatures approach the freezing point, little operation variation is seen at temperature ranges in which these reactions are carried out (12).

Adsorption, on the other hand, results in a decrease in free energy as the solute passes from solution to the adsorbed state. Thus, heat is given off as this reaction occurs. Increased solution temperature, therefore, may result in decreased adsorption efficiency. Conversely, lower temperatures may favor adsorptivity (13). Comparisons of adsorptivity of varying concentrations or types of adsorbents must thus be carried out under constant temperature conditions.

The Nature of the Substance Removed and Nature of Contact - Examination of residual lignin fragments of alum, ferric sulfate or lime treated Kraft effluent shows them to consist mainly of soluble character (6, 16). Color removal carried out with adsorbents also fail to reduce the concentration of acid soluble lignin fragments (17). The presence of these entities is thought to result from the inability of coagulation and adsorption methods to remove soluble compounds (12, 13).

Molecular shape variation of the color bodies is also thought to influence their removal to some degree. Acid soluble lignin is generally thought to exist as relatively low molecular weight spherical molecules. Long chained, high molecular weight entities predominate in the acid insoluble fraction of Kraft effluent lignin components. (6, 7, 8)

It has been theorized that the conditions of coagulation depend to some degree upon colloidal particle interaction with the floc matrix formed by the precipitation of metal salts in water. It is thought possible that smaller molecular weight particles escape enmeshment by the flocs by fitting through the gaps and tend to remain in solution as the flocs settle. (12) Conditions of adsorption depend primarily upon actual particle and substrate contact. It is similarly theorized that smaller molecular weight entities may escape adsorption by passing through the substrate matrix without making contact with adsorptive sites (13).

Contact Time - During color removal by coagulation, complete mixing of chemicals is required to optimize floc formation and interaction of reactants. Slow mixing is also carried out to maximize floc stability and increase reactant mixing and contact (14). Thus, reactants must remain together a sufficient time to allow completion of these processes. The amount of time reactants are allowed to settle will also influence the extent of removal achieved.

Adsorption reactions are considered instantaneous. Adsorption depends, however, upon particle and substrate contact and the assurance of contact depends upon the nature and time of mixing and interaction (13). Thus, experimentation is required to arrive at proper mixing and contact time for optimal performance.

Concentration and Type of Removal Aid Used - As will be shown in the next section concerning color removal method descriptions, relatively high amounts of coagulants or adsorbents were needed to maximize color removal of Kraft effluents. Color bodies appeared to be removed from the effluent by precipitation under conditions of coagulation (6, 14, 15, 16, 18). The intensity of color removal by this method appeared to increase with increasing coagulant dose. The removal of color by metal salts showed color removal progressed to a maximum level as coagulant dose increased. Increased addition of coagulant past this concentration produced no more color removal (6, 11). Residual color was thought to consist of soluble lignin (6). The ionic complexity and high color concentration of the wastewater was thought to influence coagulant dose (14).

Studies of color removal by adsorbents also showed a similar increase of color reduction with increasing adsorbent dose. A point was also reached in the process where increased adsorbent dose produced no further color reduction. It was proposed that the high concentration of lignin in the wastewater required large numbers of reactive sites upon the adsorbent and thus caused the requirement of high adsorbent dose. (1, 17) Other components in the wastewater may also have been present to compete with the lignin for adsorptive sites. The failure of increased adsorbent dose in removing color may have resulted from soluble lignin not adsorbing.

Factors influencing the types of coagulant or adsorbent chosen include the effectiveness of color removal achieved, cost and complexity of the treatment method employed, cost of reactants, method compatibility with existing treatment practice, and relative difficulty of byproduct disposal, and chemical recovery (1).

Color Reduction Methods

The following description of color treatment methods provides information about the performance and versatility of color reduction operations developed in the last few years. This list does not include information about color removal methods similar to those addressed in this study; these are described later.

Coagulation With Alum and Iron Salts - Coagulation of bleach plant effluent with alum resulted in a 90% to 95% color reduction rate and a Total Organic Carbon (TOC) removal rate of 35% to 60%. Dosages of 250 to 400 mg/L of alum were needed to produce best color removal. Dosages of 250 to 500 mg/L ferric sulfate produced similar TOC and color removal results. Adjustment of pH was required to promote optimal coagulant performance. The level of color removal efficiency achieved may be adequate for some environmental regulations, but this level of performance is not considered suitable for producing recycle water because of high residual color and TOC values.

Coagulation systems require chemical feed, mixing, and settling systems and may be fairly expensive for large operations. High volumes of sludge result from the level of chemicals used and may limit the economy of this method when disposal costs are considered (1).

Color Precipitation With Lime - Studies of treatment of colored Kraft effluent with 10 to 20 gr/L lime were carried out. Color and TOC removal rates were 90% to 99% and 35% to 50%, respectively. Adjustment of pH was made during clarification to promote precipitate settling. A lime treatment system requires a chemical feed, mixing and settling systems and sludge storage. Recovery and reuse of lime is though to be possible with existing Kraft production lime recovery systems. (15, 16, 18)

A system using less lime has been developed for separated flows. Experimental methods also exist that use a combination of pressure, lime and pH adjustment to facilitate color precipitation and settling (1).

Activated Carbon Treatment - Activated carbon was used in combinations with other treatment methods by Sullivan to successfully produce high quality reusable water from Kraft effluent. Used alone, a dosage of 10 gr/L activated carbon reduced color and TOC from combined Kraft mill effluent by 99% and 88%, respectively. Carbon dose was found to be lower for producing good color removal in wastewater pretreated by coagulation. Reduction of wastewater pH promoted color removal. (17)

Activated carbon is best used as a polishing step in combined treatment because of its low capacity for wastewater organics (1). Combination treatment schemes such as coagulation, biological treatment, demineralization, and activated carbon treatment reduced color, TOC, and dissolved solids to sufficient levels to meet NCASI standards for recycle water. Powdered activated carbon addition to biotreatment has also been found to enhance detoxification of effluent. (17)

Adsorption Upon Artificial Resins - Adsorption of Kraft produced color bodies upon synthetic media resulted in color and TOC removal of 75% and 25%, respectively. Synthetic media were judged to be inferior for color removal treatment because of their relatively high cost and loading rate. (1) Artificial resins may play a role in water recycle, however, because of their effectiveness in dissolved solids reduction (17).

Ultrafiltration - Experimental ultrafiltration of Kraft wastewater by Lundahl, et al., and Murature (19, 20) resulted in color and TOC removal of 99% and 80%, respectively. Filter loading rates were reduced by coagulation of the wastewater prior to filtration. Filtered color was disposed of by incineration. Ultrafiltration systems were thought to be easily incorporated into existing Kraft wastewater treatment facilities and were also thought useful because of their high operation rate (1, 19).

Evaporation and Reverse Osmosis - Evaporation or reverse osmosis systems have been shown to remove color from Kraft wastewater. These methods were found impractical for large-scale treatment because of high operation costs (1).

Polyelectrolytes

Since their introduction in the late 1950's, polyelectrolytes have been found useful in many types of water treatment operations. Interest in their use continues to remain high as advances in modern chemistry result in increasingly versatile water treatment aids. Polyelectrolyte use has only recently been considered for pulp and paper wastewater treatment and shows promise in economizing some treatment methods.

Polyelectrolyte Structure and Behavior - Polyelectrolytes are high molecular weight, polymeric molecules containing many ionizable groups. As is true for all polymers, polyelectrolytes are comprised of chemically-linked identical or heterogeneous monomers (21). While the term "polyelectrolyte" describes those polymers that are charged, the term "polymer" is most commonly used to describe polyelectrolytes used in water and wastewater treatment (22).

The type and variation of monomer employed in the structure of a polymer determines the type and density of the polymer's charge. Charged polymers are grouped as cationic or anionic. Those containing no net charge are called non ionic. Polymers are also grouped with respect to their molecular weight, which ranges from 50,000 to the millions. The variability of molecular weight, charge, and monomeric constituents of polymers makes them a diverse group of compounds exhibiting many properties. (21)

The high charge density and high molecular weight resulting from the linking of many ionic monomers impart specific behavior to polymers in aqueous systems. Most polymers used in water treatment have a characteristic chain-like structure which cause these molecules to be relatively insoluble. The density of electrical charge upon this chain, however, helps hold the molecule in solution as a colloidal particle. This type of structure results in the polymer assuming an extended, string like form in pure water. The charge and hydrophobicity of the polymer also cause it to be attracted to surfaces of opposite charge or interfaces of solution such as solids, the container, or the surface of the solution. (21)

The attraction of polymers to particles makes them useful in water treatment. This attraction may be physical or chemical in nature and, owing to the complexity of a given polymer structure, highly specific toward the substance with which it is to react and the conditions under which reactions will occur. Specialized reactivity of polymers may make them very efficient at removing specific impurities in wastewater. (22)

While the actual reaction between polymers and particles may be unpredictable, polymers are thought to remove particles from water by chemical precipitation or enmeshment and charge destabilization. In either instance the reaction of polymers and particles depends greatly upon actual contact of the reactants. (22, 23)

A general description of the reaction of polymers and particles is provided below:

As polymer enters the water it releases counter ions and accumulates a high charge density along its surface, resulting in polymer extension. Colloidal particles may then become attached to the polymer by charge attraction or chemical reaction. The charge of the colloidal entity may be neutralized and the colloid and polymer complex may condense with other polymer and colloid particles into a settlable floc. Removal of colloids may also occur as polymer molecules cover the particles and result in their aggregation with each other into settlable groups. (22)

Performance Variation of Polymers - Disruption of the mode of polymer and colloid contact may result in reduced reactivity of polymer and colloid entities. Variation of polymer and colloid reactivity may result from colloid and polymer charge incompatibility, reduced polymer solubility, interfering ions or particles, and excess polymer concentration. The pH of the solution may influence the effect of colloid, ion, and particle charge upon polymer behavior, and alter polymer solubility. (22, 23, 24)

Colloidal Particle Charge - Reaction of polymers and colloids depending upon charge attraction may not occur if the reactants are of similar charge. In general, polymers react best with compounds of opposite charge. Thus, cationic polymers are the first choice for removing negatively charged compounds and anionic polymers are used to remove positively charge entities. A variation in the pH of a reaction solution may influence the charge attraction of colloidal particles by altering their ionization state. (22, 23)

Polymer Solubility - Reduction in polymer solubility results in the polymer molecule existing in a coiled, condensed configuration. A polymer in this state is thought to have few contact sites available on its surface and tends to have lower particle reactivity. The pH of a solution may reduce polymer solubility by effecting counter-ion release. Ionic compounds present in solution may also influence counter ion activity and polymer surface charge, resulting in reduced polymer extension. (21)

Interfering Ions and Particles - Ions present in solution may alter polymer solubility, as mentioned, or may compete with colloidal particles for polymer reactive sites. The ionic character of the reaction solution may also influence the charge and reactivity of the colloid particles to be removed. (24)

Other particles in solution may also react with the added polymer. As a result, increased polymer concentration may be required to remove the desired material (25).

Excess Polymer Concentration - Coagulation reactions of polymers and colloidal materials generally proceed with increases in material removal in polymer concentration to a maximum removal rate. Beyond a maximum removal concentration, however, further addition of polymer may cause a decrease in material removal (22, 23, 24). Reduction in removals is thought to result from colloid restabilization or reactive site reduction by attraction by excess polymer molecules. Excessive polymer molecules may engulf colloidal particles and produce a protective, stabilizing surface layer around them. As a result, colloids are restabilized in solution or may no longer carry sites for bridging with other polymer molecules. The renewed stability of the particles thus reduces their aggregation and removal. (22, 24)

Polymer Testing - In spite of the fact that many polymers are marketed for specific purposes and treatment applications,their optimal performance in any given situation is best discovered through experimentation. Screening of many types of polymers may be required to arrive at the specific compound that will give the best result for specific treatment needs. (11, 22) Difficulty encountered in choosing a polymer for a particular application may be increased by a general reluctance of manufacturers to disclose specific details about polymer composition and chemical properties.

Polymers must generally be tested for specific applications before being used in full-scale systems. Testing must be carried out in such a way as to portray realistic treatment conditions. (22) Thus, polymers considered as coagulants may be screened by jar test methods. Jar tests with polymers should be designed to assess performance variation due to pH change, wastewater composition change, agitation time and intensity, dosage of polymer and other chemicals applied, and the sequence in which chemicals are added. Information about the volume, stability, and settleability of sludge produced may also be discovered from jar testing with polymers. (23, 24)

Polymer Uses and Advantages - Polymers have successfully been used to remove colloids from water, improve floc stability and settleability, improve sludge dewatering, and improve filtration performance (22). Anionic polymers appear to work well as coagulation aids when used with metal salts (13). Cationic polymers tend to work well alone as coagulants because of their attraction to many negatively charge colloids. Lower molecular weight polymers are thought to reduce colloidal particle charge density by coating the particles and reducing repulsion between them. High molecular weight polymers attract and agglomerate colloids by trapping them within their extended configurations. (22)

Polymers are useful in many applications because they are easy to handle, store and apply, generally provide efficient performance at very low application rates, and dramatically reduce sludge volume of some treatment methods. In addition, existing treatment facilities may be made more efficient by addition of polymers. Alum coagulation of turbidity, for example, can be carried out at an improved rate by the addition of the proper polymer. (13, 22)

Polymer Use in Pulp and Paper Wastewater Treatment - The use of polymeric compounds in the production of paper is widespread in the pulp and paper industry (1). Specific polymers are used to condition pulp for paper making and improve coatings applied to finished paper. Polymers and similar compounds are also used to control foaming and dispersion problems in pulp and paper facilities. The industry is, therefore, well acquainted with the general use and application of polymer compounds. The use of polymers in treating pulp and paper waste is limited, however, to lab and pilot plant studies.

An alum and polymer treatment study of pulp and paper wastewater by Hayes and Monroe (11) established a color removal rate of 90%. BOD and COD were reduced by 50%. Wastewater was treated with 300 mg/L alum and one mg/L of a long-chained, cationic polymer. A highly stable floc resulted and was removed from suspension by flotation with dispersed air. After considerable screening, high molecular weight cationic polymers were found to be superior over medium molecular weight compounds in promoting floc stability. Optimal color removal occurred in a pH range of 6.5 to 7, and increased polymer dose broadened effective pH range. Optimal floc production depended upon proper mixing. Contact time was determined through jar tests. Coating of color particles by the polymer was reported to improve flocculation.

An alum, lime, and polymer combination was used by Coertze (26) to remove suspended solids from pulping wastewater. Polymer addition was found to improve floc stability. The chemically treated wastewater was clarified by flotation of flocs with dissolved air application. No information was presented about color or dissolved solids reduction. The treatment method was carried out as a pilot plan and was used to clarify a wastewater flow of 4000 m^3 per day. The system was described as providing adequate solids removal for local ordinances.

Surfactants

Compounds comprised of a polar or ionic portion attached to an aliphatic or nonpolar portion are called surface active agents, or more commonly, surfactants. These compounds contain many types of chemical groups and thus exhibit a wide range of properties such as wetting, emulsifying, dispersing, and flocculating agents. Many industries use surfactants in production or operation. The pulp and paper industry, for example, employs surfactants for pulp conditioning and paper finishing.

Surfactant Structure - A general structural model of a surfactant molecule may be envisioned as a unit composed of an ionizing or soluble head attached to a nonpolar or hydrophobic tail. This structure is the basis for the unique properties of surfactants in aqueous solution. These include the tendency of surfactants to be attracted to interfaces in solution, their ability to form micelles, and their altering of the surface character of solution. (27)

Adsorptivity - The tendency of surfactants to collect upon container walls, particles and the surface of a solution is known as adsorption. In pure water, the surfactant molecule becomes soluble as the polar end of its structure reacts with water molecules by ionization. The nonpolar end, while insoluble, is essentially pulled into solution by the reactivity of the ionic portion. Subjected to the repulsive forces of the water around it, the nonpolar portion of the surfactant will tend to orient itself in an energetically favorable position at the interface of solution. Thus, surfactant molecules accumulate at the surface of a solution with the polar ends facing into the water and the aliphatic portion forced onto or above the surface. In addition, the ionized portion may itself be attracted to particles or interfaces of opposite charge. A double layer of surfactant molecules may then result as the solution facing aliphatic ends attract a layer of surfactant molecules. These molecules will attach themselves to the existing layer by their nonpolar ends and face their ionizing portion toward the solution. Adsorptivity resulting from charge attraction is common for cationic surfactants. (28)

The adsorptive behavior of surfactants depends not only upon the nature of the surfactant, but also upon the entities with which it may react and the presence of ions and other surfactants in solution. The surface character or reactive ability of a particle may influence, for example, the way in which a surfactant will be attracted to it. The extent of this reaction may be influenced by the presence of other compounds in solution. (27)

The adsorption of a surfactant upon the surface of colloidal particles may result in particle aggregation. The nature of the reactants may influence the type of aggregation occurring and cause the formation of flocs or chemical precipitates. In cases where surfactant concentration is relatively high, double layers of surfactant molecules may form upon particles and cause their surfaces to become restabilized in solution by formation of a new, ionic layer. (28)

A particle surface may also be such that it attracts the nonpolar portion of the surfactant molecule. In this case a layer of surfactant forms upon the particle with the ionizing portion facing into solution. The surface character of the particle may thus be changed from hydrophobic to hydrophilic. The particle may then become soluble. (28)

Adsorptive reactivity of surfactants may also depend upon the components of the reaction solution and its pH. Ions present in solution, for example, may react with the surfactant to precipitate it or alter its surface in such a way as to render it unreactive with other compounds. Surfactants may also react selectively with ions over compounds for which they are intended. (29)

Many compounds exhibit surfactant properties. The extent to which these compounds react with other surfactants depends upon the nature of the compounds in question. Schwartz (29) cited studies showing that mixed surfactant behavior was unpredictable. These studies suggested that experimentation was often needed to establish the behavior of mixed surfactant solutions.

The variation of the pH of the reaction solution may alter the way in which a surfactant will behave. The character of ions and particles present in solution may vary as pH is changed and result in changes in reactivity with a surfactant. In addition, pH may influence the solubility of a surfactant or alter its behavior toward other compounds by altering its ionizing behavior. (27)

Micelles - Surfactants tend to become increasingly soluble as temperature of solution increases. At relatively low temperatures surfactants dissolve into a dilute solution of individual ions. Solution concentration slowly increases with rising temperature to a critical point at which solubility increases sharply. The sudden change in solubility is attributed to the formation of highly soluble entities called micelles.

Micelles are a configuration of a continuous layer of surfactant molecules in a three dimensional bubblelike form. Surfactant molecules are situated in this form with their polar ends facing into solution and their nonpolar ends grouped to the interior. Micelle shape, ease of formation, and stability depends upon the character of the nonpolar portion of the molecule and the presence of ions and other surfactants in solution. (28)

Micelle formation generally occurs more readily as the molecular weight of the nonpolar portion increases. Micelle shape variation results from the chemical composition of the nonpolar end. The nonpolar end of the molecule may also influence the formation of double layers of the micelle wall. (28, 29)

Surfactant molecules or micelles may react with ions to form insoluble precipitates. Ions may also incorporate themselves upon the micelle surface or interior and alter its stability and reactivity. Other surfactants in solution may also cause precipitation of the chosen surfactant micelle or alter its stability by changing its layering character.

Properties of micelles include the ability to solubilize, precipitate, or disperse other compounds in solution (28). Nonpolar compounds, for example, may become dissolved or dispersed in water by being incorporated into the micelle interior. Ionic particles may become attracted to the outside of the micelle and the resulting complex may become settlable.

Micelles may form or react differently with other compounds with changes in solution pH or the addition of other surfactants (28, 29). As mentioned earlier, pH variation may influence the reactivity of compounds and ions in solution and may alter the surface character of the micelle through ionic charge variation. Nonpolar or surfactant compounds in solution may incorporate themselves into the micelle wall or interior and alter the surface character or stability of the micelle. Unpredictable enhancement or inhibition of micelle properties may result from the addition of ions or other surfactants and studies of micelle behavior suggest experimentation may be needed to arrive at micelle character in mixed solution. (29)

Solution Surface Alteration - The tendency of surfactant molecules to accumulate at surfaces of solution and to align themselves into a defined layer results in alteration of the surface character of their aqueous environment (28). In pure water, the attraction of water molecules to each other results in an energetically compromised state in which the surface layer of water molecules is maintained at a minimum. The attractive inward pull upon surface molecules by interior molecules reduces surface spreading. This surface tension provides integrity to water droplets upon surfaces, causing them to hold their smallest shape and resist dispersal. The attractive interaction of water molecules similarly squeezes nonpolar or hydrophobic compounds from solution. Surfactant molecules accumulate at the surface of a solution in an energetically favorable position when acted upon by the repelling force of water molecules. Because surfactant molecules are repelled from the bulk solution, they tend to maintain a state of potential energy at the surface. The result is a reduction of the surface tension of the solution.

Changes in surface tension of a surfactant solution may lead to increased wetting, spreading, or adhesive potential of the solution (28, 29). Foaming character of the surface may also be enhanced. The specific surface effect of a surfactant depends, again, upon the nature of the surfactant and its reactive environment. The density of the surface layer, for example, may depend upon the nonpolar character of the surfactant and the tendency of other surfactants to be incorporated into the existing layer. New compounds added to the surface layer may aid or curtail the effects of the surfactant in question. Surface elasticity and viscosity are also dependent upon the nonpolar nature of the surfactant molecule and the presence of other compounds in the layer. In general, long chained or heavily branched aliphatic portions tend to interact more strongly at the surface than short chained portions and result in increased surface stability. Increased density of the surface layer resulting from the incorporation of other compounds may also increase stability.

Foaming Ability - An important surface characteristic of some surfactants is their ability to promote foaming (27, 28, 29). While many surfactants exhibit some degree of foaming ability, those that are charged and form high viscosity, elastic surface layers tend to produce the most stable foams. Nonpolar portions of the surfactant contribute to elasticity and viscosity. The charge of the surfactant maintains foam stability by helping to reduce draining of the foam matrix. The importance of charge in foam stability is explained as follows.

Alternating layers of surfactant molecules and liquid make up the foam structure. As liquid drains from the layers, foam structure weakens. Surface charge in the surfactant layers repel, however, as the draining layers come closer together. Repulsion of the layers occurs as they reach a certain proximity because of their charge. As a result, the layers won't touch and liquid is held between them by capillary action. (28)

Foam production and stability also depends upon the concentration of surfactant in solution (28, 29). At surfactant concentration below that required for micelle formation, foam density depends upon bulk solution concentration. Foam density after micelle formation is influenced by the rate at which free surfactant accumulates at the surface.

The production of foam in mixed solutions depends upon the effects of pH variation, the presence of ions and other compounds, and temperature and agitation of the solution (28, 29). Changes in pH, for example, alter the interaction of nonpolar entities of some surfactants and changes their surface stability. Variation in pH may also influence free surfactant concentration and cause decreased foam stability by reducing surfactant solubility. Ions may react with free surfactant and reduce surfactant concentration or may incorporate themselves into the surface layer and alter its ability to maintain a stable foam. Other surfactants present may increase or decrease the foaming ability of the surfactant in question. Depending upon its structure, the compound may incorporate itself into the existing surface layer or completely crowd out the layer and form a new one. Either case may result in foaming alteration.

