A COAGULATION STUDY: COMPARISON OF ALUMINUM SULFATE AND POLYBASIC ALUMINUM CHLORIDE

By

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To My Family,

George, Amal, and Fadi Jada'a,

for the joy and love they bring into my life

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INTRODUCTION

Coagulation is defined as the process whereby destabilization of a given suspension or solution is effected. That is, the function of coagulation is to overcome those factors which promote the stability of a given system. On the other hand, flocculation is defined as the process whereby destabilized particles, or particles formed as a result of destabilization, are induced to come together, make contact and thereby form large agglomerates. The coagulation-flocculation process could either (a) alter the surface properties of particulate material thus increasing the adsorptivity of the particles to a given filter medium or generating a tendency for aggregation of small particles into larger units, or (b) precepitate dissolved matter thereby creating particulate material for which separation by sedimentation and/or filtration is feasible. Such a conversion of the stable state of a given dispersion or solution to an unstable state is termed destabilization.

Impurities in water vary in size by about six orders of magnitude, from a few angstroms for soluble substances to a few hundred microns for suspended materials. The removal of a large proportion of these impurities in water and wastewater treatment is accomplished by sedimentation. However, because many of these impurities are too small for gravitational settling alone to be an effective removal process, the coagulation of these particles into large, more readily settleable aggregates is essential for successful separation by sedimentation.

Turbidity may be attributed to the presence of suspended matter, causing light scattering and resulting in lack of clarity of a water. Suspended matter giving rise to turbidity include silt, bacteria, algae, viruses, macromolecules and material derived from organic soil matter, mineral substances, and many industrial pollutants, Hence, it is apparent that removal of turbidity from water involves the removal of a wide variety of substances.

Most of the color in waters arises from organic compounds leached from soil and decayed vegetation. Surface waters may at times appear to be highly colored, because of the colored suspended matter, when in reality they are not. Color caused by the presence of suspended matter is referred to as apparent color, and is differentiated from color derived from colloidal organic sources, which is referred to as true color. Presence of coloring matter in water is an indication of pollution of some form, and therefore steps are invariably taken to remove color from waters during treatment.

The presence of such a diversity of material, ranging from clay particles through various biological forms to organic and inorganic substances in solution, occur to differing extents simultaneously in a given water source and thereby present considerable difficulties during both optimization and control of coagulation and flocculation. Optimization is influenced by the properties of the material present, characteristics of the different coagulants which may be applied, method of addition of coagulants to the water, and with a particular combination of such factors, the characteristics of flocs formed for a given set of flocculation parameters such as the magnitude of induced velocity gradients and their duration. Control is influenced largely by changes in water quality and, in cases where a range of materials are present, the relative concentration of each at a given time.

Trihalomethanes are organohalogen compounds named as derivatives of the gas methane "CH_4", as the name implies. When three of the four hydrogen atoms of methane are replaced by chlorine, bromine, or iodine, ten distinct compounds are possible by various combinations of those three halogen atoms. The different compounds are listed in Table I.

Current analytical methods applied to drinking waters can detect the chlorinated, brominated and the iodated trihalomethanes (1). However, because of the chemical instability of the iodated compounds, only trichloromethane (chloroform), bromodichloromethane, dibromochloromethane, and tribromomethane (bromoform) have been denoted in the trihalomethane regulation (2) as total trihalomethane (TTHM).

Trihalomethanes have been detected in drinking water supplies in varying concentrations as a result of the conventional practice for disinfecting waters, chlorination (3, 4). When chlorine (Cl_2) is added to water supplies containing organic matter, a chemical interaction takes place causing the formation of trihalomethanes and other halogenated forms of organic compounds (3, 4). The organic content of natural water supplies is derived partly from naturally occurring products of biological activity in the aquatic and the terrestrial environments, and partly from human activity. Those naturally occurring organics are referred to as "Humic Substances" (Humic Acids and Fulvic Acids) (5, 6, 7). These substances have been described as being predominantly aromatic, chemically complexed polyelectrolytes that are acidic, having an amorphous like structure (8, 9). They contain a variety of acidic functional groups such as carboxylic, phenolic, alcoholic, ketonic, quinnoid, and methoxyl. These groups are present in varying concentrations that affect the stability of the humic-substances in water. Under most pH conditions found in water supplies, humic substances are negatively charged macromolecules ranging in molecular weight from a few hundreds to tens of thousands. The concentration of humic acids in waters is very low, in contrast to fulvic acids that comprise the bulk of natural organic matter (8, 10).

Humic substances, both humic acids and fulvic acids, act as the main precursor for the trihalomethane producing reaction, although some other organic monomers such as aminophenol, dimethylphenol, diethylaniline and others have been found to produce high levels of chloroform ($CHCl_3$) upon chlorination (11, 12). The actual levels of TTHMs in drinking waters vary depending upon the concentration of chlorine applied, contact time, the type and chemical composition of the raw water, pH, temperature, season, and finally the treatment techniques practiced.