Solution temperature variation may alter free surfactant concentration and change surface surfactant density or change viscosity and elasticity of the foam. Agitation of the solution may overcome cohesive forces of the surface and cause breakdown of foam layers. (29)

EHDABr - Ethylhexadecyldimethlammoniumbromide (EHDABr, mw 378.48), a commercially available product well known for its foaming ability, produced the best results of the surfactants screened. EHDABr is a member of the family of quaternary ammonium compounds, which are useful disinfectants, fabric softeners, and ore flotation compounds (29). Quaternary ammonium compounds exhibit a high density positive surface charge and adsorb upon oppositely charged surfaces. They are thought to kill bacteria by altering their cell membrane properties and have been found to agglomerate bacterial cells. As ore flotation compounds they react with a conditioning agent adsorbed upon mineral particles. The resulting mixed film envelopes air bubbles and allows the mineral to float to the surface for collection. Quaternary ammonium compounds also adsorb upon fabrics and are durable fabric softeners. The softening action of the surfactant is attributed to the aliphatic portion of the molecule, which reduces friction between the individual cloth fibers. The charge of these compounds also makes them useful as binders for noncharged surfactants.

Foam Flotation

The process of foam flotation carried out in this study is a specific type of adsorptive bubble separation. All adsorptive bubble separation techniques are based upon surface active characteristics of compounds. Molecular, colloidal or larger materials are separated from solution by becoming selectively adsorbed upon rising bubbles. The substance removed, called a colligend, may be naturally surface active or made so by its reaction with a suitable surface active compound, called a collector. The collector may also produce a supporting foam for the collected material or foaming may be induced by an additional surface active compound.

Nomenclature - Figure 1 shows the accepted scheme of classification of adsorptive bubble separation techniques compiled by Karger, Grieves and Lemlich (30). This characterization is a compromise between rational systemization and actual definition usage and may include overlapping terms. As indicated, bubble separation may be carried out with or without foam. Bubble fractionation, for example, is the transfer of material from liquid to its surface by adsorption upon rising bubbles. Solvent sublation is the transfer of material from the bulk liquid to a solvent.

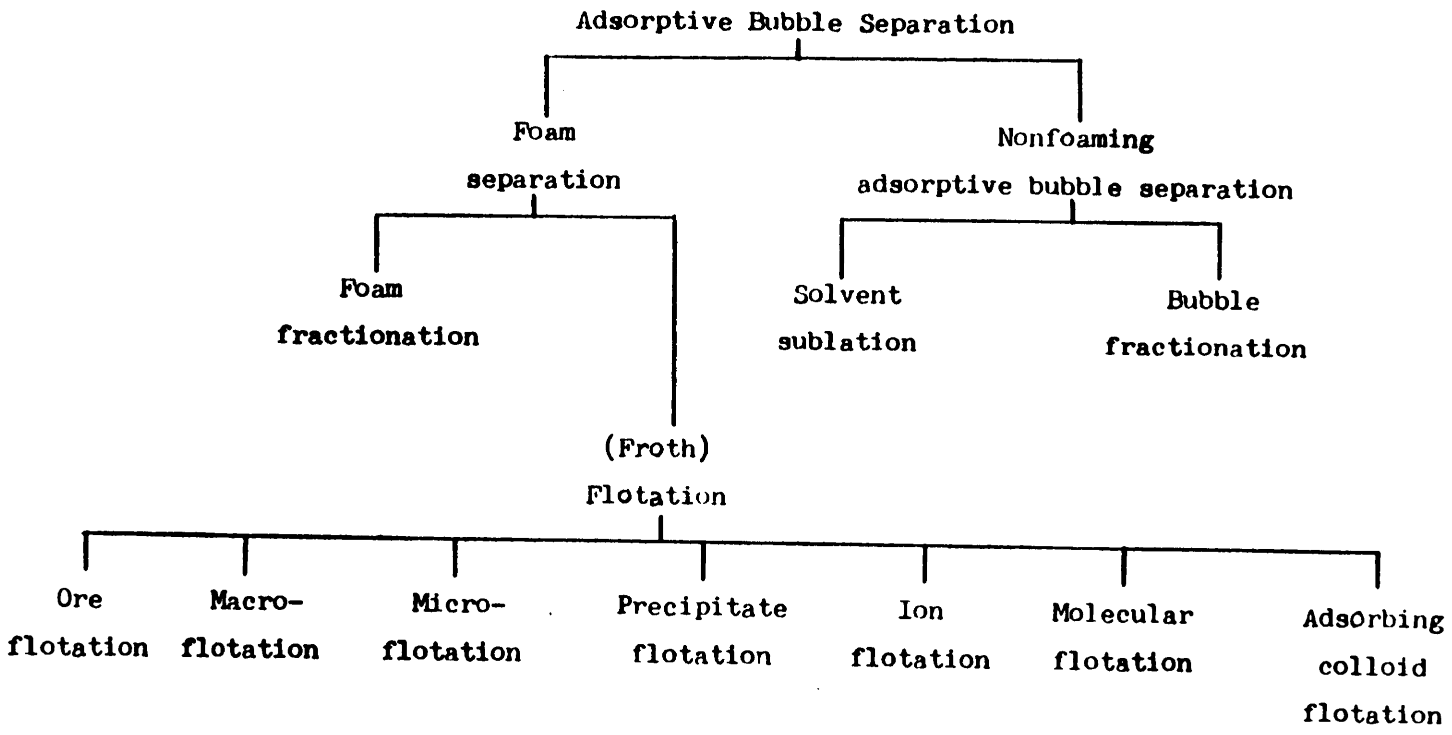


Figure 1. Nomenclature of Adsorptive Bubble Separation Techniques (30)

The larger division is divided into Foam Fractionation, a method of separating compounds by their foaming character, and froth flotation methods. Froth flotation methods are diverse in operation and may apply to the separation of specific compounds. Ore flotation, for example, is the separation of minerals from suspended impurities. This process relies upon the adsorptivity of fine-grained, mineral particles upon a collector. Macroflotation applies to the removal by foam of relatively large particles such as flocs and mineral aggregates. Microflotation describes the flotation of microscopic materials such as colloids and bacteria.

Precipitate Flotation involves the removal of a formed precipitate. The precipitate may result from reaction with a specific additive or may come about from reaction with the collector. Ion and Molecular Flotation processes are names given to the separation of surface inactive ions by reaction with a collector. The resulting hydrophobic material is usually an insoluble product. Adsorbing colloid flotation is the separation of a solute by its adsorption upon a colloid. The complexed result is then rendered floatable by reaction with a collector.

<u>Ion Flotation</u> - Lemlich (31) suggested flotation processes generally occur by the mechanism of Ion or Precipitate flotation. Ion flotation, as described by

Pinfold (32) is based upon reaction of dissolved materials with a collector. The chemical reaction occurring produces a hydrophobic molecule that will adsorb upon rising bubbles. Ion flotation occurs in dilute solutions of colligend and generally requires small foam volume. Because the collector/colligend reaction is a chemical one, stoichiometric amounts of collector are required for removal of ions. Slightly greater amounts of collector are needed if the collector is both reactant and foaming agent. If the colligend concentration is such that precipitation occurs upon collector addition, the method of separation changes to that of precipitate flotation and the dynamics of ion flotation no longer apply to the removal system.

Precipitate Flotation - Pinfold (33) described Precipitate flotation occurring as the result of : 1) a formed precipitate adsorbing upon a collector, 2) the reaction of hydrophilic ions into a hydrophobic result, or 3) hydrophilic ions precipitating in reaction with the collector.

An existing precipitate becomes attracted to bubbles when collector molecules are adsorbed upon it and change the surface character of the precipitate. There is generally a low collector/colligend ratio in precipitate flotation because the reaction between components is one of physical entrapment of the colligend by the collector. Free collector must exist in the system if it is to provide foaming activity.

Formation of an insoluble precipitate from soluble ion reaction may result in a floatable aggregation. In this separation method the collector functions primarily as a foaming agent and the precipitate adsorbs upon bubbles because of its own hydrophobic character. Precipitates exhibiting floating behavior by adsorption upon bubbles are themselves thought to contain polar and nonpolar portions.

Because precipitation floatation comes about as the result of a relatively high colligend concentration, the amount of foam required for good removal is large. Provisions are made in precipitate flotation systems to accommodate high foam volume and the collector employed must produce a stable, supporting foam (33).

Batch Flotation Design and Operation

Foam flotation operations are carried out in column configurations and may function as batch or continuous processes (31, 34). Batch operation is the most basic method and is achieved by introducing air bubbles through a special sparger into a liquid pool in the column. Foam produced at the surface of the pool rises in the column and is removed at a specific height. A stage of batch operation is completed when foaming no longer occurs. Collector and colligend concentration influence foaming time and volume of foam produced. Collected foam is collapsed before further treatment and is called foamate.

Optimal batch operation depends upon sufficient pool mixing, correct collector/colligend ratio, correct sparger submergence (pool depth), and foam removal at the proper height (35). Foam height and stability must be such that maximum draining of foam occurs before coalescence results in colligend return to the pool. Final concentration of colligend in the foamate depends upon the air flow rate, which must be controlled to not remove the collector before it has reacted with the colligend.

Continuous Flow Flotation Design

A column operating in a continuous flow mode is similar in configuration to a batch operation column, with some additions (34). These include influent and effluent ports and may include provisions for refluxing foamate from the collapsing apparatus. Influent ports may occur in the solution pool, at the liquid/foam interface, or along the height of the foam column. Effluent ports are generally placed at the bottom of the pool. Reflux of foamate for enrichment of the rising foam is carried out by introducing foamate through a port just below the foam removal opening. The optimal location of any of thee ports in a specific system depends upon factors specific to the reactants and the type of foam resulting, and the degree of separation desired.

Successful design of a continuous flow system also depends upon control of pool depth, sparger type, air flow rate, column height, and foam collection and collapsing (35). These factors play an important role in maximizing colligend concentration in the foamate with minimal collector application.

<u>Sparger Type, Pool Depth, Air Flow</u> - Sparger type, pool depth, and air flow variations control the contact time of the collector and colligend. Sparger type, for example, influences the size and shape of bubbles. Spargers producing small, uniformly sized bubbles are generally preferred in flotation operations. Small bubbles provide good adsorptive surface area because of their large surface to volume ratio. They rise slowly in liquid and extend adsorptive surface residence time. Small bubbles also promote the formation of stable foam. Pool depth must also set to maximize bubble residence and ensure proper mixing. Too deep pool depths may result, however, in bubbles shearing as they gain velocity in rising.

The rate at which air is introduced into the column will also influence bubble contact time. In addition, air flow rate will determine pool mixing and liquid content of foam. In general, a high air flow rate increases throughput of the column and tends to produce a wet foam (35, 36).

Thus, best removal of colligend usually occurs with small bubbles applied at a low air flow rate. Dryer foam develops in this way and bubbles are subjected to less shear from turbulence. Low air flow rates also result in lower foam volume production, reducing the need for large collection columns.

Column Height - The height of the foam column controls the extent of draining of the foam as it rises (34, 35). The rising foam must be allowed to drain sufficiently to increase colligend concentration and reduce liquid carryover, but must be collected before coalescence occurs. The application of foamate as reflux generally requires a higher foam column than a system operating without reflux. Columns should be designed for foam removal at different heights to allow for determination of optimal foam removal height.

Foam Collapsing - Foam collected from the column may be collapsed by heat or chemical antifoaming agents, if no undesirable changes result (35). Unstable foams may be broken by the impact of foam running back against itself. Stable foams may be collapsed by rotating paddles or by ultrasound. The rate of foam removal and collapse may be controlled somewhat by the size of the removal port.

Continuous Flow Operation

Successful operation of a continuous-flow, foam flotation system depends upon the control of variables influencing column performance. These include the effects of: collector/colligend ratio, the nature of the collector, mixing and contact time of reactants, pH, ionic strength and temperature of solution, and method of column monitoring during operation. (32 - 35)

Collector/Colligend Ratio - The collector/colligend ratio providing the best separation of colligend depends upon the nature of the collector/colligend reaction, the colligend concentration, and the behavior of the collector in solution. Ion flotation requires slightly greater than stoichiometric amounts of collector for a given colligend concentration. Collector concentration below this amount will reduce colligend separation by foam instability resulting from low free collector concentration. Under conditions of precipitate flotation, enough collector must be present to promote hydrophobicity of the precipitate and produce foam. Insufficient collector concentration may result in reduced precipitate and reaction and reduction of foaming.

Collector concentration in excess of that required for optimal removal may reduce separation efficiency. When colligend is present as an ion, excess collector may envelop the ion and eliminate adsorptive sites for bubbles. When micelles result from excess collector concentration, ions may adsorb upon or in the micelles. Separation is reduced because micelles are hydrophilic and will not attach to bubbles.

Excess collector concentration may reduce separation in precipitation flotation systems by forming double layers upon precipitate particles. The precipitate particle is thus rendered hydrophilic and will not float on bubbles. Excess collector may also compete with colligend particles for adsorptive sites on bubbles.

Excessively low colligend concentration may reduce efficiency of separation by resulting in reduced collector concentration. If the amount of collector present is insufficient to promote foaming, flotation will be incomplete. The addition of extra collector may result in separation at the expense of collector wasting. If colligend concentration is high enough to result in precipitation, the separation mode of the flotation system may be altered from its original design.

<u>The Nature of the Collector</u> - The nature and behavior of the collector in solution may also determine the collector/colligend ratio. The unique reactivity of a collector with the colligend and other components of the

reaction solution will determine the amount of free collector present for foam production after reactions have occurred. In addition, specific collectors may be required to produce expected results in mixed solutions, where the properties of the collector may be altered by reaction with impurities.

Mixing and Contact Time - The rate and location of influent introduction into the flotation system influences mixing and may determine reaction time. Depending upon the nature of the collector/colligend reaction, separation efficiency may depend upon addition of influent to the pool, the interface, or the foam itself. Experimentation may be required to arrive at the influent addition method providing best mixing for the reactants in question.

Flow rate of the influent will also control residence time of the treated solution. Adjustment may be needed to achieve proper contact time for the collector and colligend. Precipitate flotation may be enhanced by allowed time for the formation of large, stable aggregates which float more readily than small particles.

Ionic Strength and pH Variation - The pH and related ionic strength of the reactant solution may greatly influence collector/colligend reaction, free collector concentration, and stability of the reactants. The effects of pH changes upon separation performance may be summarized as follows: 1) hydrolysis of the ions to be separated may be altered, changing their reactivity with the collector; 2) change of collector ionization may alter its mode or capacity of adsorption or reactions; 3) precipitation rates of ions may change and alter the dynamics of removal; 4) changes may occur in the ionic character of other ions and resulting in ionic strength changes of solution; and 5) foam stability may be changed.

The ionic character of the colligend solution may influence collector activity (37). Ions charged oppositely to the collector may compete with colligend for adsorption or reaction with the collector. Ions in solution may also react with the colligend and alter its adsorptive behavior. The charge and size of ionic species may determine the extent of reaction with the collector or colligend and experimentation may be required to find collectors for optimal separation in mixed ionic solutions.

Temperature Effects - Temperature changes may alter the rate of adsorption of reactants and may cause changes in foam stability. Because adsorption is an exothermic reaction, excessively high temperatures may reduce adsorption rates. Increase in temperature also reduces foam stability by disrupting the foam structure and changing the concentration of free collector in solution.

System Monitoring - A method of monitoring an operating continuous-flow system must be carried out that is suitable for the material separated and the type of separation occurring. In general, the withdrawal and analysis of samples from an operating system provide information about the extent of colligend separation and when it occurs. Analysis of flow rates of the system may be carried out by measurement of effluent and foamate flow.

Uses and Advantages of Foam Flotation Systems

Foam flotation processes have been successfully carried out for trace metal separation and analysis, mineral and chemical purification, wastewater detoxification, radioactive isotope separation, bacteria separation, and has been tested for replacing primary settling of municiple and industrial wastewater (31 - 35).

Foam flotation systems are compact in size, often easily fitted into existing treatment systems, and efficient in operation. They produce a highly concentrated waste and generally function at a high rate. They are easily modified for changing effluent and promote aeration of wastewater. When used in place of coagulation methods, foam flotation systems require less equipment and reduce sludge volume.

EHDABr Flotation Studies

Grieves and Bhattacharya (38) used a batch flotation system to separate cyanide ions complexed with ferric sulfate. They found good mixing of reactants enhanced flotation. Excessive mixing, however, caused the formation of stabilizing double layers upon ion complexes and reduced separation. Variation of pH altered ion characteristics and changed flotation behavior of ions. Chloride and sulfate ions were found to inhibit complexed cyanide separation by competing for adsorption with the collector. Foam quantity and stability increased with increasing free collector concentration.

Grieves and Wilson (39) used EHDABr to separate dichromate ions from an acid solution. EHDABr reacted immediately with dichromate ions to form an insoluble precipitate. Eighty five percent of the dichromate ions were removed with stoichiometric amounts of EHDABr and slightly more collector was needed to sustain foaming. Temperature variation, gas flow, and bubble size variation effected flotation performance. The researchers suggested keeping temperature constant. Precipitate shearing from rising bubbles was reduced by maintaining a low gas flow rate and using a sparger that produced small bubbles.

Devivo and Karger (34) used EHDABr to float colloidal kaolin. They varied pH, collector/colligend ratio to influence adsorptive capacity of the system. Variation of pH was found to alter the charge characteristics of colloidal particles. Small bubbles enhanced flotation by reducing breakup of the EHDA-Br/kaolin complex.

Grieves and Choinard (34) floated phenol adsorbed upon powdered activated carbon with EHDABr. They found pH variation improved phenol adsorption and overdosing of collector reduced flotation by stabilizing carbon particles.

EHDABr was used by Bretz (40) to float certain strains of bacteria. EHDABr adsorbed upon the surface of the cells or reacted with cell membranes to render the bacteria hydrophobic. Foam character depended upon free EHDABr concentration. Changes in pH altered reactivity of the collector with bacteria cell walls in an unknown way and resulted in flotation changes.

Grieves, Walkowiak, and Bhattacharya (41) studied the selectivity of EHDABr and other quaternary ammonium compounds for anions in solution (34). They concluded that quaternary ammonium surfactants were useful for separating mixed ion solutions. The extent of selectivity was influenced by anion's charge structure and degree of hydration. In general, the least hydrated anion in a mixture was preferentially floated for anions of like charge. For anions of differing charge intensity, lower charged species floated preferentially.

Boardman and Bishop (42) removed 100% of suspended, powdered activated carbon with EHDABr in a continuous flow foam flotation system. They determined that effluent EHDABr concentration was controlled by the loading rate of the influent and by influent EHDABr concentration.

Kraft Wastewater Flotation

Ng *et al*. (43) found naturally occurring surfactants in Kraft Production wastewater could be floated as a foam. Kraft wastewater was subjected to dispersed air in a continuous-flow system. Fatty acids and resin acids in the wastewater produced a thin foam that was removed, collapsed, and treated by aeration. The system functioned as a 25 million gallon per day pilot plant. The system reduced toxicity and odor of the wastewater. Adjustment of wastewater pH affected performance of the system by altering foaming behavior of the fatty acids and resin acids.

METHODS AND MATERIALS

Parameters Studied and Their Measurement

The following methods of analysis were carried out upon the untreated and treated wastewater to establish the efficiency of the treatment applied.

Color - Color analysis was carried out by the method standardized by the National Council of Air and Stream Improvement of the pulp and paper industry (43). The method relies upon the comparison of wastewater color to a Platinum-Cobalt (Pt-Co) color standard (#500 APHA, Fisher Scientific, Fairlawn, NJ).

A Pt-Co standard curve was developed for light absorbance at 465 nanometers, and a solution pH of 7.6. Experimental samples were vacuum filtered through a 0.8 um filter and adjusted to pH 7.6. Absorbance readings were obtained for the samples and compared to a standard curve. Color levels for the samples were recorded as Pt-Co units (PCU). Absorbance measurements were made with a Beckman DU-6 Spectrophotometer (Irvine, CA).

Total Organic Carbon - Total Organic Carbon measurements for the wastewater and EHDABr solutions were made with a Dohrmann, DC-80, Carbon Analyzer (Santa Clara, CA). A 15 milliliter (mL) sample was acidified with H_3PO_4 and purged with oxygen for 10 minutes. A 200 microliter (uL) portion of a stirred sample was transferred to the

Carbon Analyzer for analysis. TOC levels were obtained as milligrams per liter (mg/L).

Total Suspended Solids - Total suspended solids measurements were made as described in Standard Methods for the Examination of Water and Wastewater (44). A sample volume of 25 mls was vacuum filtered through an 0.8 um filter. Samples were analyzed in triplicate and results were recorded as an average of the values obtained. Total suspended solids levels were recorded as mg/L.

Ethylhexadecyldimethylammoniumbromide (EHDABr) -

Measurement of EHDABr levels were made with a surfactant analysis method developed by Cullum and described by Boardman (41). The method involved titration of a charged surfactant with a surfactant of opposite charge. A solution of sodium dodecyl sulfate (SDS) was used to titrate EHDABr.

The analysis was carried out by Cullum as follows. Solutions of SDS and EHDABr of equal normality were made. A 25 mL sample of EHDABr solution was put in a 300 ml stoppered bottle and acidified with 1 mL N HCl. To this was added 1 mL of methylene blue solution (0.0004% in water), 25 mLs of pure water, and 50 mLs chloroform. Titration with SDS was made with vigorous agitation of the mixture following each SDS addition. Titration was completed when the methylene blue color migrated from the top aqueous layer to the chloroform layer. EHDABr concentration was determined from the relationship:

(normality of SDS) (mLs titrated) =

(normality of EHDABr) (sample volume, mLs).

The analysis was modified because the colored wastewater obscured the disappearance of blue color from the aqueous layer. The possibility that a titration end point could be established by the appearance of color in the chloroform layer was investigated.

A standard addition was made with the appearance of methylene blue color in the chloroform layer as the titration endpoint. The standard addition method was described in Instrumental Methods of Analysis (45). The standard curve (Appendix A) used to demonstrate the accuracy of the modified titration method was used to determine EHDABr levels in experimental samples.

General Experimentation Approach

Polymers were screened for their ability to coagulate color in the wastewater. A group of polymers exhibiting color removal ability was further evaluated by jar tests. The effects of Ph variation and PAC addition upon the performance of the polymers were evaluated by jar tests. Polymer dose for the evaluation of the effects of pH or PAC upon polymer performance was that used in jar tests with polymers alone. A pH promoting good color removal was chosen for each polymer. Color removal performance for each polymer at the chosen pH was then evaluated by jar test.

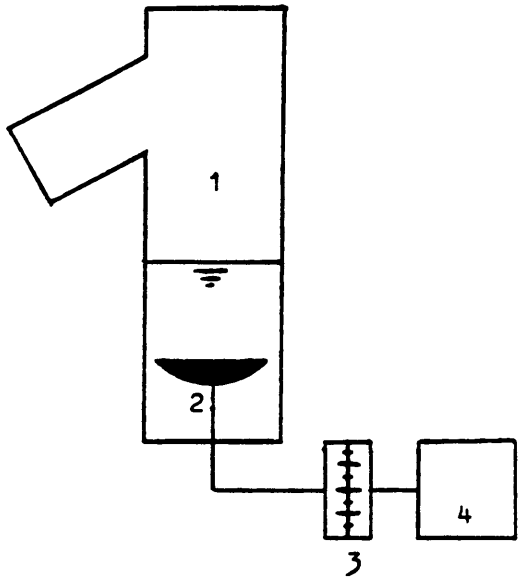
Surfactants were screened for foaming ability in the wastewater. The foam producing ability of EHDABr was verified by screening. The color removal performance of EHDABr was then evaluated by jar test. The effects of pH variation and PAC addition upon EHDABr performance were evaluated by jar tests and batch flotation. EHDABr dose for the evaluation of the effects of pH or PAC upon EHDABr performance was less than that used in jar tests with EHDABr alone. A pH point promoting good color removal was chosen. Color removal performance at the chosen pH was then evaluated by jar test.

EHDABr was used in a continuous-flow, foam flotation system to treat the wastewater. The results of jar tests were used to establish EHDABr doses in the flotation system. Flotation trials with varying EHDABr dose and varying detention time were made. Performance of the system was evaluated by color, TOC, SS, and EHDABr removal ability. Trials for each EHDABr dose and detention time were repeated once. The trial thought to give best column performance was repeated three times.

Experimental Materials Screening

Polymer Screening - Stock solutions were made from concentrated polymers according to manufacturers' instructions. Wastewater samples of 200 mL were treated with a range of 50 to 300 mg/L of the polymers. Polymers were mixed with the wastewater by one half minute of vigorous agitation. The mixture was then slow-mixed for 30 minutes and allowed to settle. Color analysis of the sample was then made and floc settling behavior observed. Polymers exhibiting coagulating behavior and color removal ability were further evaluated by jar tests.

<u>Surfactant Screening</u> - Stock solutions were made from concentrated surfactants according to manufacturers' instructions. One liter (L) samples of wastewater were treated with a range of 50 to 300 mg/L surfactants. The mixture was added to a glass flotation column. The column was 40 cm tall with a diameter of 6.5 cm. Air flow was maintained at 1500 cm^3/min. Air entered the column through a PTM, 3 micron, grade H, stainless steel sparger (Cortland NY). A representation of the column is shown in Figure 2. Foaming character of the mixture was observed. Collected foam was allowed to collapse and analyzed for color concentration. Surfactants were chosen for further study by their ability to produce a stable foam that supported color flotation. The following compounds were screened: sodium dodecyl sulfate; EHDABr; and Tretolite surfactants AR-18, AR-20, AR-21, AR-25, AR-27, ATF-7, AW-4, EWS-270, EWS-271, and J-118.



1. Column
2. Sparger
3. Rotameter
4. Compressed Air

Figure 2. Surfactant Screening and Batch Flotation Column

Color Removal by Coagulation

Jar Tests - A stock solution of polymer or EHDABr was made. A 500 ml sample of wastewater was added to each of six square-bottomed, 1 L jars. The jars were placed under a multiple stir apparatus and stirred at 100 rpm. Polymer or EHDABr was introduced from the stock solution. Dosages ranged from 50 to 300 mg/L for each jar test performed. High rate mixing continued for 3 minutes after polymer or EHDABr addition. Slow mixing followed at 20 rpm for 30 minutes. Samples were settled for 1 hour before being analyzed for color.

Adjustment of pH - Adjustment of pH was made with 0.1 N sulfuric acid or 0.1 N sodium hydroxide. A Fisher, Model 610, pH meter and probe (Fairlawn, NJ) were used to obtain pH readings.

Coagulation pH Variation - A 500 mL sample of wastewater was added to each of 6 jar test jars. A change in pH was made in each of the jars. The range in pH of the jars was 3 to 9. Jar test procedures were then carried out as described above with polymer or EHDABr. Color analyses were performed following each jar test.

PAC Addition - A stock solution of Watercarb Plus PAC (Husky Industries, Dunnellon, FL) was prepared. Wastewater samples in jar test jars were stirred at 100 rpm. PAC was added to the jars from the stock solution. The dosage of

PAC ranged from 50 to 200 mg/L in each jar test. The jars were rapidly mixed for 3 minutes. A dose of Polymer or EHDA/Br was then added to the jars and the jar test proceeded as described earlier. As before, color analyses were performed at the completion of the jar tests.

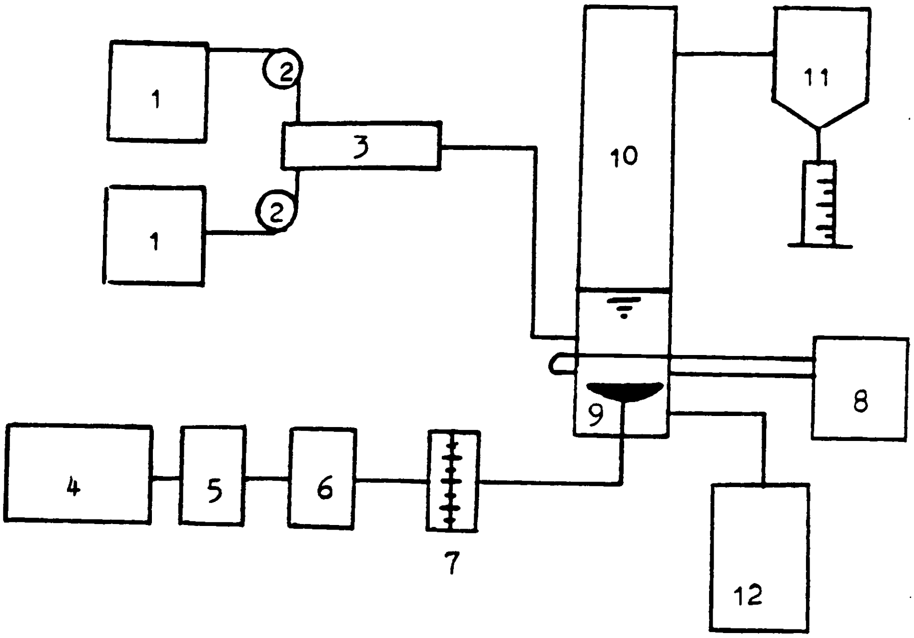
Batch Flotation Color Removal

Wastewater samples that underwent jar tests for EHDABr pH optimization, and EHDABr/PAC treatment were treated by batch flotation. Wastewater samples were added one at a time to the column shown in Figure 2. Each sample was aerated until foaming no longer occurred. The liquid remaining in the column was analyzed for color.

Continuous-flow, Foam Flotation

Flotation Column Design - An adaptation was made of the continuous-flow, foam flotation system designed by Boardman (41) for conducting this study. A diagram of the column system appears in Figure 3. The numbers in the following description correspond to those used in the figure.

The following components made up the flotation system: 1) the EHDABr stock solution and wastewater were held in separate 20 liter containers; 2) positive displacement, pumps, Model 374 (Colmar, PA), delivered the surfactant and the wastewater; 3) a 3 cm diameter glass tube accepted the pumped reactants and allowed them to mix; 4) an air compressor delivered compressed air; 5) air was cleaned of



1. Reactant Containers
2. Pumps
3. Mixing Chamber
4. Compressed Air
5. Hydrator
6. Air Filter
7. Rotameter
8. Water Jacket
9. Sparger
10. Column
11. Foam Breaker
12. Effluent Tank

Figure 3. Continuous-flow, Foam Flotation Column

particulates in a cotton trap; 6) air was hydrated in a water trap; 7) a rotameter controlled air flow into the column; 8) column temperature was maintained by a waterfilled tube connected to a water bath; 9) a PTM sparger (grade H, Cortland, NY) produced bubbles from the air flow; 10) a 68 cm by 6.5 cm cylindrical column supported the reactant pool and rising foam, 11) a spinning paddle inside a closed funnel collapsed foam from the top of the column, and 12) a 20 liter container collected effluent from below the column sparger. A collection vessel was provided for collapsed foam below the foam breaking unit. Ports for collection of samples were located in the wastewater feed line, the mixed reactants feed line, and the effluent line.

Continuous-flow, Flotation Operation - Air flow into the column was maintained at 1500 cm^3/min in all flotation trials. Column temperature was maintained at 25° C throughout the study.

Column EHDABr concentration and detention time were controlled by adjustment of EHDABr flow from the stock solution and adjustment of the wastewater flow. Flow rates were monitored at the beginning and end of the operation interval.

Column operation continued for 30 minutes before the sampling interval was initiated. Samples were obtained from the wastewater inflow, the combined wastewater and EHDABr inflow, and the effluent flow throughout the sampling time. Analyses for color, TOC, SS, and EHDABr residual were performed.

Effluent and foamate were collected throughout the sampling interval and their volumes were recorded. Observation of column operation continued throughout the trial.

RESULTS AND DISCUSSION

This chapter will present the results of experiments using polymers to remove color followed by the results of EHDABr treatments. Discussion of all results will immediately follow their presentation.

Polymer Treatment

Polymer Screening - Some of the cationic polymers screened produced measurable color removal. None of the nonionic or anionic polymers screened produced measurable color removal. Positively charged polymers appeared to react with negatively charged color producing lignin particles, as supported by Singley's (22) theory of polymer behavior. The cationic polymers, Nalco 7107, Tretolite J-118, Betz 1190, and Magnifloc 581-C were chosen to complete the polymer study. Their choice was based upon the results of the screening trial.

Color Removal With Polymers - The results of color coagulation by cationic polymers in jar tests appear in Figure 4. The untreated wastewater was at pH 6.3 and had a color concentration of 2430 PCU. Figure 4 shows that increasing polymer doses caused increasing color removal for all polymers tested. Color removal did not increase, however, beyond a specific dosage of all polymers tested. The Nalco polymer, for example, produced its lowest color

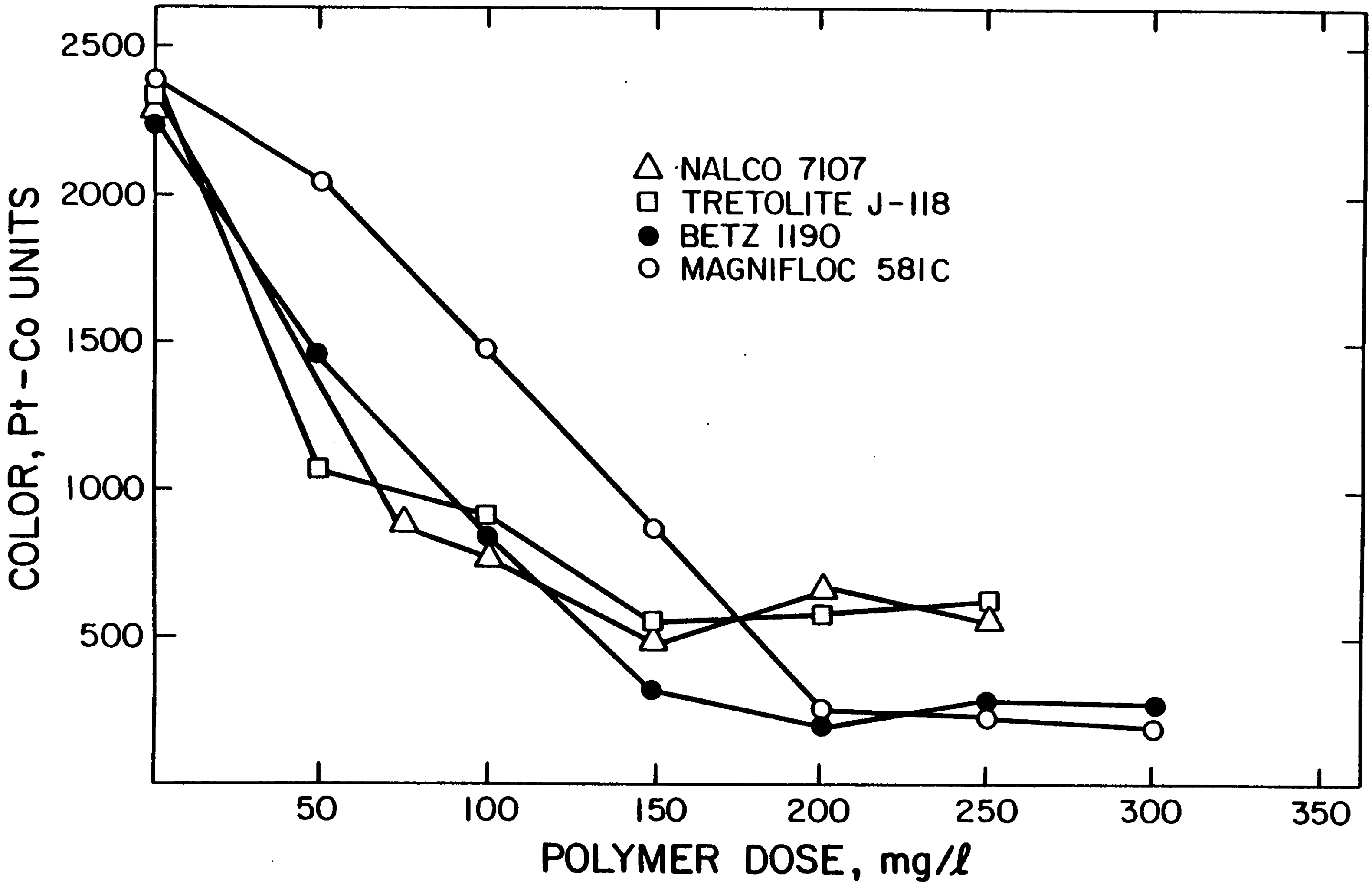


Figure 4. Color Residuals After Coagulation and Settling with Cationic Polymers at pH 6.3

level of 546 PCU at a 150 mg/L dose. Dosages of 200 and 250 mg/L of the Nalco polymer resulted in color levels of 660 PCU and 574 PCU, respectively.

The Tretolite polymer produced its lowest color level at 500 PCU at a dose of 150 mg/L. Color levels of 583 PCU and 650 PCU occurred at Tretolite doses of 200 and 250 mg/L, respectively.

The Betz polymer gave a color level of 300 PCU at a 150 mg/L dose. A Betz dose of 200 mg/L resulted in a color level of 210 PCU and further dosage increase to 250 and 300 mg/L resulted in respective color levels of 250 PCU and 240 PCU. A 200 mg/L dose of Magnifloc polymer produced a color level of 240 PCU. Increase of Magnifloc doses to 250 and 300 mg/L resulted in PCU levels of 220 and 210, respectively. A Magnifloc dose of 150 mg/L produced a PCU of 880.

The Betz and Magnifloc polymers gave better color removal than the Nalco and Tretolite polymers. The Betz polymer provided the best color removal of all the polymers at dosages of 150 mg/L, which constituted the best results at the lowest dose for all polymers tested.

The color removal that occurred with polymers was similar to that noted for alum, by McLachlan (6), and with lime, by Dugal et al. (16). The work of these researchers showed that increasing coagulant dose produced increased color removal. They also found that a point was reached where a further coagulant dose increase did not increase color removal. Both studies reported that the residual color remaining after coagulation was comprised of soluble lignin fragments which were not precipitated by the coagulants.

Polymer Color Coagulation and pH - The effect of pH upon color removal with 200 mg/L of the four cationic polymers is shown in Figure 5. Initial wastewater color was 2390 PCU. The Nalco polymer gave a color level of 520 PCU at pH 3.5. Color removal for the Nalco polymer was reduced at pH 6, where it produced a color level of 540 PCU. Further decrease of color removal performance occurred as pH increased to 8, where the Nalco polymer gave a color level of 600 PCU. The Tretolite polymer showed a color increase of 500 to 620 PCU between pH 3.5 and 5, and a color increase of 622 to 992 PCU between pH 6 and 9. The Magnifloc polymer gave a color level of 610 PCU at pH 3.5. Color removal improved to 400 PCU for the Magnifloc at pH 6, and remained stable to pH 9 and 410 PCU. The Betz polymer produced a PCU of 290 at pH 3.5. Color removal levels remained the same for the Betz polymer between pH 3.5 and pH 8 and increased to 340 PCU at pH 9.

The color removal performance of the Betz polymer was least effected by pH variation. The Nalco and Tretolite

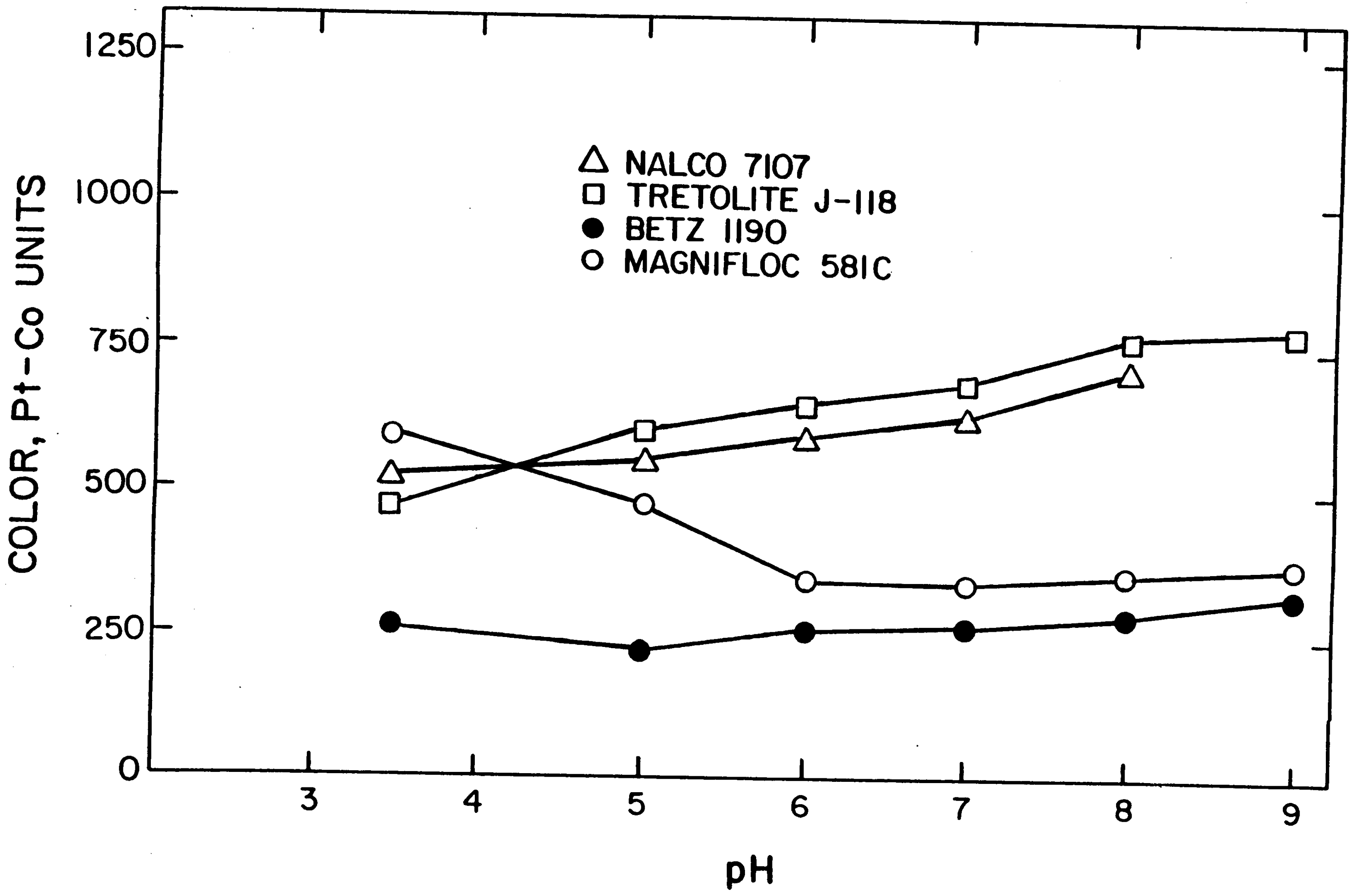


Figure 5. Color Residuals After Coagulation and Settling with Cationic Polymers at Varying pH

polymer showed reduced color removal ability as pH increased from 3.5 to 9. Performance of the Magnifloc polymer improved between pH 3.5 and 6 and remained relatively constant as pH increased to 9.

Color Coagulation at Acidic pH with Polymers - The bleach plant wastewater component of the biotreated wastewater used in this study had a pH range of 2.1 to 4.9. The average color level of the bleach plant wastewater was 2505 PCU. This color level was 64% of the total average color level of the wastewater before biotreatment (Table 1). However, samples of the bleach plant wastewater were not available at the time of this study. The pH of the biotreated wastewater was thus made acidic to simulate the character of the bleach plant wastewater. Wastewater pH was adjusted for each polymer as follows: Nalco, pH 3.5; Tretolite, pH 3.5; Betz, pH 5. Magnifloc performance was best at pH 6 or greater, (Figure 5) so its pH was maintained at 6.3 for this series of jar tests.