Trihalomethanes are characterized as being potential carcinogens (cancer-causing compounds), with possible health hazard implications. Due to the possible hazards associated with THMs, the United States Environmental Protection Agency (USEPA) added a Maximum Contaminant Level (MCL) for the THMs to the Primary Interim Drinking Water Regulations in 1979. This MCL has been set at 0.10 mg/ℓ and covers the most common types of THMs mentioned before (TTHMs). Water containing THMs in excess of 0.10 mg/ℓ is considered to be in violation of the USEPA's MCL.

Several approaches have been attempted and extensively studied to remove trihalomethanes from drinking waters, or at least minimize their concentrations to accepted levels in accordance with the Drinking Water Regulations. Five different methods have been listed as being the "Best Generally Available Treatment Methods for Reducing TTHMs Levels", usually called "Type I Technology":

1. Use chloramines ($Cl_2 + NH_3$) as an alternative or additional disinfectants. Although their disinfection action is not as effective as hypochlorous acid (HOCl) or the hypochlorite ion (OCl^-), very minimal TTHM formation is achieved.

2. Use chlorine dioxide (ClO_2) as an alternative or additional disinfectant. Again, very low TTHM levels are detected.

3. Move the point of chlorination, and substitute chloramines, hydrogen peroxide (H_2O_2) or potassium permanganate ($KMnO_4$) as preoxidants. TTHM reduction is good depending on specific modifications.

4. Improve the clarification process (coagulation, flocculation, sedimentation, filtration). TTHM reduction is usually good depending mainly on the process practiced, that includes variables such as the type and dose of coagulant used, flocculation time, type and method of filtration.

5. Use Powdered Activated Carbon (PAC) seasonally or intermittently, with the limit being 10 mg/ℓ. Post disinfection is required in this case. TTHM reduction is generally good.

This study was designed to treat the water for the removal of turbidity, organic matter, and trihalomethanes and their precursors; improving clarification was the method chosen. Water from Lakes Carl Blackwell and McMurtry, that are the main water supplies for the City of Stillwater, Oklahoma, were the subject of this study. The main objective of this study was to evaluate the efficiency of Polybasic Aluminum Chloride (PBAC) as a coagulant in reducing turbidity, organics, trihalomethanes and trihalomethane precursors in the water, as compared to Aluminum Sulfate (Alum), a conventional coagulant. Other objectives of this study were to (a) determine what dosage of each coagulant is required for both optimum turbidity and organics (humic substances) removal, (b) determine the mechanism by which PBAC acts as a coagulant in the course of the treatment process, and (c) study the preferential removal of the precursors based on molecular weight studies.

TABLE I

STRUCTURAL FORMULAS AND NAMES OF THE TRIHALOMETHANES (13)

Name	Formula
Trichloromethane (chloroform)	$CHCl_3$
Bromodichloromethane	$CHBrCl_2$
Dibromochloromethane	$CHBr_2Cl$
Tribromomethane (Bromoform)	$CHBr_3$
Dichloroiodomethane	$CHCl_2I$
Bromochloroiodomethane	$CHClBrI$
Chlorodiiodomethane	$CHClI_2$
Dibromoiodomethane	$CHBr_2I$
Bromodiiodomethane	$CHBrI_2$
Triiodomethane (Iodoform)	CHI_3

CHAPTER II

LITERATURE REVIEW

Coagulation

Reduction of the amount of particulate and dissolved organic matter in natural waters may be achieved through improved coagulation, by adsorption on suitable material such as Granular Activated Carbon (GAC), by membrane processes such as ultrafiltration or reverse osmosis, and by chemical oxidation. However, membrane processes and chemical oxidation are unlikely to be cost effective as compared to coagulation and granular activated carbon. Coagulation has several advantages over GAC including: (a) little or no required capital investment, (b) minimal increase in unit operating costs, (c) well known technology. However, coagulation may not be effective enough to achieve the required precursor reduction to allow chlorination and still meet the proposed THM standard. It is also less effective than GAC for the removal of organics of synthetic origin.

Since chlorination of most natural waters for bacterial and viral disinfection produces chlorinated byproducts, with potential chronic health risks, including the THM group, a major reassessment of water treatment practices has taken place in this country (14). Available technical options to meet proposed THM standards (15) include:

(1) Substituting new disinfectants for chlorine,

(2) Reducing the THM precursor concentration and altering the point of Cl_2 addition (elimination of pre Cl_2) and,

(3) Removing THM and other chlorinated compounds produced during treatment.

Should chlorination be retained as a potable water treatment method, removal of the trihalomethane precursors prior to chlorination is an obvious treatment strategy now used by several water utilities (16, 17). This treatment strategy is likely to be used more extensively in the future.