The results of polymer coagulation at acidic pH are shown in Figure 6. The untreated wastewater color level was 2500 PCU. All polymers gave decreasing color level with increasing dose. The Nalco produced its lowest color level at 555 PCU at a 250 mg/L dosage. A Tretolite concentration of 250 mg/L produced its lowest color level of 484 PCU. The Betz polymer produced its lowest color level of 240 PCU at a

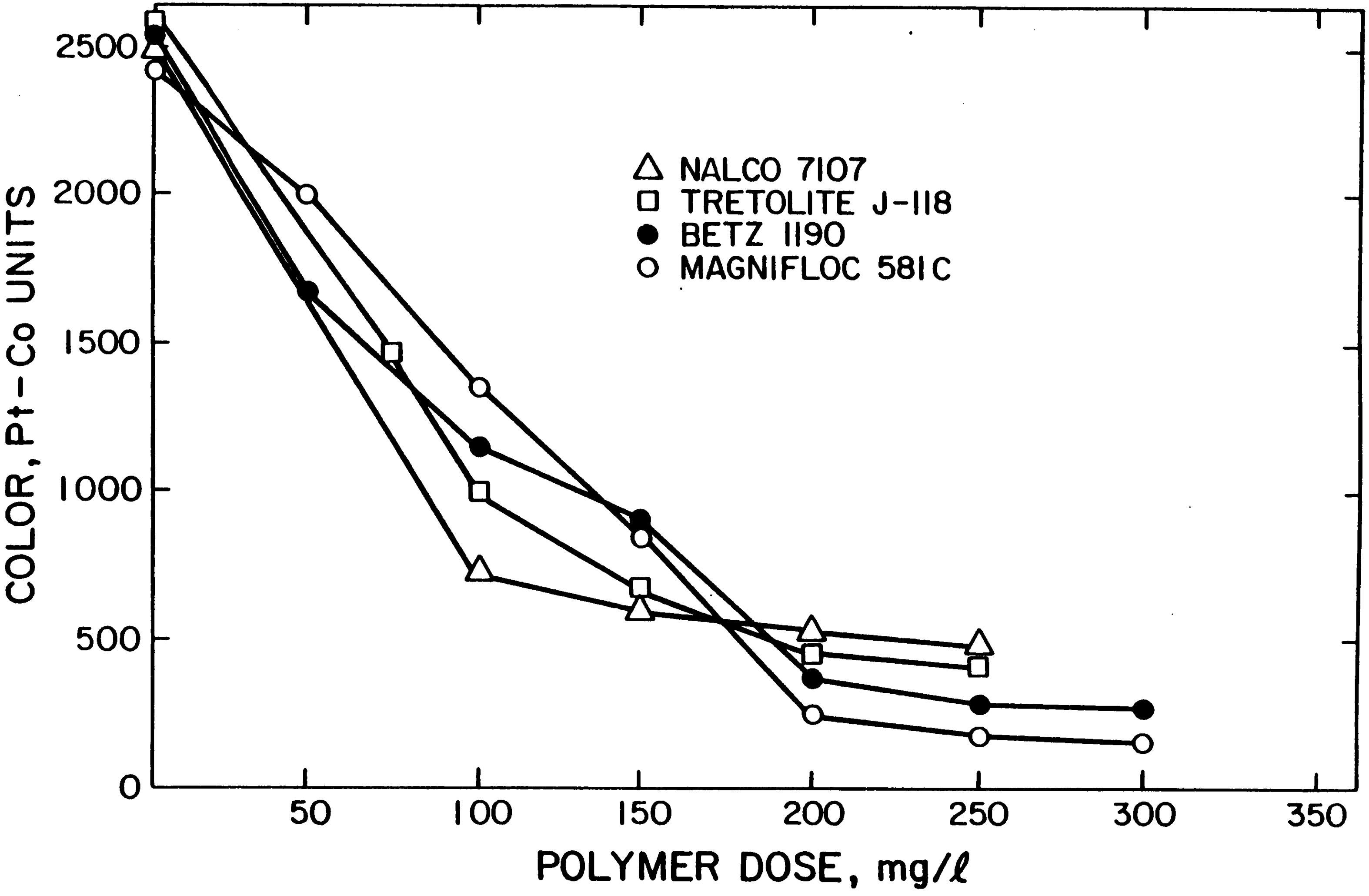


Figure 6. Color Residuals After Coagulation and Settling with Cationic Polymers at Chosen pH

250 mg/L dose. The Magnifloc polymer gave a color level of 243 PCU at a 200 mg/L dose. The lowest color level achieved by the Magnifloc polymer was 202 PCU at a 300 mg/L dose.

These results showed that the performance of the Nalco and Treolite polymers at pH 3.5 did not vary greatly from their performance at pH 6.3. Performance of the Magnifloc polymer was the same in this jar test as in the first test (Figure 4). The color level for 150 mg/L of the Betz polymer was 300 PCU at pH 6.3 and 890 PCU at pH 5. This suggested that the Betz performance was reduced by a pH change of 6.3 to 5. This result appeared to contradict the results of the coagulation of pH analysis (Figure 5), which showed that the Betz performance was not affected by pH changes of 3.5 to 9.

Color Coagulation by PAC and Polymers - The results of PAC additions with 150 mg/l of polymers are presented in Figure 7. Color levels at zero mg/L PAC were taken from Figure 4. This figure showed the results of jartests with varying polymer doses. Wastewater pH was 6.5 and the color level was 2480 PCU. Color levels achieved with 50 mg/L PAC and the polymers were as follows: Nalco, 500 PCU; Tretolite, 600 PCU; Betz, 450 PCU; and Magnifloc, 682 PCU.

Color levels did not decrease when PAC concentration increased from 50 to 100 mg/L. Color levels at 150 mg/L PAC were Nalco, 470 PCU, Tretolite, 510 PCU; Betz, 420 PCU; and

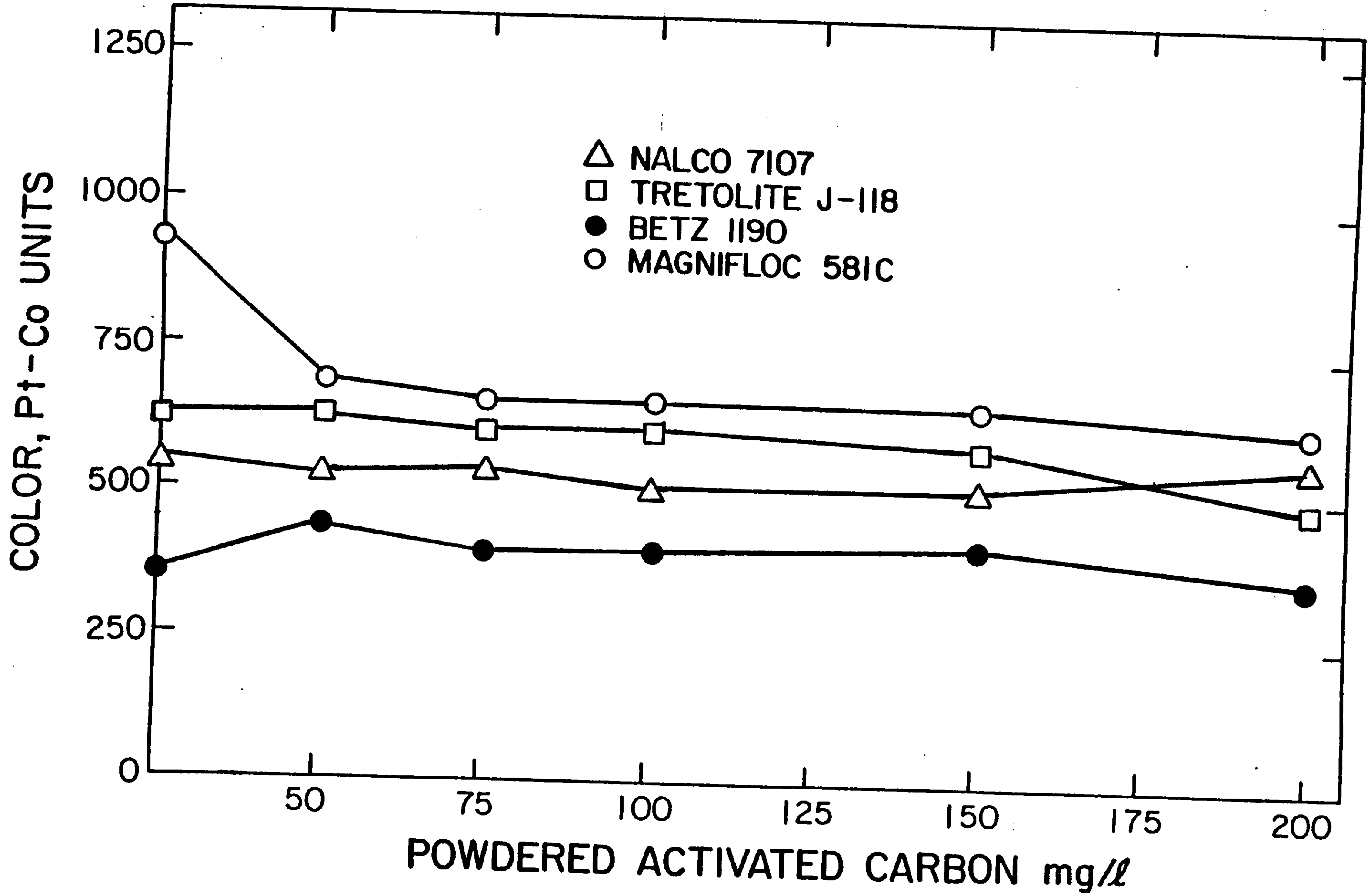


Figure 7. Color Residuals After Coagulation and Settling with PAC and 150 mg/L Cationic Polymers at pH 6.5

Magnifloc, 586 PCU. Color levels did not decrease between PAC increase of 150 to 200 mg/L.

Table 3 summarizes the color levels that resulted from 50 mg/L PAC added to 150 mg/L polymers to performance of 150 mg/L polymers alone. These results showed that a 50 mg/L dose of PAC improved the performance of the Magnifloc performance only. Performance levels of 50 mg/L PAC and polymers did not improve as the PAC dosage was increased to 200 mg/L.

EHDABr Treatment

Surfactant Screening - EHDABr produced a stable foam under the screening conditions. EHDABr also coagulated color bodies when mixed with the wastewater. All other surfactants tested yielded unstable foams and/or no color removal (Surfactant Screening Section in METHODS AND MATERIALS).

Garrett (28) and Schwartz (29) proposed that the surfactant foaming ability may be reduced by the presence of other surfactants or reactive compounds in solution. Ng et al. (43) demonstrated that resin acids in pulp and paper wastewater produced weak foams under aeration. Resin acids may have reacted with the surfactants screened and reduced their foaming ability. The foaming ability may have been further reduced by the reaction of the surfactants with chlorides present in the wastewater.

Table 3. Color Levels From Coagulation and Settling by PAC and Polymers, and Polymers Alone *

Polymer	Color, PCU Polymer & PAC	Polymer Alone
Nalco 7107	500	500
Tretolite J-118	600	546
Betz 1190	450	300
Magnifloc 581C	682	880

* From Figure 4 and Figure 7

It was thought that EHDABr coagulated lignin fragments because of its cationic charge. Grieves et al. (41) showed that EHDABr was attracted to compounds of opposite charge. Grieves et al. (38, 39) also showed that EHDABr will precipitate compounds of opposite charge.

Color Removal by Coagulation and Settling, and Batch Flotation with EHDABr - Figure 8 illustrates the color removal performance of 100 mg/L EHDABr at a pH range of 3 to 9. The color level of the untreated wastewater was 2380 PCU. Color levels at pH 3 from coagulation and settling, and batch flotation were 492 and 462 PCU, respectively. Color removal was constant as the pH was increased from 3 to 8. Color levels at pH 9 after coagulation and settling, and batch flotation were 706 and 500 PCU, respectively.

The performance of EHDABr was not greatly affected by pH changes in the range from 3 to 9. The amount of color removed by batch flotation was the same as that removed by coagulation and settling.

The results of EHDABr coagulation at pH 5 and pH 6.3 appear in Figures 9. Initial wastewater color level was 2077 PCU. Best color removal was achieved at an EHDABr dose of 100 mg/L. Color levels for this dose at pH 5 and 6.3 were 459 and 480 PCU, respectively. Increased color removal did not occur as EHDABr dose was increased from 100 to 250 mg/L.

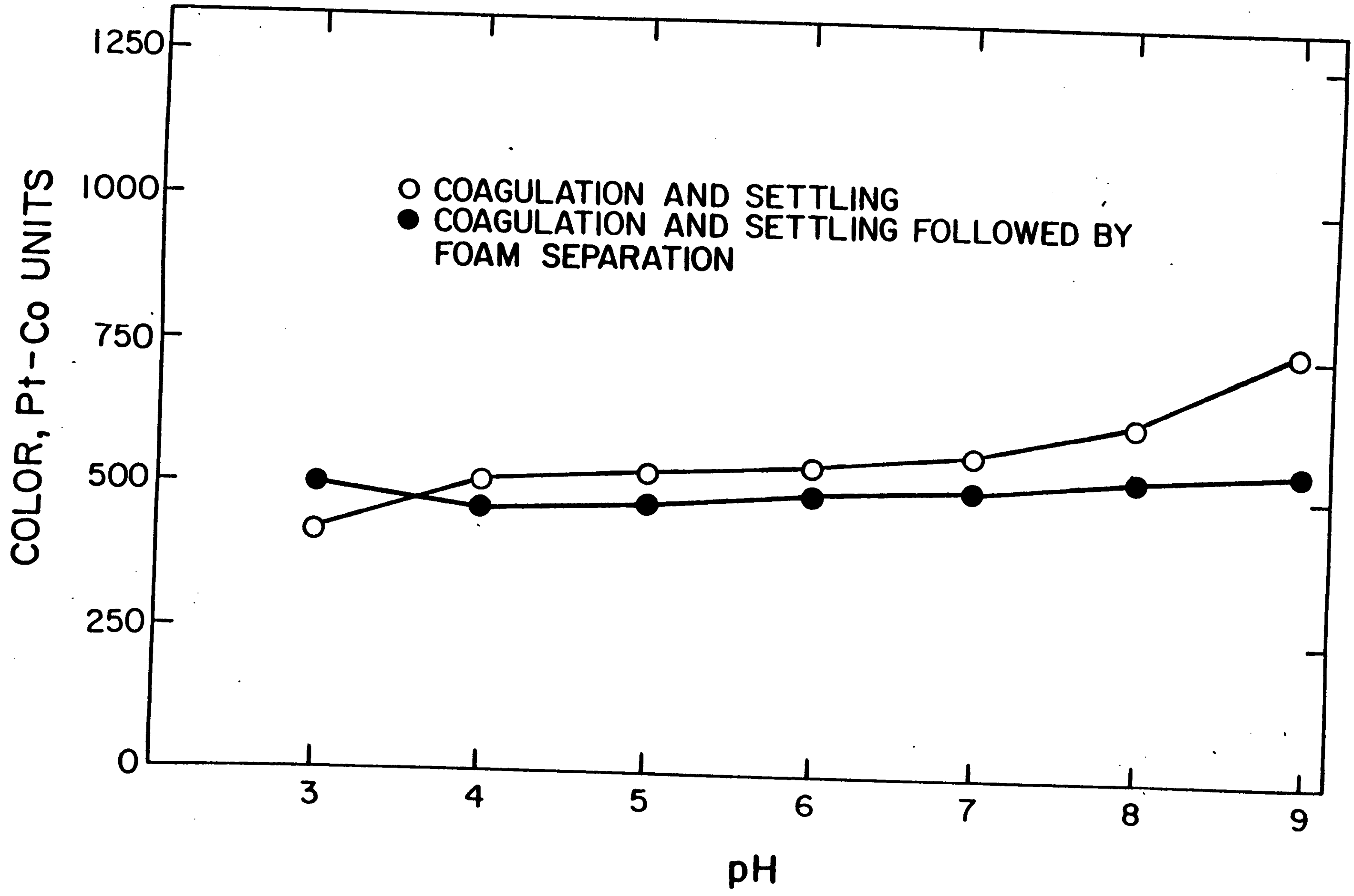


Figure 8. Color Residuals After Coagulation and Settling, and Batch Flotation with EHDABr at Varying pH

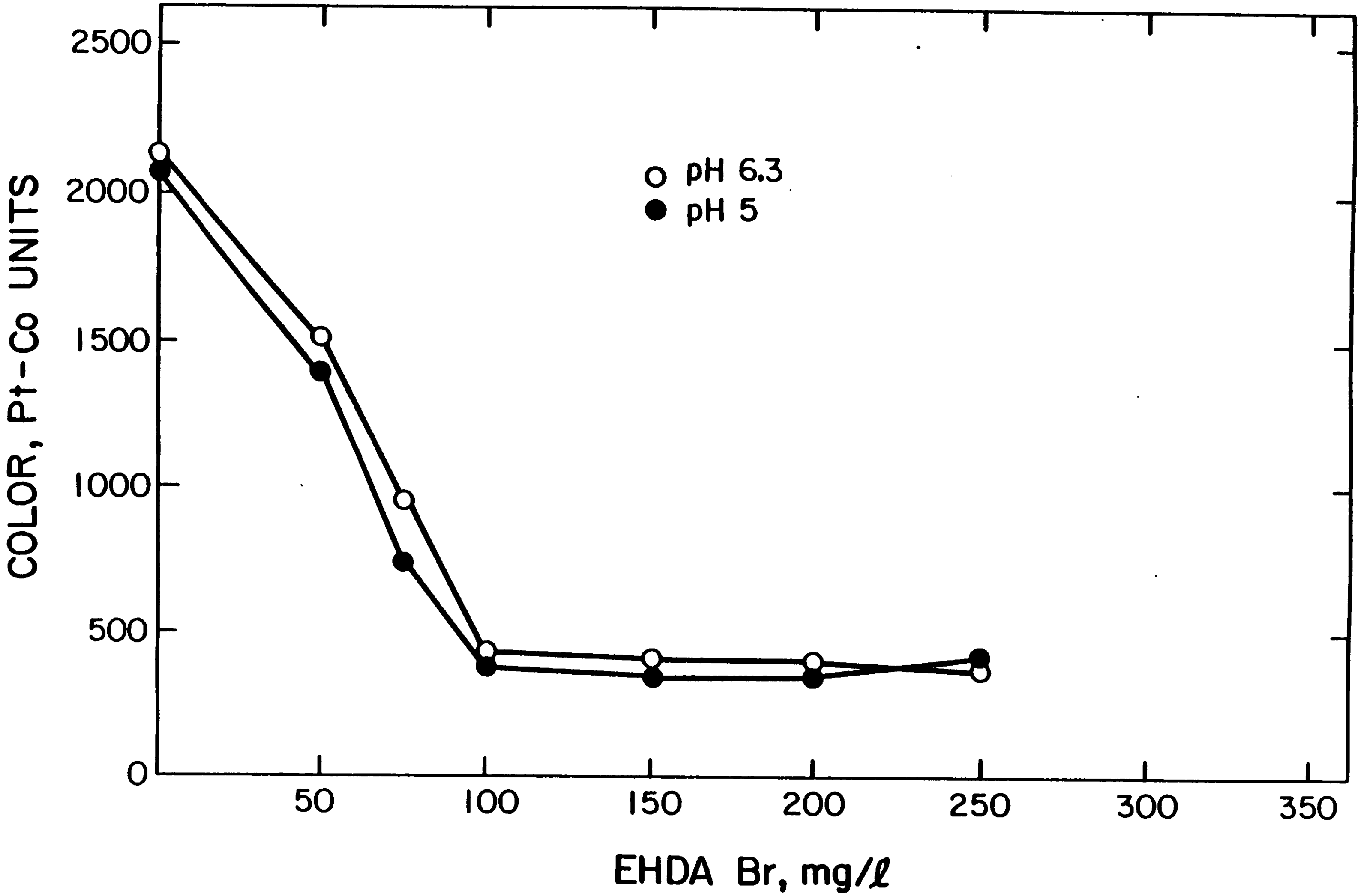


Figure 9. Color Residuals After Coagulation and Settling with EHDABr at pH 5 and pH 6.3

The results in Figure 9 support the results that showed EHDABr performance is not greatly affected by pH change (Figure 8). EHDABr at 100 mg/L removed 77% of the wastewater color at pH 6.3.

Coagulation and Settling, and Batch Flotation by EHDABr and PAC - The results of using 80 mg/L EHDABr and varying PAC doses appear in Figure 10. The color level shown at zero mg/L PAC originated from the jartest results shown in Figure 9 at pH 6.3. The wastewater had a color level of 2064 PCU and was at pH 6.3. The figure shows that color removal by coagulation and settling or batch flotation was similar at all PAC doses. A PAC dose of 10 mg/L resulted in color levels of 450 and 411 PCU for batch flotation and coagulation, respectively. The maximum PAC dose of 60 mg/L produced color levels of 370 and 452 PCU for batch flotation and coagulation and settling, respectively.

Addition of 10 mg/L PAC and 80 mg/L EHDABr resulted in color levels achieved by coagulation with 100 mg/L EHDABr alone (Figure 9). An increase in the PAC concentration above 10 mg/L resulted in no color removal improvement.

Column Operation - It was observed during column operation that colored flocs were deposited upon the interior of the wastewater-EHDABr mixing tube and tubing carrying the EHDABr-wastewater mixture. Colored flocs were also deposited in the foam collection tubing and were darker

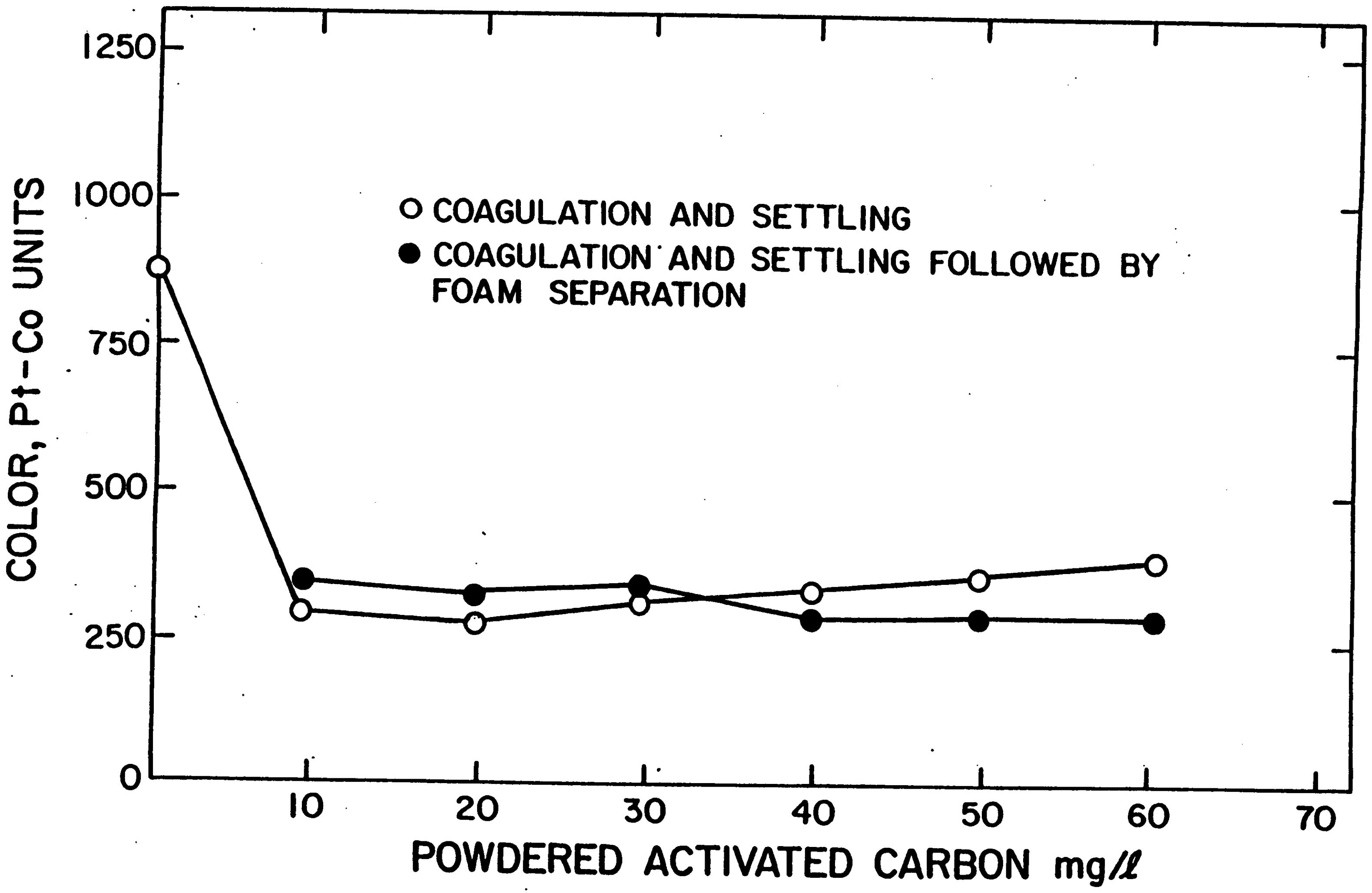


Figure 10. Color Residuals After Coagulation and Settling, and Batch Flotation with PAC and 80 mg/L EHDABr at pH 6.3

in color than the influent deposits.

Color deposition resulted from the sedimentation and adsorption of EHDABr color complexes upon tubing interior. The adsorptive behavior of EHDABr was reported by Garrett (28) and Schwartz (29), who suggested that the adsorptive character of EHDABr and other surfactants caused them to attract to glassware, plastics, and fabrics. The darker color observed in the collection tubing suggested that foam contained high concentrations of EHDABr-color complexes.

The foam rising in the column visually appeared to be of consistent density. EHDABr concentrations of 200 mg/L or greater produced denser foams than the 150 mg/L dosage. All concentrations of EHDABr produced a light brown foam. Foam color at 150 mg/L EHDABr was lighter in intensity than the higher EHDABr doses. Foam color was constant from the bottom to the top of the column.

Differences in foam density and color seen for varying EHDABr doses suggested that increasing EHDABr doses improved foam density and color flotation or removal. The constancy of color observed in the foam column suggested that the concentration of color bodies was fairly uniform throughout the column of foam.

Mixing of column pool contents appeared to be vigorous and well distributed within the column pool. Flocculated color particles appeared to be dispersed by the mixing activity.

The pH of the wastewater used in the trial ranged between 6.0 and 6.8. The pH of the effluent from the trials ranged from 6.0 to 7.0. An increase in pH was seen in the wastewater after some flotation trials. The increase in pH ranged from 0 to 0.4 pH units.

Flotation Performance Without EHDABr - The results of continuous-flow, foam flotation experiments without EHDABr addition are summarized in Table 4. The wastewater pH was 6.4. Part A of the table shows that influent color levels were 2433 and 2457 PCU at the beginning and end of the sampling period, respectively. Effluent color level at the beginning of the trial was 2456 PCU and 2507 PCU at the end. The influent TSS concentration was 48 mg/L at the beginning of the trial and 38 mg/L at the end. Effluent TSS levels were 32 mg/L and 29 mg/L for the beginning and end of the sampling period, respectively. Influent TOC levels at the beginning and end of the sampling interval were 196 mg/L and 204 mg/L. Effluent TOC levels were 165 mg/L at the beginning of the sampling interval and 195 mg/L at the end.

Part B of Table 4 shows that 11.9 liters of influent produced 72 mLs of foamate liquid. Foamate color was 2428 PCU. Foamate TOC and TSS levels were 179 mg/L and 136 mg/L, respectively.

Table 4. Continuous-flow, Foam Flotation Without EHDABr

A. Flotation Performance

Time, min	Color, PCU		TSS, mg/L		TOC, mg/L	
	influent	effluent	influent	effluent	influent	effluent
0	2433	2456	48	32	196	165
60	2457	2507	38	29	204	195

B. Flow of Foamate

Detention Time, min	Effluent Volume, mL	Foamate			
		Volume, mL	Color, PCU	TSS, mg/L	TOC, mg/L
5	11,910	72	2428	179	136

Wastewater color was not reduced by flotation without EHDABr. Color was not concentrated in the foamate. The TOC concentration was reduced in the wastewater but TOC was not concentrated in the foamate. This suggested that TOC reduction resulted from aeration in the column. TOC reduction by aeration was also observed by Ng (43), who showed that volatile organic compounds were removed from Kraft wastewater by aeration. The TSS concentration was reduced by flotation. Foamate TSS was of a higher concentration than the influent and this suggested that some of the influent TSS was concentrated in the foamate.

Continuous-flow, Foam Flotation with EHDABr

The results of flotation trials conducted at varying EHDABr dose and detention time are presented in this section. Color, TSS, TOC, and EHDABr levels for flotation trials 1-4 will be presented in graphs. The data for trials 1-4 are tabulated in Appendix B. The results of replicate trials, numbers 5-10, are presented in tabular form.

Color Flotation - The results of flotation with 150 mg/L EHDABr at a 10 minute detention time are shown in Figure 11. Influent color did not vary substantially during the trial. Beginning and ending influent color levels were 2150 and 2210 PCU, respectively. Effluent color levels increased from 350 PCU at the beginning to 620 PCU at the end of the trial. Color levels of the EHDABr-wastewater

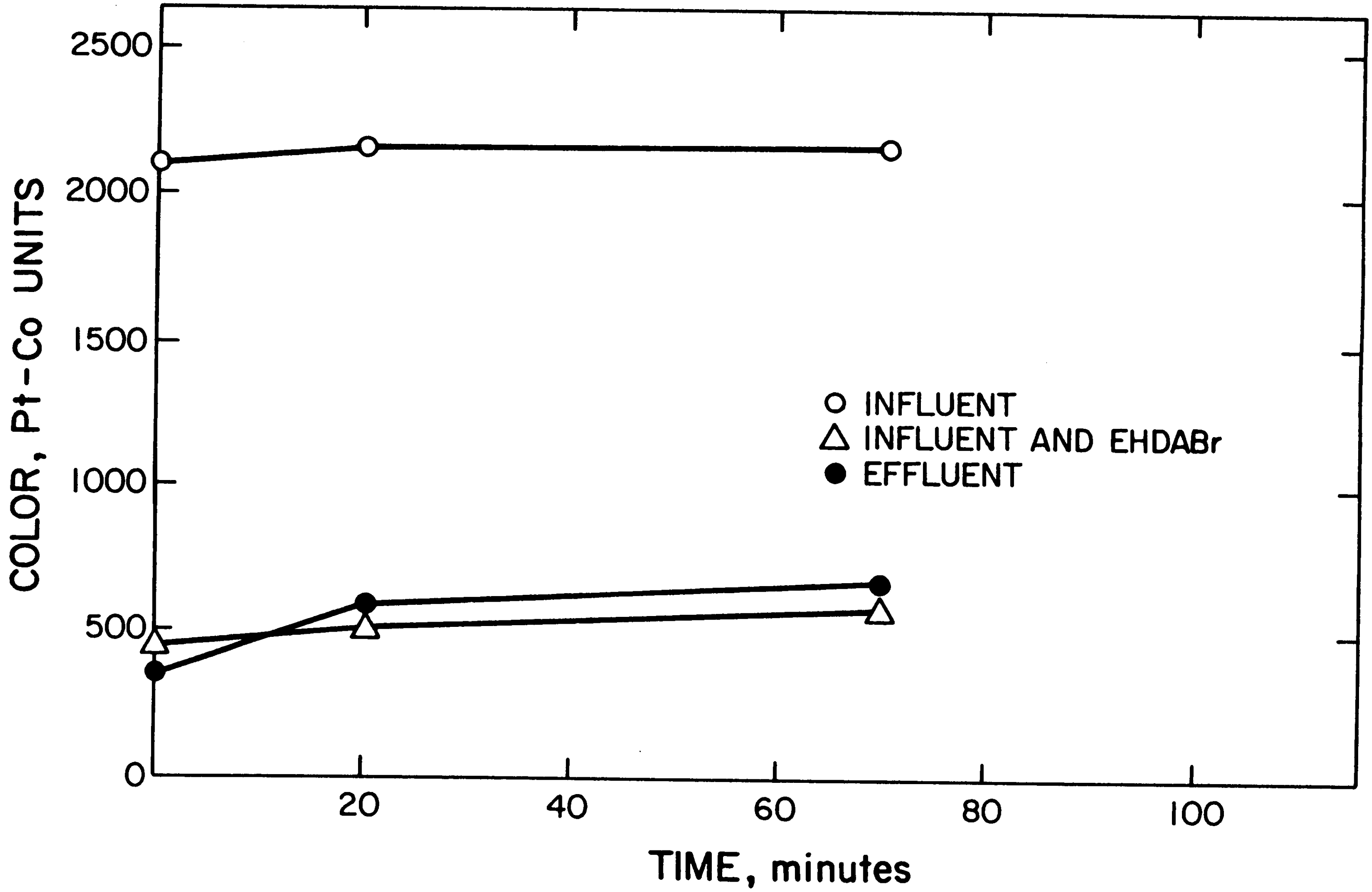


Figure 11. Color levels From Flotation by 150 mg/L EHDABr at a 10 Minute Column Detention Time and pH 6.2

complex ranged from 410 PCU to 550 PCU at the beginning and end of the trial. Color levels were reduced by 83 and 72% at the beginning and end of the trial, respectively. Results of the replicate trial, number 5, appear in Table 4. The table shows that color removal in trial 5 ranged from 78 to 65% at the start and end of the trial, respectively. The color removed by trials 1 and 5 ranged from 65 to 83%. The performance reduction observed during the sampling interval of trial 1 suggested that the system did not operate at steady state.

The color removals observed in trials 1 and 5 appeared to be improved over the 77% color removal seen in coagulation and settling with 150 mg/L EHDABr (Figure 9). The higher color removal seen at the beginning of the trials may have resulted, however, from the system not having achieved steady operation. The concentration of EHDABr in the column may have, as a result, been higher at the beginning of the sampling period than at the end. The high initial EHDABr column concentration may have resulted in relatively high color removal. As the system reached steady state operation, unreacted EHDABr may have been removed from the column with increased efficiency. The EHDABr available for reaction with color may have thus decreased. A decrease in color removal by flotation may have then occurred.

Table 5. Replicate Continuous-flow, Foam Flotation Trials with EHDABr

Trial	EHDABr/ Det. Time	Time, min.	Color, PCU				TSS, mg/L				TOC, mg/L			EHDABr, mg/L	
			*R	M	E	%	R	M	E	%	R	E	%	E	%
5	150/10	0	2340	666	502	78	28	308	160	47	183	124	32	110	26
		73	2510	871	616	65	38	286	152	46	180	133	26	75	50
6	200/10	0	2860	724	1003	74	39	340	144	58	172	109	36	89	57
		66	2760	701	995	74	29	240	92	62	178	125	29	60	60
7	250/10	0	2600	472	310	88	92	432	150	65	210	90	57	87	56
		62	2700	391	326	88	64	464	162	65	209	92	55	82	59
8	200/ 5	0	2540	344	279	89	104	440	158	64	203	100	50	91	54
		62	2420	387	251	89	84	468	174	63	201	101	50	91	54
9	200/ 5	0	2490	356	301	88	48	380	128	66	193	72	63	75	62
		60	2332	368	228	90	60	420	142	66	195	74	62	82	59
10	200/ 5	0	2270	426	287	87	128	452	160	65	210	78	62	69	66
		60	2611	414	240	90	116	452	164	64	213	77	63	71	64

* R= Raw influent, M= EHDABr/wastewater complex, E= Effluent, %= percent removed

Color removal performance at the end of trials 1 and 5 ranged from 65 to 72%. This range of removal was poorer than that from coagulation and settling by 150 mg/L EHDABr. Lemlich (35) provided an explaination for this performance difference by pointing out that flotation requires a sufficient surfactant concentration to sustain both colligend precipitation and foam production. The difference in color removal performance observed between coagulation and settling, and flotation may have resulted from some of the EHDABr in the flotation system being used for foam production instead of coagulation of color. An increase in EHDABr concentration may have been required in flotation to replace the EHDABr used for foam production to provide comparable color removal to that of coagulation and settling.

Figure 12 illustrates the results of trial 2, in which 200 mg/L EHDABr was used at a 5 minute detention time. The influent color levels ranged from 2350 PCU at the beginning to 2260 PCU at the end of the sampling period. Effluent color varied from 250 to 230 PCU from the beginning to the end of the trial. EHDABr-wastewater complex color levels remained at or near 320 PCU throughout the trial. Replicate trials 8-10 are shown in Table 5. Influent color ranged from 2332 to 2611 PCU and effluent color ranged from 228 to 301 PCU in the replicate trials. Color removals in trial 2

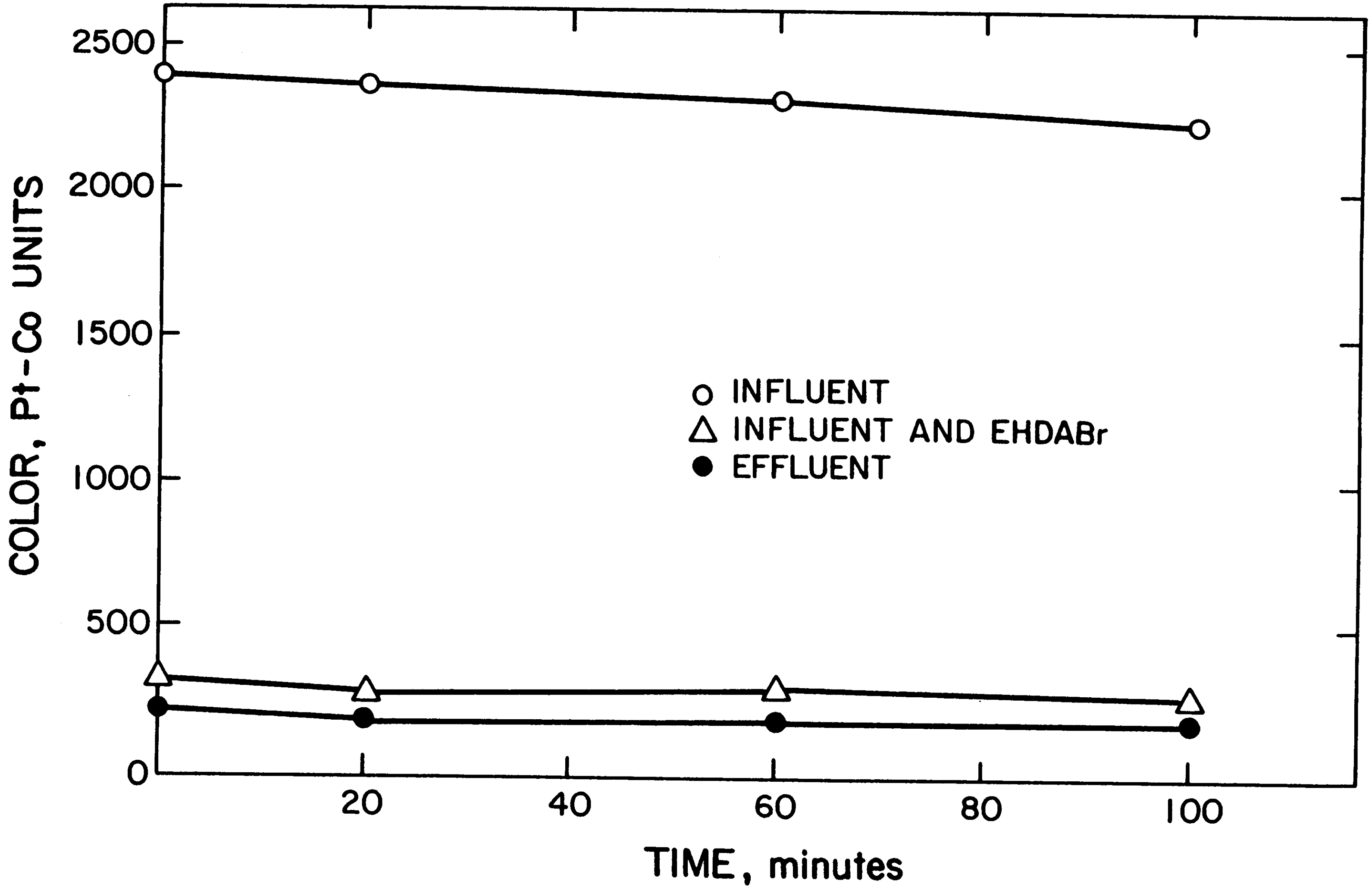


Figure 12. Color Levels From Flotation by 200 mg/L EHDABr at a 5 Minute Column Detention Time and pH 6.2

and trials 8-10 ranged from 87 to 91%.

The constancy of color removal observed in trial 2 suggested the system was operating at or near steady state. Flotation with 200 mg/L EHDABr removed 10 to 14% more color than coagulation and settling with 200 mg/L EHDABr (Figure 9).

The results of flotation with 200 mg/L EHDABr at a 10 minute detention time are shown in Figure 13. This was flotation trial 3. Influent color ranged from 2050 PCU to 1850 PCU from beginning to the end of the trial. Effluent color levels ranged from 220 PCU to 180 PCU at the beginning and end of the trial, respectively. EHDABr-wastewater complex color levels were 220 PCU at trial start and 280 PCU at the end. The replicate trial 6, shown in Table 5, had initial and ending influent color levels of 2860 and 2760 PCU, respectively. Effluent color levels ranged from 1003 to 995 PCU at the beginning and end of the trial, respectively. A range of 74 to 92% of the wastewater color was removed in trials 3 and 6.

The constancy of color removal seen in trial 3 suggested that steady state operation occurred. The performance of 200 mg/L EHDABr at a 10 minute detention time was similar to that observed at a 5 minute detention time (Figure 12).

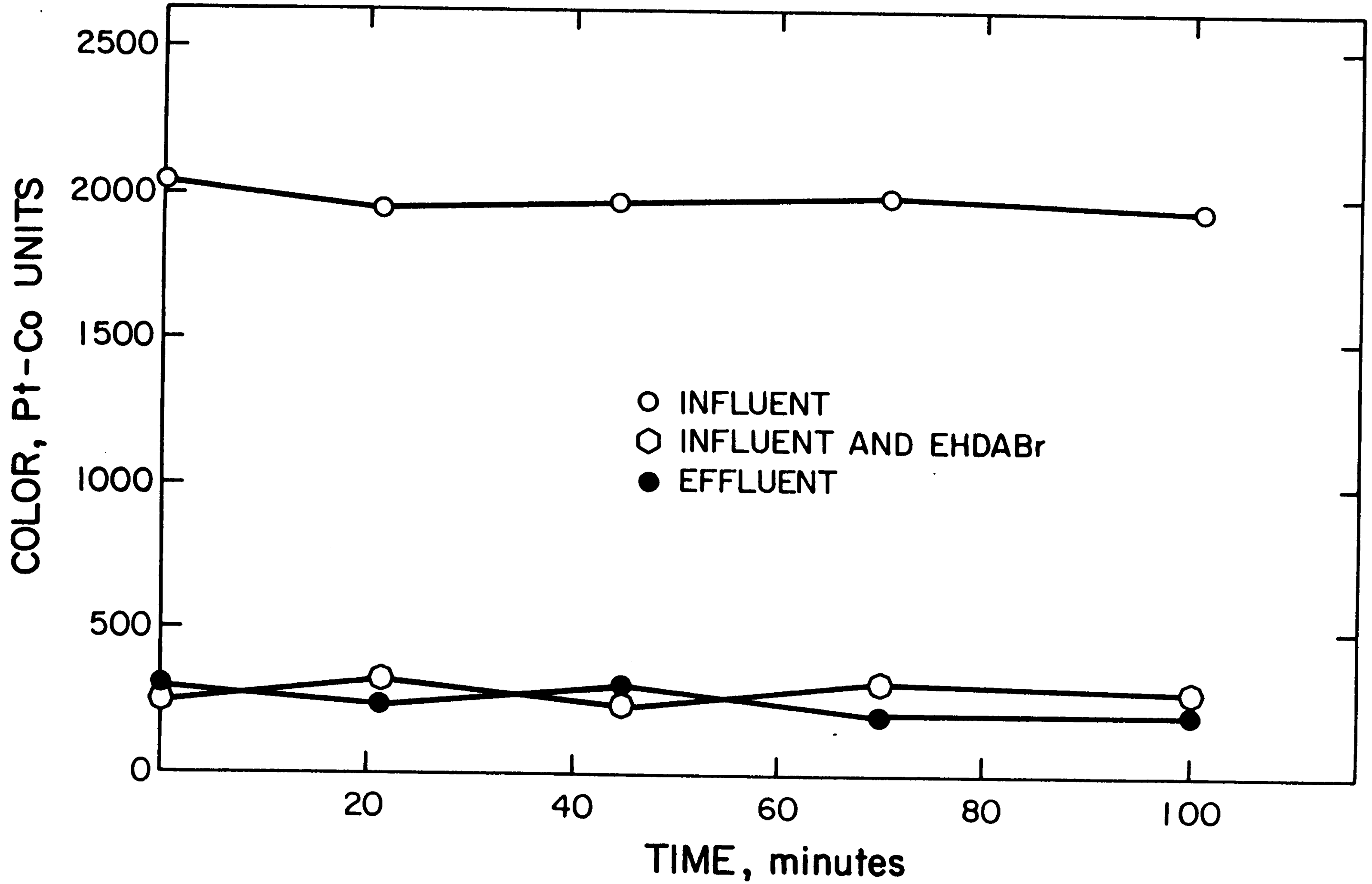


Figure 13. Color Levels From Flotation by 200 mg/L EHDABr at a 10 Minute Column Detention Time and pH 6.3

The data produced in trial 4 are shown in figure 14. This trial was conducted with 250 mg/L EHDABr at a 10 minute detention time. Influent color was 2050 PCU and 1950 PCU at the start and end of the trial, respectively. Effluent color levels were 160 PCU at the beginning and 310 PCU at the end of the trial. The color level of the wastewater and EHDABr complex was 280 PCU from the beginning to the end of the trial.

The constancy of color removal performance seen in Trial 7, a replicate of trial 4, is summarized in Table 5. Influent color levels were 2600 PCU and 2700 PCU at the beginning and end of the trial, respectively. Effluent color level was 310 PCU at the start and 326 PCU at the end of the trial. The range of color removed in trial 4 and 7 was 84 to 92%. The constancy of color removal performance observed in trial 4 suggested the trial operated near steady state.

The results of trials 1-4 suggested the following: 1) color removal by flotation with 150 mg/L EHDABr was poorer than color removal by coagulation and settling at the same EHDABr dose; 2) 200 mg/L EHDABr gave the best color flotation and removed more color than 200 mg/L EHDABr by coagulation and settling; 3) no difference was observed in color removal at flotation detention times of 5 or 10 minutes; 4) 250 mg/L EHDABr produced the same color removal

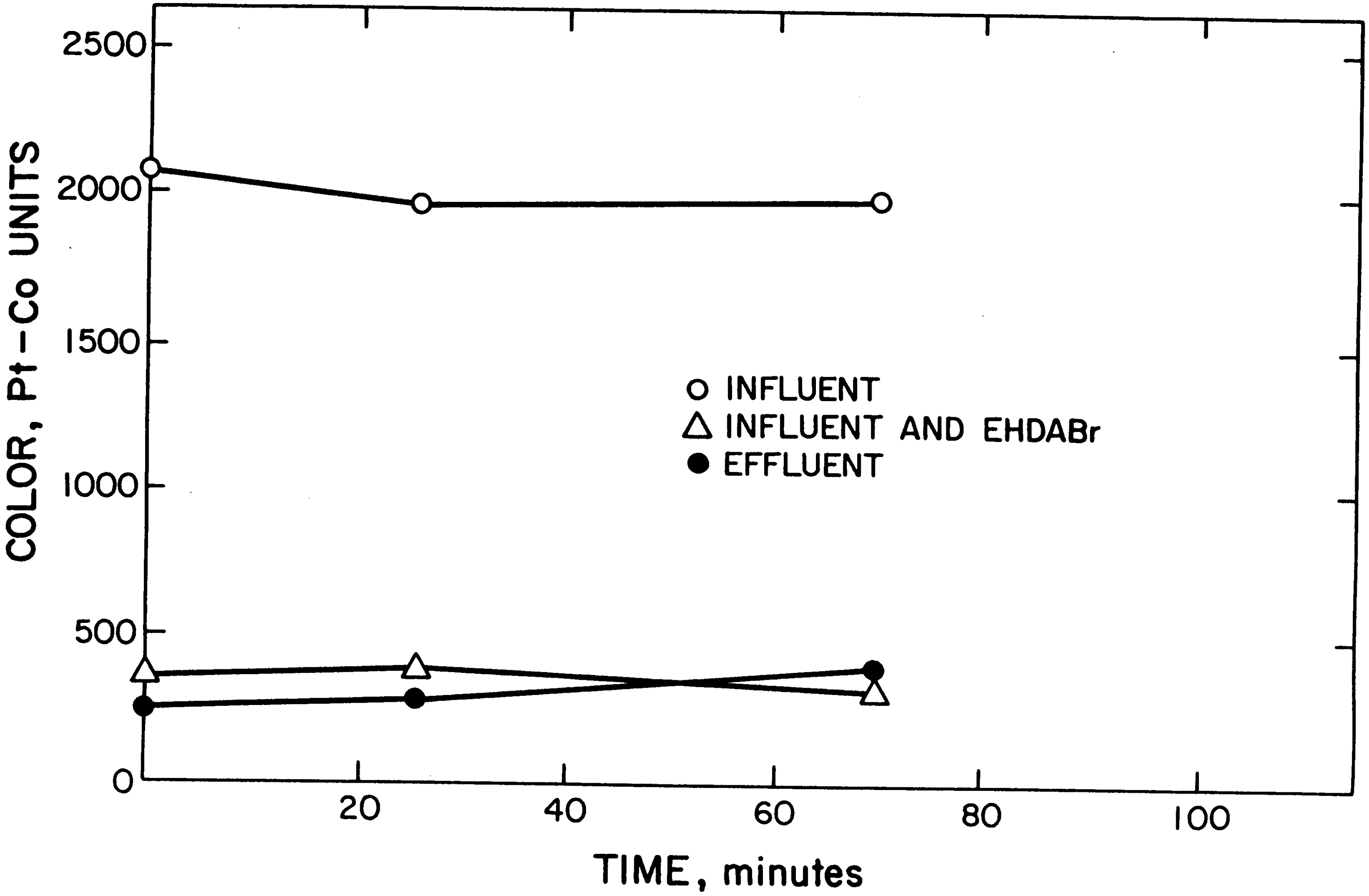


Figure 14. Color Levels From Flotation by 250 mg/L EHDABr at a 10 Minute Column Detention Time and pH 6.2

as 200 mg/L EHDABr in flotation; 5) the level of color removed by flotation was the same as that precipitated by EHDABr during column operation.

TOC Flotation - This section concerns the changes in TOC levels that occurred during trials 1-4 and the replicate trials. The results of TOC analysis of a pure EHDABr solution are also presented.

EHDABr has the molecular formula $CH_3(CH_2)_{15}N(Br)(CH_3)_2C_2H_5$ and a molecular weight of 378.48. The molecular formula showed that the Carbon in EHDABr constitutes 63% of the surfactant's molecular weight. This suggested that each mg/L of EHDABr would produce a theoretical TOC of 0.63 mg/L. The results of TOC analysis of a pure EHDABr solution, however, showed that 1 mg/L EHDABr resulted in a solution TOC level of 0.02 mg/L. The results of the analysis of EHDABr TOC levels are presented in Appendix C. This suggested that EHDABr was difficult to oxidize by the analytical method used in this research. The complexing of EHDABr with the wastewater produced a compound that was also difficult to analyze for TOC concentration. As a result, no data was available on the TOC levels of EHDABr-wastewater complexes formed prior to flotation. Because the maximum EHDABr dose of 250 mg/L used in this study would have resulted in a detectable wastewater TOC level increase of 5 mg/L, the TOC levels obtained from the trials most likely resulted from the wastewater alone.

Figure 15 presents the results of TOC removal in trial 1. An EHDABr dose of 150 mg/L was used at a 10 minute detention time. Influent TOC was 117 mg/L at the initiation of the trial and 130 mg/L at the end. Effluent TOC levels at the beginning and end of the trial were 43 and 117 mg/L, respectively. Results of the replicate, trial 5, appear in Table 5.

Influent TOC in the beginning of the trial was 183 mg/L and 180 mg/L at the end. Effluent TOC was 124 mg/L at the beginning of the trial and 134 mg/L at the end. The range of TOC removal for trials 1 and 5 was 26 to 63%.

The decrease of TOC removal performance observed between the beginning and end of the trial suggested that the system was not operating at steady state during the sampling period.

The results of TOC removal in trial 2 appear in Figure 16. EHDABr was used at a 200 mg/L dose and a 5 minute detention time. Influent TOC levels were 172 mg/L at the beginning and 176 mg/L at the end of the trial. Effluent TOC levels were 69 and 71 mg/L at the beginning and end of the trial, respectively. The constancy of TOC removal observed throughout the trial suggested steady state operation.

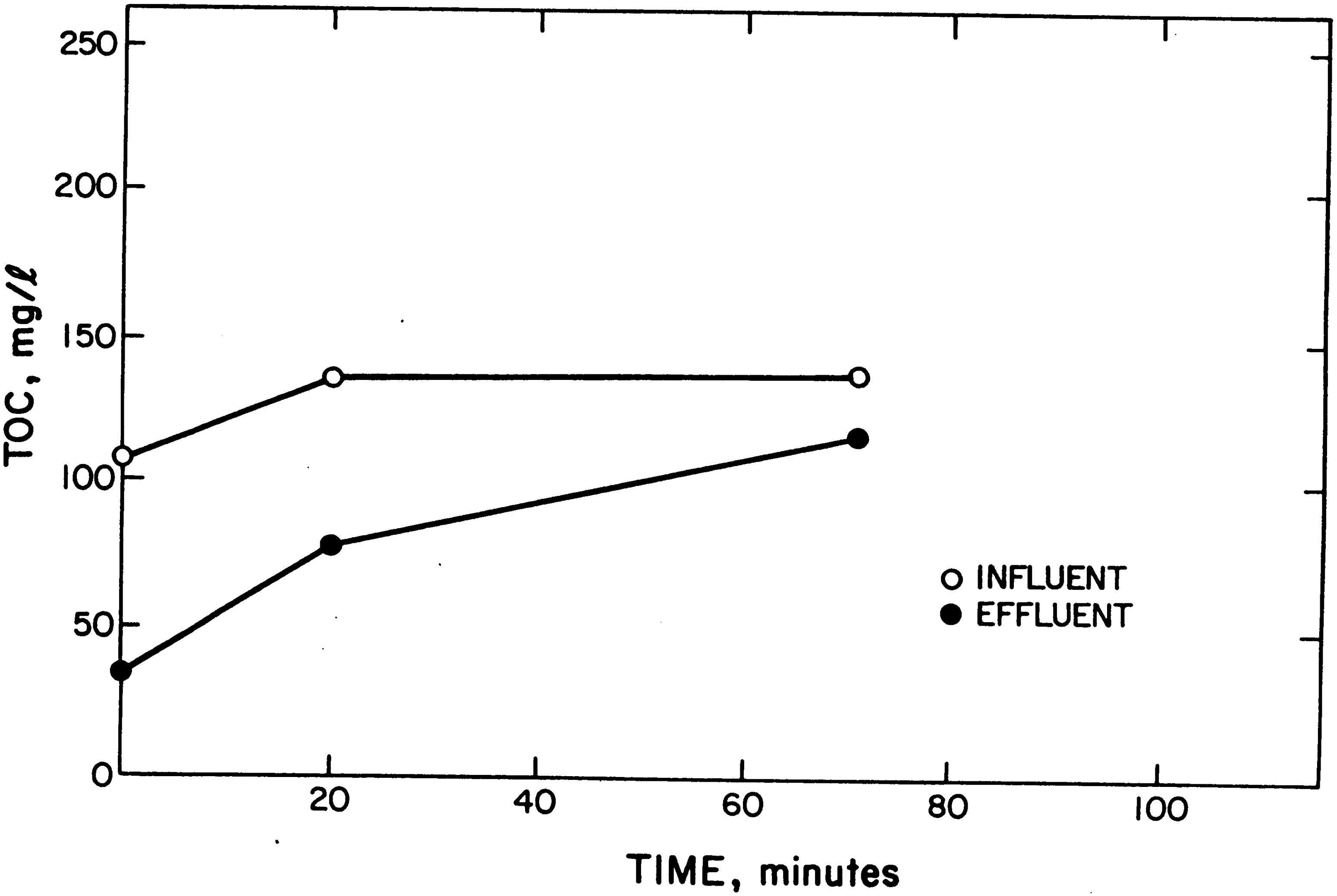


Figure 15. TOC levels From Flotation by 150 mg/L EHDABr at a 10 Minute Column Detention Time

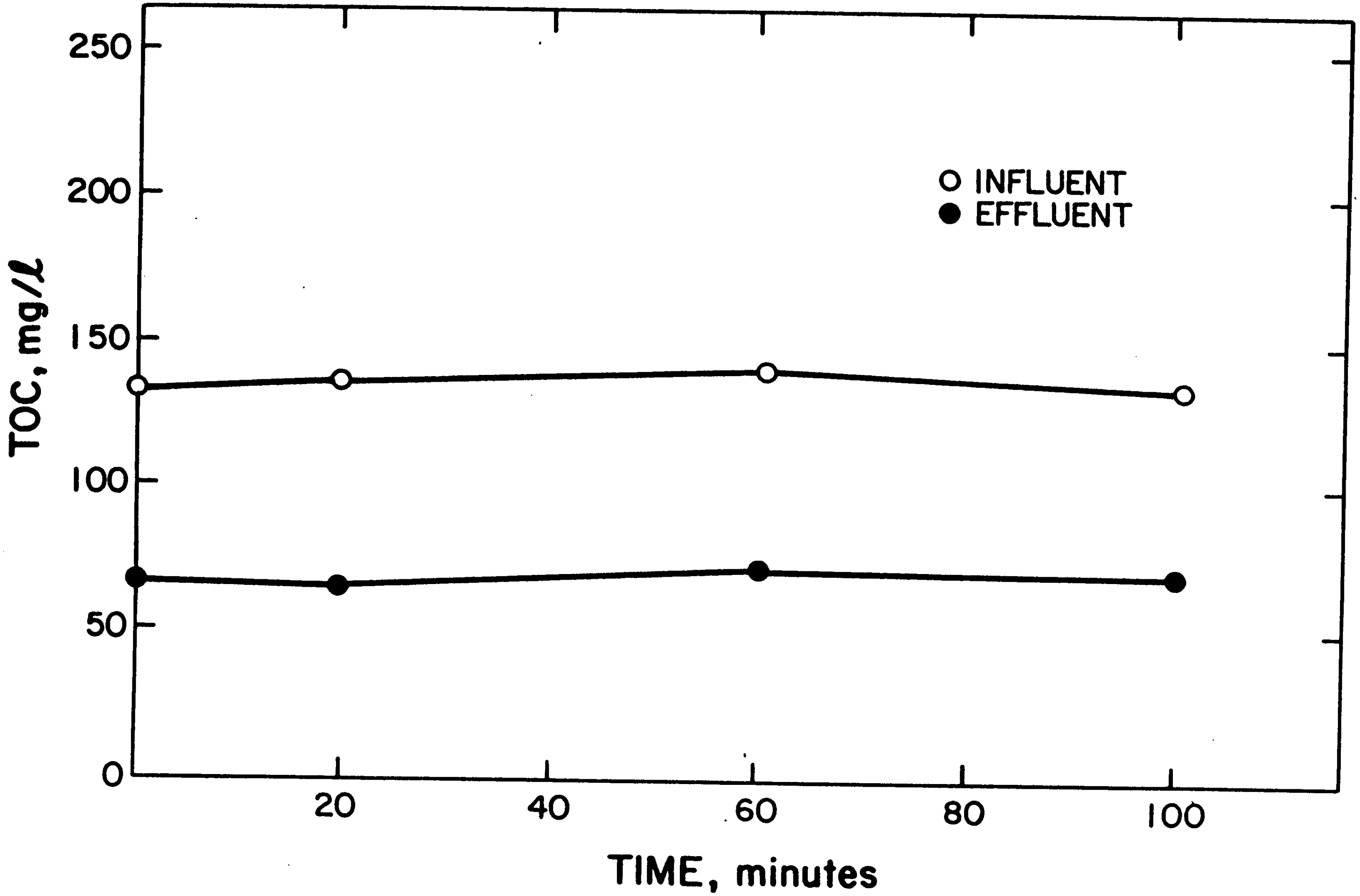


Figure 16. TOC Levels From Flotation by 200 mg/L EHDABr at a 5 Minute Column Detention Time

TOC influent levels of the replicate trials, numbers 8-10, ranged from 193 to 210 mg/L at the beginning of the trials and 195 to 213 mg/L at the end (Table 5). Effluent TOC levels ranged from 72 to 100 mg/L at the beginning of the trials and 74 to 101 mg/L at the end. The range of TOC removal for trials 2, and 8-10 was 55 to 64%.

The TOC removal performance of trial 3, in which 200 mg/L EHDABr was used at a 10 minute detention time, is presented in Figure 17. Influent TOC levels ranged between 180 and 200 mg/L throughout the trial. Effluent TOC levels were 105 mg/L at the beginning of the trial and 137 mg/L at the end. Although effluent TOC levels increased during the trial, the system may have operated at steady state because influent TOC levels also increased.

The results of the replicate trial, number 6, appear in Table 5. Influent TOC levels ranged from 172 mg/L to 178 mg/L at the start and end of the trial, respectively. Effluent TOC levels were 109 mg/L at the beginning and 125 mg/L at the end of the trial. TOC removal for trials 3 and 6 ranged between 29 and 44%.

An EHDABr dose of 250 mg/L was used in trial 4 at a 10 minute detention time. The results of this trial appear in Figure 18. Influent TOC levels ranged from 192 to 197 mg/L throughout the trial. Effluent TOC concentration was 90 mg/L at trial start and 103 mg/L at trial end. Replicate

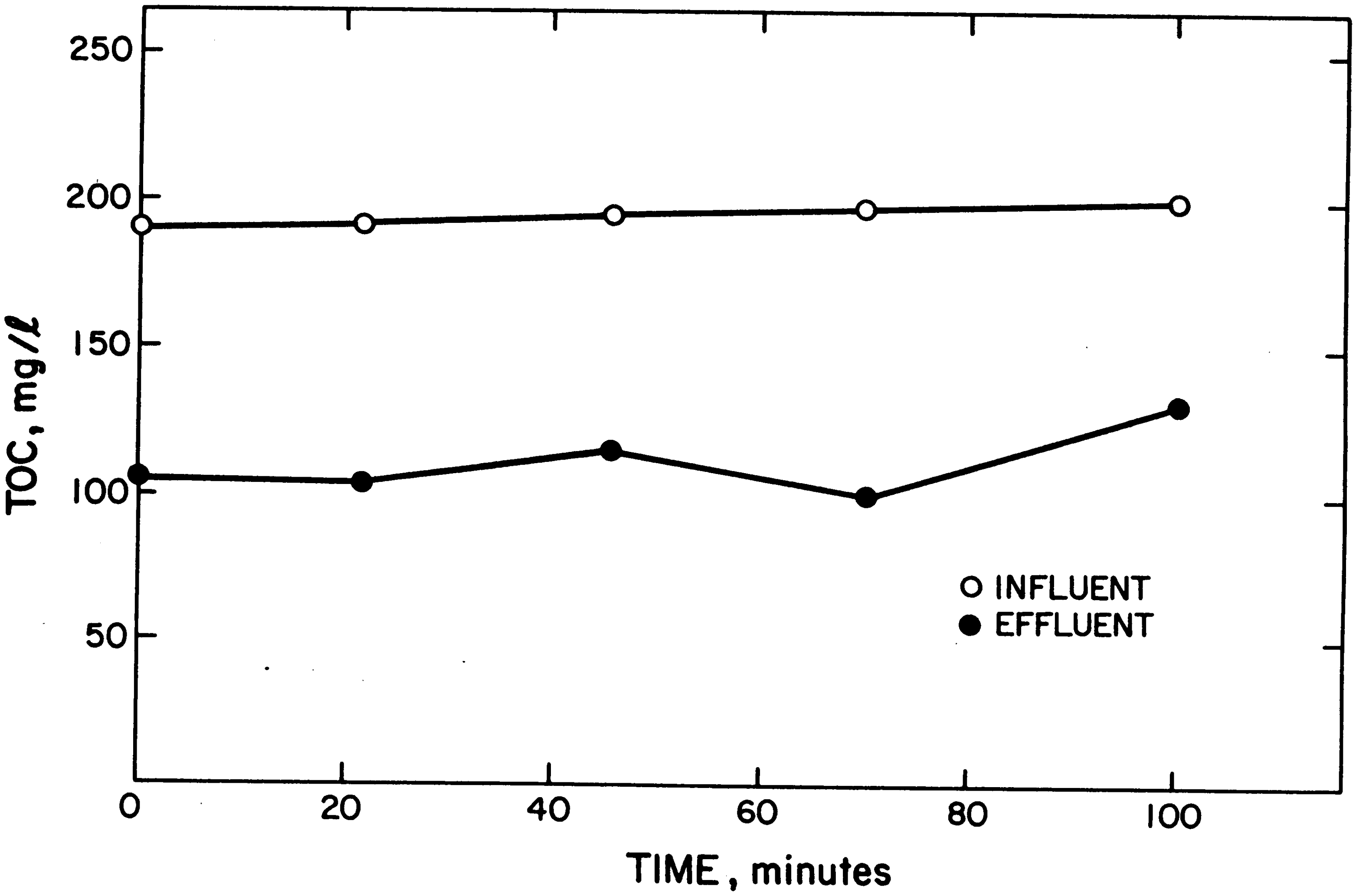


Figure 17. TOC Levels From Flotation by 200 mg/L EHDABr at a 10 Minute Column Detention Time

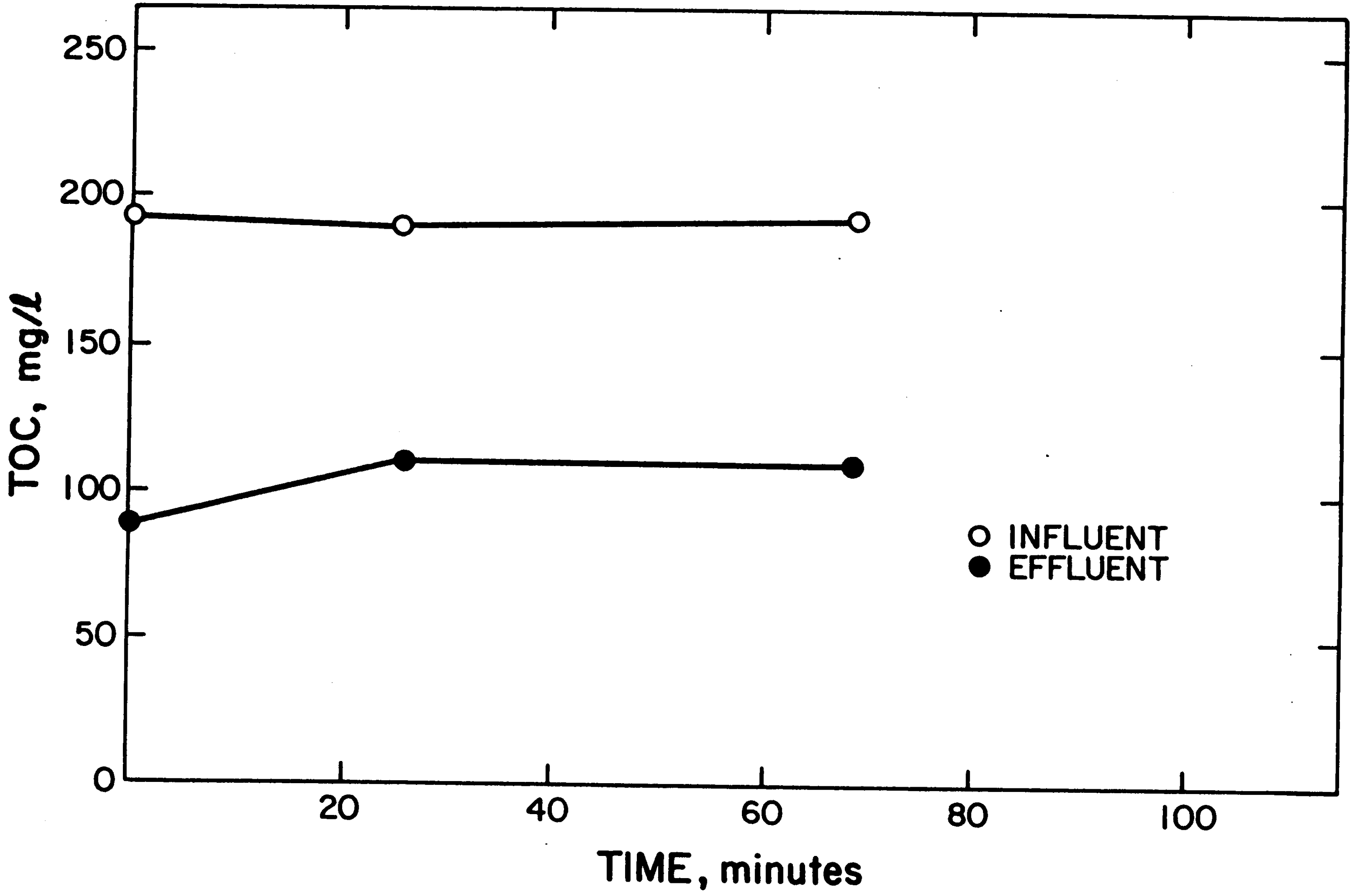


Figure 18. TOC Levels From Flotation by 250 mg/L EHDABr at a 10 Minute Column Detention Time

trial 7, shown in Table 5, had an influent TOC level of 201 to 203 mg/L throughout the trial. Effluent TOC levels were 90 and 92 mg/L at trial start and end, respectively. TOC removal range of trials 4 and 7 was 37 to 57%.

The TOC removal results of trials 1-4 suggested the following: 1) EHDABr dose of 150 mg/L produced the lowest TOC removals; 2) 200 mg/L EHDABr gave best TOC removal; 3) detention time of 5 minutes gave better TOC removal than 10 minutes at EHDABr dose of 200 mg/L; 4) 250 mg/L EHDABr at a 10 minute detention time gave better TOC removal than 200 mg/L EHDABr at a 10 minute detention time.

TOC removal may have been reduced when detention time increased from 5 to 10 minutes because the removal of EHDABr may have been improved as detention time increased. As a result, the EHDABr available for reaction with TOC components of the wastewater may have been lower in the 10 minute detention time than the 5 minute time. This was supported by the fact that 250 mg/L EHDABr improved TOC removal at a 10 minute detention time over 200 mg/L EHDABr at the same detention time. The increased influent concentration of the 250 mg/L dose over the 200 mg/L dose may have replenished the column EHDABr concentration that was removed by the longer detention time.

Dugal _et_ _al_. (7) showed that up to 63% of Kraft wastewater TOC was made up of acid insoluble lignin.

Removal of acid insoluble lignin would have resulted in TOC removal as well. As a result, the TOC reduction that was observed in the flotation trials may have been removed as colored particles flocculated and floated by EHDABr. Residual wastewater TOC may have consisted of soluble lignin fragments and soluble organic compounds such as cellulose and the by products of biological treatment.

TSS Flotation - Figure 19 shows the results of TSS flotation with 150 mg/L EHDABr at a 10 minute detention time (trial 1). Influent TSS level was 5 mg/L throughout the trial. EHDABr-wastewater complex TSS levels ranged from 228 mg/L to 224 mg/L at the beginning and end of the trial, respectively. Effluent TSS levels were 92 mg/L at trial start and 90 mg/L at the end. The consistency of TSS removal during this trial suggested steady state occurred. Replicate trial 5, in Table 5, had an influent TSS level of 28 mg/L at the start and a TSS level of 162 mg/L at the end of the trial. The range of TSS removal for trials 1 and 5 was 45 to 64%.

Flotation results of TSS for trial 2 appear in Figure 20. An EHDABr dose of 200 mg/L was used at a detention time of 5 minutes. Influent TSS levels of 85 and 82 mg/L occurred at the beginning and end of the trial, respectively. EHDABr-wastewater complex TSS levels were 475 mg/L at the trial beginning and 463 mg/L at the end.

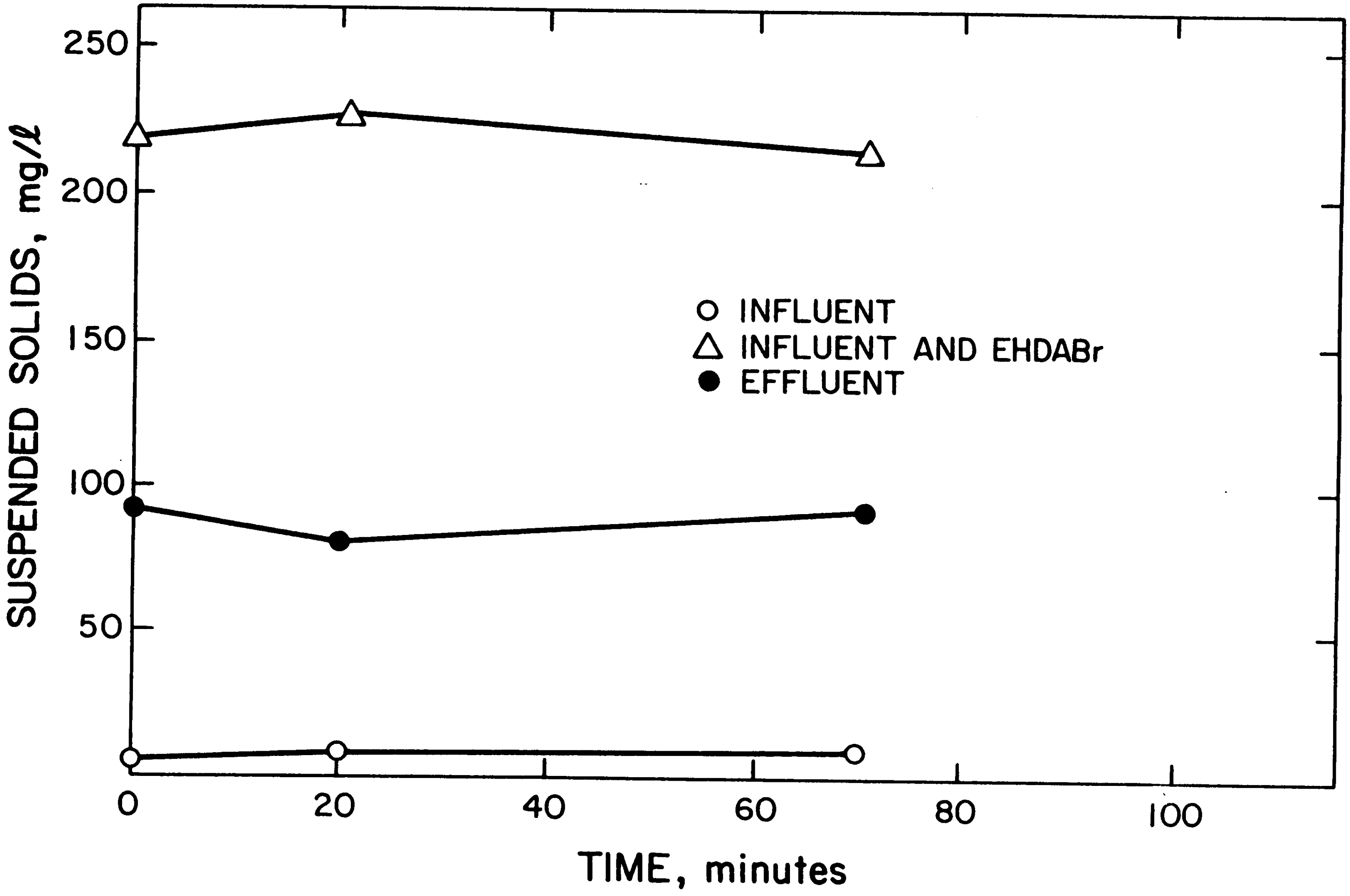


Figure 19. TSS Levels From Flotation by 150 mg/L EHDABr at a 10 Minute Column Detention Time

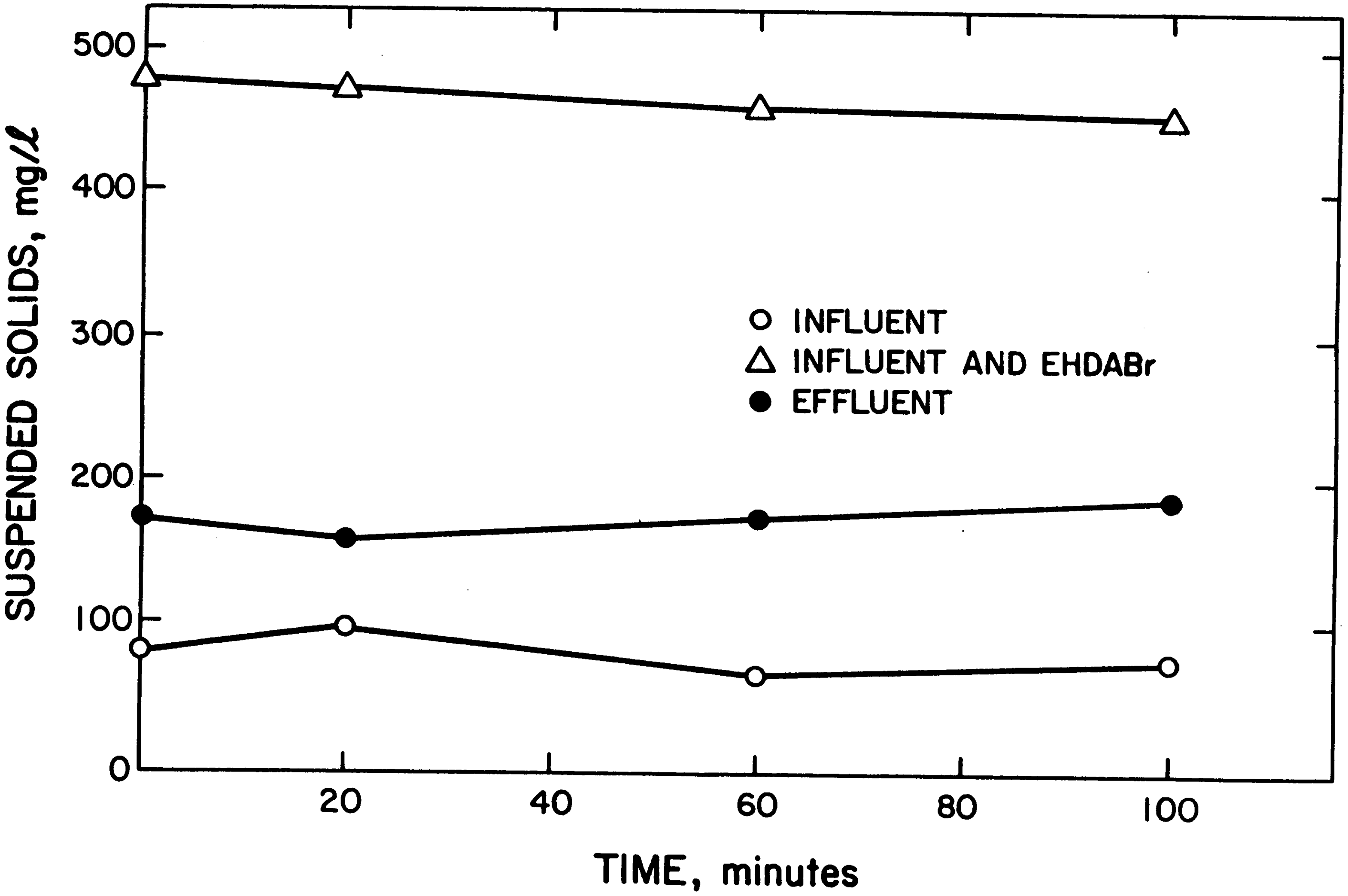


Figure 20. TSS Levels From Flotation by 200 mg/L EHDABr at a 5 Minute Column Detention Time

Effluent TSS levels ranged from 162 mg/L at the trial beginning to 186 mg/L at the trial end. The flotation of TSS appeared to be constant in the trial and suggested steady state operation occurred. Trials 8-10 were replicates of trial 2 and are shown in Table 5. Influent TSS concentration in these trials ranged from 48 to 128 mg/L at trials' start. The TSS levels found at trial end ranged from 60 to 116 mg/L for the replicates. Reduction of TSS in trials 2 and 8-10 was 60 to 66%.

Results of flotation with 200 mg/L EHDABr at a 10 minute detention time (trial 3) are illustrated in Figure 21. Influent TSS levels were 40 mg/L at the beginning of the trial. Levels of influent TSS increased to 120 mg/L at the 20 minute operation point, and changed to 100, 80, and 100 mg/L at trial time 45, 70, and 100 minutes, respectively. EHDABr-wastewater complex TSS levels began at 440 mg/L, decreased to 320 mg/L at 20 minutes of operation, and ranged between 400 and 440 mg/L during the last 55 minutes of column operation. Effluent TSS levels were initially 280 mg/L, decreased to 160, 120, and 80 mg/L at 20, 45, and 70 minutes respectively, and ended at 120 mg/L after 100 minutes of operation. The variation in effluent TSS levels occurring during this trial suggested that steady state may have been reached after 45 minutes of column operation. Trial 6 was a replicate of trial 3 and is

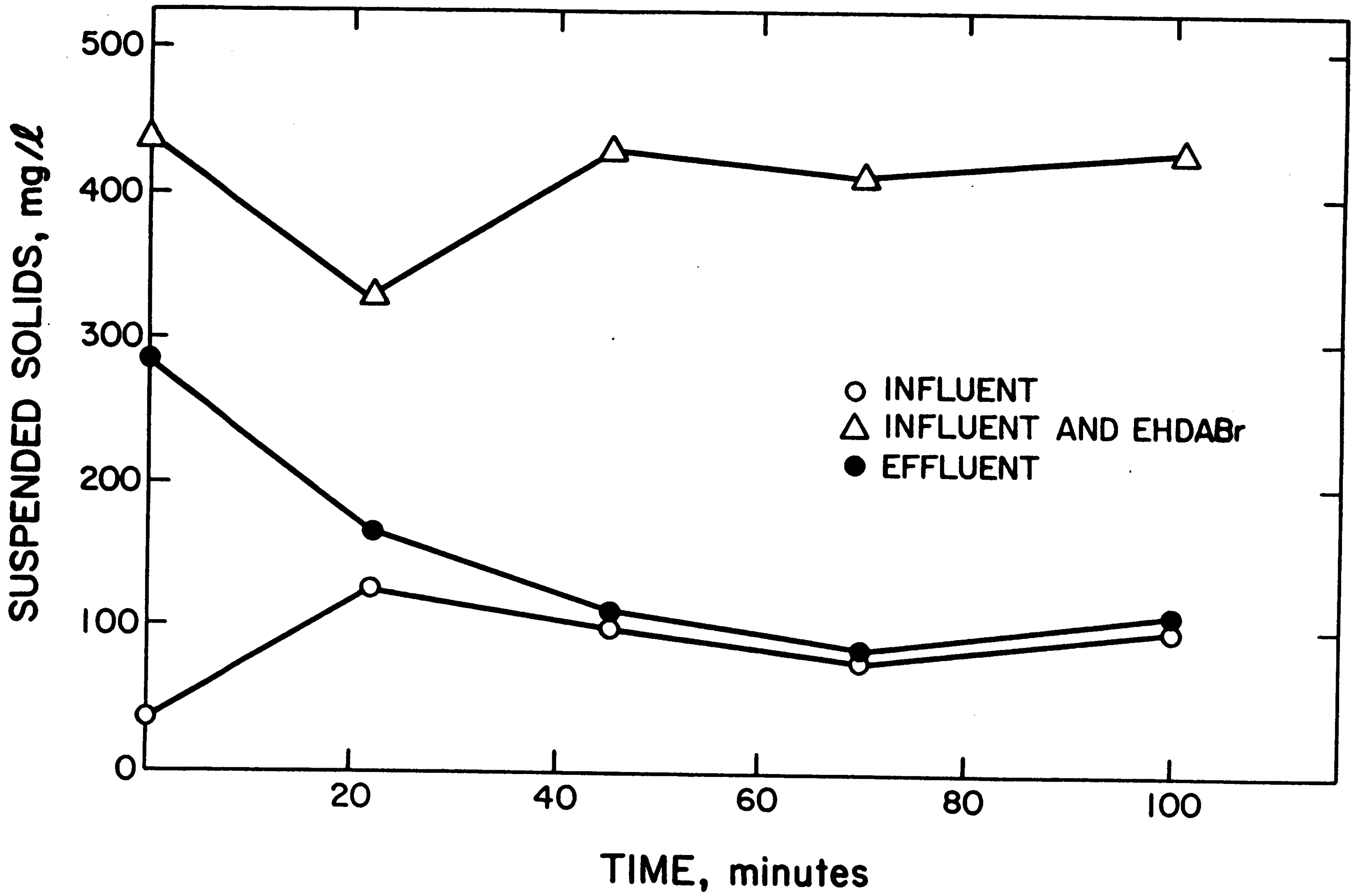


Figure 21. TSS Levels From Flotation by 200 mg/L EHDABr at a 10 Minute Column Detention Time

presented in Table 5. TSS concentration of the influent was 39 and 29 mg/L at the beginning and end of trial 6, respectively. Effluent TSS level as 144 mg/L at trial start and 92 mg/L at the end. In trials 3 and 6, 36 to 80% of the TSS of the wastewater and EHDABr mixture was removed.

A dose of 250 mg/L EHDABr was used at a 10 minute detention time in trial 4. Results of TSS flotation in this trial appear in Figure 22. Influent TSS increased steadily from 76 mg/L at trial start to 156 mg/L at trial end. EHDABr-wastewater complex TSS levels increased steadily from 426 mg/L at trial start to 528 mg/L at the conclusion of the trial. Effluent TSS was 94 mg/L at the beginning of the trial and increased steadily to 196 mg/L at the end. Trial 4 was replicated in trial 7, which appears in Table 5. Influent TSS ranged from 92 to 64 mg/L at the beginning and end of the trial, respectively. Effluent TSS was 150 mg/L at the trial start and 174 mg/L at trial conclusion. The removal range of TSS in trials 4 and 7 was 63 to 77%. Trial 4 may have reached steady state after 20 minutes of operation where removals in TSS after 20 and 70 minutes differed by only 4%.

The results of TSS flotation presented above suggested the following: 1) Influent TSS increased when EHDABr was added. Concentration of TSS increased as EHDABr dose increased from 150 to 200 mg/L, but did not increase as

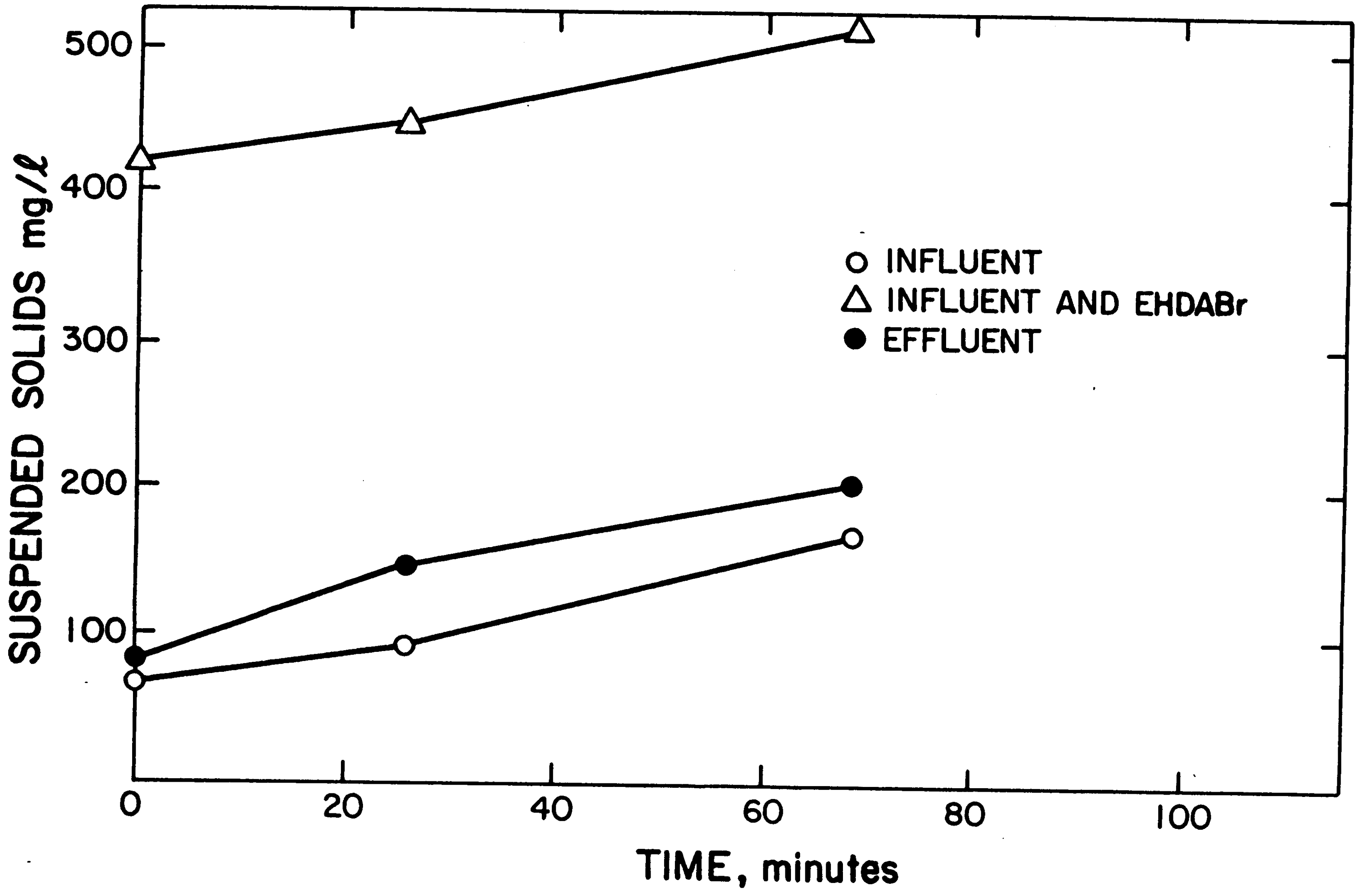


Figure 22. TSS Levels From Flotation by 250 mg/L EHDABr at a 10 Minute Column Detention Time

EHDABr dose increased from 200 to 250 mg/L; 2) flotation produced a net increase of TSS over influent TSS levels; 3) 200 mg/L EHDABr best removed TSS; 4) a 10 minute detention time gave better TSS removals than a 5 minutes detention time; 5) increases in EHDABr dose from 200 to 250 mg/L did not improve TSS flotation at 10 minute detention.

Increasing detention time from 5 to 10 minutes may have promoted TSS flotation by improving EHDABr-wastewater mixing and contact time. According to Lemlich (35), an improvement in flocculated particles flotation ability would result. The highest EHDABr dose used in flotation, 250 mg/L, may have been excessive. This was suggested by the observation that neither TSS precipitation nor flotation was increased as EHDABr was increased in concentration from 200 to 250 mg/L. The rate of column air flow may have been too low to effectively mix and remove EHDABr levels greater than 200 mg/L.

Consideration of the results of EHDABr coagulation and flotation operations suggested that TSS formation by EHDABr played a primary role in removing color.

EHDABr Flotation - Effluent EHDABr levels for trials 1-4 are shown in Figure 23. The results of trial 1, 150 mg/L EHDABr at a 10 minute detention time, show that EHDABr levels were 60, 70, and 47 mg/L at 0, 20 and 70 minutes of operation time, respectively. These results suggested that

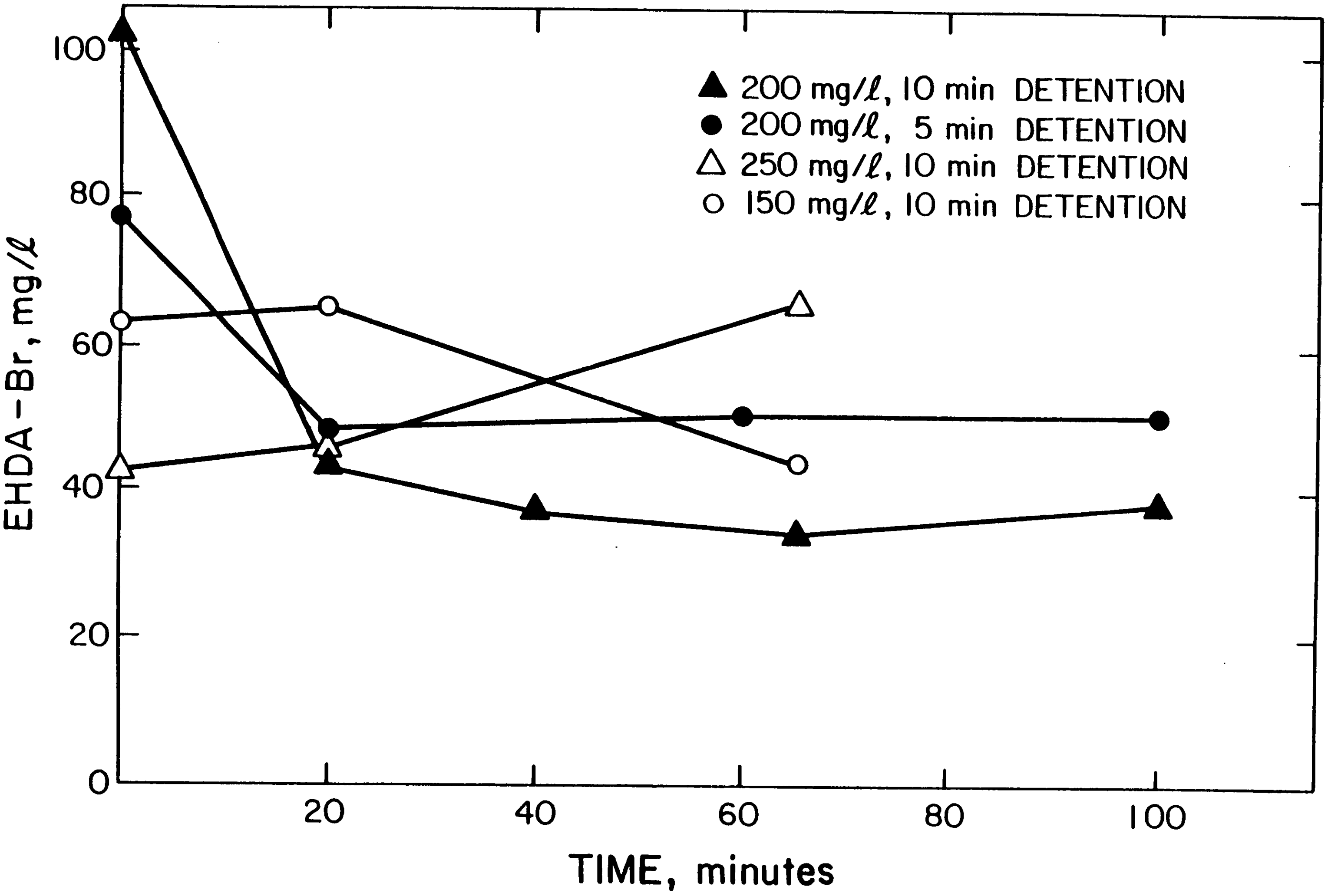


Figure 23. Levels of EHDABr in the Effluent of Flotation Trials

EHDABr flotation with 150 mg/L did not stabilize during the time in which samples were taken. In trial 2, 200 mg/L EHDABr at a 5 minute detention time, EHDABr level decreased from 77 mg/L to 58 mg/L during the first 20 minutes of sampling time. EHDABr levels then remained fairly constant until trial end, ranging from 58 to 61 mg/L after 20 and 100 minutes, respectively, of column operation time. The constancy of EHDABr effluent levels seen after 20 minutes of operation in trial 2 suggested EHDABr flotation reached steady state at this time. The results of trial 3, in which 200 mg/L EHDABr was used at a 10 minute detention time, showed that EHDABr concentration dropped from 105 to 48 mg/L in the first 20 minutes of column sampling time. EHDABr levels ranged between 35 and 38 mg/L at 40 and 100 minutes of operation time, respectively. The results of trial 3 suggested that steady state operation occurred after 20 minutes of sampling time. The results of flotation with 250 mg/L EHDABr at a 10 minute detention time, trial 4, showed that EHDABr concentration was 42 mg/L at the beginning of sampling. EHDABr concentrations increased to 46 and 75 mg/L at 22 and 70 minutes of sampling time, respectively. The steady increase of effluent EHDABr seen in trial 4 suggested that steady state flotation of EHDABr did not occur.

The results of EHDABr removal in the replicate trials are shown in Table 5. Trial 5, replicate of the trial using

150 mg/L EHDABr at a 10 minute detention time, had an EHDABr effluent level of 110 and 75 mg/L at the beginning and end of the trial, respectively. Trials 8-10 were replicates of the 200 mg/L EHDABr used at a 5 minute detention time. Effluent EHDABr levels ranged from 69 to 91 mg/L at the start and 71 to 91 mg/L at the end of these trials. Trial 6 repeated flotation with 200 mg/L at a 10 minute detention time. Effluent EHDABr levels were 89 and 60 mg/L at the start and end of the trial, respectively. The repeated trial of 250 mg/L EHDABr at a 10 minute detention time, trial 7, showed an EHDABr concentration of 87 and 82 mg/L at trial start and end, respectively. Ranges of percent EHDABr removal in all trials were as follows: 150 mg/L at 10 minute detention, 26-69%; 200 mg/L at 5 min. detention, 54-70%; 200 mg/L at 10 min. detention, 47-81%; 250 mg/L at 10 min. detention, 56-70%.

The results of EHDABr flotation in trials 1-4 suggested the following: 1) the efficiency of EHDABr flotation with 150 mg/L EHDABr was not established during the sampling time; 2) 200 mg/L EHDABr gave the best observed EHDABr removal; 3) EHDABr removal was better at a 10 minute detention time than a 5 minute detention time for flotation with 200 mg/L EHDABr; 4) 250 mg/L EHDABr at a 10 minute detention time gave increasing effluent EHDABr levels during column operation time.

Comparison of column TSS removal results and column EHDABr removal results showed that 200 mg/L EHDABr was associated with the best EHDABr and TSS removals. This suggested that EHDABr is removed in flotation as a component of TSS. This was supported by the trials in which 250 mg/L EHDABr was used at a 10 minute detention time. Removal of TSS in these trials was no greater than that seen at trials using 200 mg/L EHDABr. EHDABr levels increased in the effluent as a result, as shown in Figure 23. The results of EHDABr flotation removal thus confirmed the observation that 250 mg/L EHDABr was an excessive surfactant dose.

Foamate Production - The levels of color occurring in the foamate from the flotation trials are summarized in Table 6. The data in Table 6 were obtained from analysis of foamate production data in Appendix D. Table 6 shows the average effluent color for trials using 150 mg/L EHDABr at a 10 minute detention time was 570 PCU. Average foamate color for these trials was 413 PCU. Trials in which 200 mg/L EHDABr was used at a 5 minute detention time had average color levels of 250 PCU and 301 PCU for the effluent and foamate, respectively. The trials in which 200 mg/L EHDABr was used at a 10 minute detention time had a range of color levels of 150 to 1003 PCU in the effluent and 306 to 577 PCU in the foamate. The trials for 250 mg/L EHDABr at a 10 minute detention time had color levels of 263 and 313 PCU in

Table 6. Average Effluent and Foamate Color Levels

EHDABr Dose/ Detention Time	Trials	Average Effluent Color, PCU	Average Foamate Color, PCU
150/10	1,5	570	413
200/5	2,8-10	250	301
*200/10	3,6	150-1003	306-577
250/10	4,7	263	313

*Values were not averaged because the range was large.

the effluent and foamate, respectively. The results of foamate color analysis suggested that the foamate color level of a given trial was similar to the effluent color level of that trial. This resulted from the foamate color being concentrated in the TSS of the foamate.

Table 7 summarizes the results of foamate production. Information in Table 7 was obtained from analysis of the data in Appendix D. Part A of Table 7 shows that the average foamate flow for trials using 200 mg/L at a 5 minute detention time was 7.4 mL/min. The foamate volume for these trials was an average of 3.7% of the influent volume. Trials with 200 mg/L EHDABr at a 10 minute detention time showed an average foamate flow of 4.65 mL/min. and their foamate volume averaged 4.6% of the influent volume.

These results suggested that flotation at a 10 minute detention time produced more foamate than floatation at 5 minute's detention for a given EHDABr dose. This was supported by the fact that foamate flow of the 10 minute detention time was greater than half of the foamate flow at 5 minute's detention. This may have resulted from improved mixing and contact of the wastewater and EHDABr at a 10 minute detention time over that of the 5 minute time. This was also supported by EHDABr flotation results (Figure 23), which showed that the longer detention time removed EHDABr best.

Table 7. Foamate Flow in Continuous-flow, Flotation Experiments

A. Foamate Production for 200 mg/L EHDABr

Trials	Detention Time, min	Average Foamate Flow, mL/min	Average Foamate percent of Influent
2,8-10	5	7.4	3.7
3,6	10	4.65	4.6

B. Foamate Production for the 10 Minute Detention Time

Trials	EHDABr, mg/L	Average Foamate Flow, mL/min	Average Foamate percent of Influent
1,5	150	2.7	2.7
3,6	200	4.65	4.6
4,7	250	4.75	4.9

Part B of Table 7 shows that 150 mg/L EHDABr at a 10 minute detention time produced an average foamate flow rate of 2.7 mL/min. and the foamate volume averaged 2.7% of the influent for these trials. An EHDABr concentration of 200 mg/L at the same detention time produced a foamate flow of 4.65 mL/min. and average foamate volume which was 4.6% of the influent volume. An EHDABr dose of 250 mg/L gave an average foamate flow rate of 4.75 mL/min. and foamate volume which averaged 4.9% of the influent volume.

These results showed that for a 10 minute detention time, an increase of EHDABr from 150 mg/L to 200 mg/L produced an increase in foamate flow. Increase of EHDABr dose from 200 to 250 mg/L resulted in a slight increase in foamate flow. These results supported the work of Grieves et al. (38) and Lemlich (35), who showed that foam production and foamate volume depended upon column collector concentration. Column observations also established that an increase of EHDABr dose from 150 to 200 mg/L resulted in an increase in foam density. Foam production may have increased only slightly when EHDABr concentration was increased from 200 to 250 mg/L because the maximum foam production ability of the system may have been achieved with an EHDABr dosage of about 200 mg/L. This was supported by EHDABr removal results (Figure 23), which showed that EHDABr effluent levels increased over time when flotation was conducted with 250 mg/L EHDABr.

Table 8 addresses the rate of foamate TSS collection. The information in this table was derived from foamate data in Appendix D. Part A of Table 8 shows that in trials with 200 mg/L EHDABr, the average foamate collection rate of TSS was 32 mg/min. The range of foamate TSS in these trials was 4004 to 5058 mg/L. The average foamate TSS collection rate of trials conducted at a 10 minute detention time was 19.4 mg/min. Foamate TSS in these trials ranged from 3922 to 4392 mg/L.

These results suggested that the 10 minute detention time produced more foamate TSS than the 5 minute detention time at a given EHDABr dose. This may have resulted from the 10 minute detention time providing better mixing and contact time of the EHDABr and the wastewater. The results of TSS flotation removal also showed that EHDABr at 200 mg/L gave better TSS removal at a 10 minute detention time than a 5 minute time.

Part B of Table 8 shows the rate of TSS collection in the foamate for different EHDABr doses in 10 minute detention time trials. EHDABr at 150 mg/L provided an average foamate TSS collection rate of 3 mg/min. Foamate TSS concentration ranged from 1096 to 1147 mg/L. A 200 mg/L EHDABr dose provided an average foamate TSS collection rate of 19.4 mg/min. The foamate TSS concentration range for

Table 8. Average Foamate TSS Collection

A. Foamate TSS Collection for 200 mg/L EHDABr

Trials	Detention Time, min	Foamate TSS mg/L	Average Foamate TSS Collection, mg/min
2,8-10	5	4004-5058	32.0
3,6	10	3922-4392	19.4

B. Foamate TSS Collection for the 10 Minute Detention Time

Trials	EHDABr, mg/L	Foamate TSS mg/L	Average Foamate TSS Collection, mg/min
1,5	150	1096-1147	3.0
3,6	200	3922-4392	19.4
4,7	250	3396-4056	17.2

these trials was 3922 to 4392 mg/L. A 250 mg/L EHDABr concentration gave an average foamate TSS collection rate of 17.2 mg/min. Foamate TSS concentration ranged from 3396 to 4056 mg/L for trials using 250 mg/L EHDABr.

These results supported the results of the flotation TSS measurements, which showed that 200 mg/L EHDABr at a 10 minute detention time removed TSS best. These results also supported the observation that 250 mg/L EHDABr was an excessive dose.

Comparison of Polymer Performance and EHDABr Performance

A 150 mg/L dose of the Betz polymer produced the best polymer color removal of 89%. EHDABr removed 77% of the wastewater color by coagulation and settling, and 89% of the color by continuous-flow, foam flotation. EHDABr doses providing this performance were 100 mg/L and 200 mg/L for coagulation and settling, and continuous-flow flotation, respectively. The following factors must be considered in evaluating whether polymer or EHDABr addition would be best for treatment of pulp and paper wastewater:

1) the relative costs of polymers and EHDABr;

2) the relative costs of coagulation facilities, and flotation facilities;

3) comparison of the amount and character of the waste products of coagulation and settling, and flotation and disposal costs of the waste materials;

4) comparison of the performance levels of polymers and EHDABr to the degree of color removal required.

SUMMARY AND CONCLUSIONS

The first part of this study concerned the evaluation of color removal by organic polymers in Kraft Process pulp and paper wastewater. Color removal ability was established through jar tests. The effects of pH and powdered activated carbon additions upon polymer performance in jar tests were also studied. The four cationic polymers chosen for this study were: Nalco 7107, Tretolite J-118, Betz 1190, and Magnifloc 581-C. The following conclusions about color removal effected by polymers were made:

1) A 150 mg/L dose of Betz polymer removed 87% of the wastewater color. This was the best color removal performance at the lowest polymer dose. The Nalco polymer removed 77% of the color with a 150 mg/L dose, the Tretolite polymer removed 79% of the color with a 150 mg/L dose, and the Magnifloc polymer removed 91% of the color with a 300 mg/L dose.

2) The Betz polymer performance was unaffected by pH variation of 3.5 to 9. Magnifloc performance was reduced at pH 3.5 to 6 and was unaffected by pH change of 6 to 9. The performance of the Nalco and Tretolite polymers decreased as pH increased from 3.5 to 8.

3) Color removal at less than optimal dosages of polymers was improved by PAC addition.

In the second part of this study, the ability of the surfactant, EHDABr, to remove color was studied.

Experiments with jar tests, batch flotation, and continuous-flow flotation were conducted with EHDABr. The effects of pH and PAC additions upon EHDABr performance in jar tests and batch flotation were established. The ability of EHDABr to remove color, TOC, and TSS by continuous-flow flotation was studied. The levels of EHDABr occurring in the flotation effluent were also established. The following conclusions were made about EHDABr performance:

1) EHDABr removed color bodies from the wastewater by precipitating them.

2) A 200 mg/L EHDABr dose at a 5 minute detention time removed 90% of the color and 64% of the TOC from the wastewater by continuous-flow flotation. This was the best color and TOC removal performance of continuous-flow flotation. Color and TOC removal by 200 mg/L at a 10 minute detention time was 90% and 44%, respectively. Effluent EHDABr levels were lower for the 10 minute detention time than the 5 minute detention time.

3) Continuous-flow flotation operations resulted in a net TSS increase in the wastewater. The TSS levels increased because of the precipitation of color by EHDABr. The best removal of the TSS formed occurred with 200 mg/L EDHBr. A 10 minute detention time produced the best TSS removal of 80%; TSS removal at the 5 minute detention time was 66%.

4) A 100 mg/L dose of EHDABr removed 77% of the wastewater color by coagulation and settling. Higher EHDABr doses did not improve color removal.

5) The performance of EHDABr in jar tests and batch flotation was not effected by pH variation of 3 to 9.

6) Color removal at less than optimal EHDABr dose was improved by PAC addition in jar tests and batch flotation.

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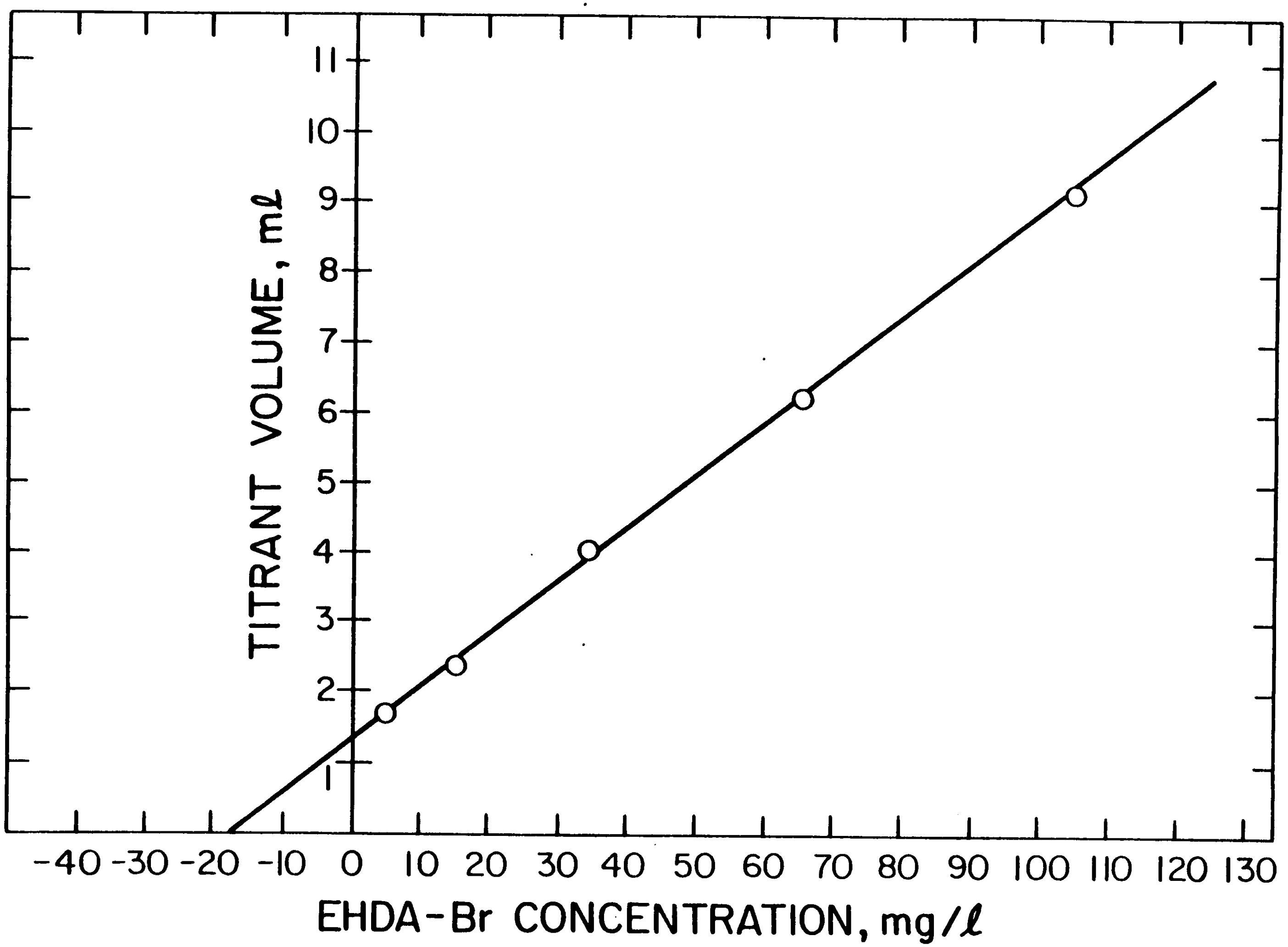

Appendix A. Standard Additions Characteristics of Titimetric Analysis of EHDABr in Kraft biotreated Wastewater

Appendix B. Results of Continuous-flow, Flotation Trials with EHDABr

Trial	EHDABr/ Det. Time	Time, min.	Color, PCU				TSS, mg/L				TOC, mg/L			EHDABr, mg/L	
			*R	M	E	%	R	M	E	%	R	E	%	E	%
1	150/10	0	2150	410	350	83	5	228	92	45	117	43	63	62	59
		22	2200	410	510	76	5	230	85	64	133	76	42	70	54
		70	2210	550	620	72	5	224	90	59	130	117	10	47	69
2	200/ 5	0	2350	320	250	89	85	475	162	66	172	69	59	77	61
		20	2310	270	210	91	96	472	150	63	173	69	60	58	71
		60	2410	320	230	90	65	465	170	63	172	61	64	60	70
		100	2260	320	230	90	82	463	186	60	176	71	59	61	70
3	200/10	0	2050	220	220	89	40	440	280	36	180	105	41	105	47
		22	1950	360	190	90	120	320	160	50	180	103	42	48	76
		45	1950	280	310	84	100	440	120	73	190	117	38	35	83
		70	1980	310	150	92	80	400	80	80	190	105	44	32	84
		100	1850	280	180	90	100	440	120	73	200	137	31	38	81
4	250/10	0	2050	280	160	92	76	426	94	77	195	90	53	42	84
		22	1950	280	210	89	84	436	144	67	192	120	37	46	82
		70	1950	280	310	84	156	528	196	63	197	103	47	75	70

* R= Raw influent, M= EHDABr/wastewater complex, E= Effluent, %= percent removed

Appendix C. TOC Analysis of 100 mg/L EHDABr

Sample	TOC, mg/L
1	1.094
	1.869
	1.802
2	2.011
	2.040
	1.986
3	2.211
	2.167
	2.107

Appendix D. Foamate Character in Continuous-flow, Foam Flotation Trials

Trial	EHDABr/ Det. Time	Sample Time, min	Foamate, mL	Influent, L	Foamate TSS, mg/L
1	150/10	70	200	6.92	1147
2	200/ 5	100	700	19.95	4004
3	200/10	100	480	9.92	4392
4	250/10	70	340	6.94	3396
5	150/10	73	190	7.28	1096
6	200/10	66	300	6.55	3922
7	250/10	62	290	6.14	4056
8	200/ 5	62	460	12.36	5058
9	200/ 5	60	480	11.98	4096
10	200/ 5	60	420	11.94	4280

Trial	Foamate TSS, mg	Foamate % influent	Foamate Color, PCU	Foamate Flow, mL/min	Foamate TSS Flow, mg/min
1	229	2.9	432	2.8	3.3
2	2802	3.5	244	7.0	28.0
3	2108	4.8	306	4.8	21.0
4	1145	4.9	275	4.8	16.5
5	208	2.6	395	2.6	2.8
6	1176	4.5	577	4.5	17.8
7	1176	4.9	352	4.7	19.0
8	2326	3.7	294	7.4	37.5
9	1966	4.0	324	8.0	32.7
10	1797	3.5	344	7.0	29.9

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