Coagulation of Humic Substances With Inorganic Salts

Humic substances consist of three broad categories of organic acids, as summarized in Table II. The fulvic acids appear to be most prevalent in natural waters; the humic acids occur least, and are more insoluble (8, 18). Most fulvic acids are of lower molecular weight, ranging from approximately 200 to 1000 (19). Humic acids exhibit molecular weight up to 200,000 and are of correspondingly larger size (20). The equivalent weight and charge density of these organic colloids are an approximate measure of their ease of coagulation. Generally the fulvic acids have a low equivalent weight and a correspondingly high charged density; that is, a large number of ionogenic (ion-producing) groups per unit mass (9). Humic acids have a high equivalent weight and a correspondingly low charge density (9). Thus higher doses of inorganic or organic coagulants may be needed to coagulate equal mass concentrations of fulvic acids as compared to humic acids. Humic acids in addition, appear to contribute more to color per unit weight, because of their large molecular size.

A number of structural models have been proposed for humus, notably the work of Dragunov (21), Christman and Ghassemi (22), and Kleinhempel (23). The structure of a humus molecule in its simplified form is given in Figure 1. It is a huge amorphous mass of polyhetero condensate with certain functional groups protruding from its surface that react with chlorine to produce trihalomethanes. The earliest proposed structure for a humic acid molecule was given by Dragunov (21) and is given in Figure 2. The functional groups shown in Figure 2 are some of those that have been shown in the literature to participate in the THM reaction (24, 25).

A number of investigations reported in the literature deal specifically with the coagulation of humic substances. Hall and Packham (26) concentrated humic substances from river water by means of a strongly basic macroporous anion exchange resin. The organics were eluted from the resin with 2 Molar Sodium Chloride and separated into humic and fulvic fractions. Studies were conducted on the coagulation of the humic and fulvic acid in the presence of kaolinite and alone. Hall and Packham found a stoichiometric relation between

TABLE II

CLASSIFICATION OF HUMIC SUBSTANCES (74)

Characteristics	Fulvic Acids	Humic Acids	Hymatomelanic Acids
Occurrence	Most prevalent	Least prevalent	Intermediate
M.W., size	Low M.W. (200-1000)	high M.W. (to 200,000)	in between
Equivalent Wt.	low	high	intermediate
Charge Density	high	low	intermediate
Light Scattering	low	high	intermediate

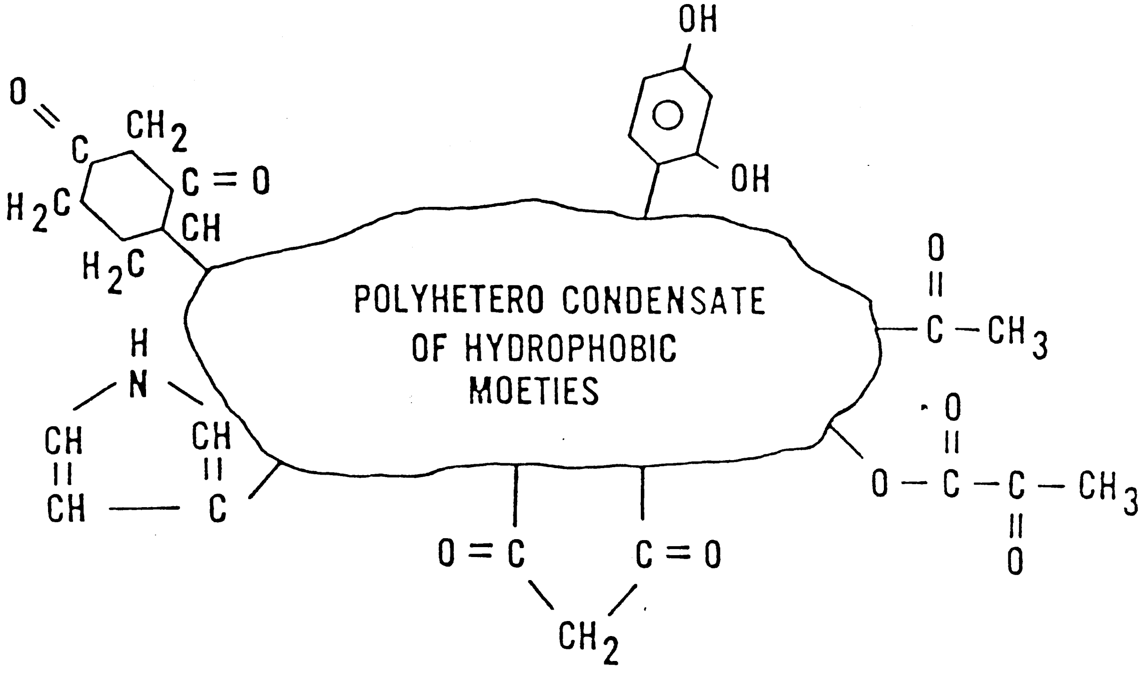


Figure 1: Model Humic Compound.

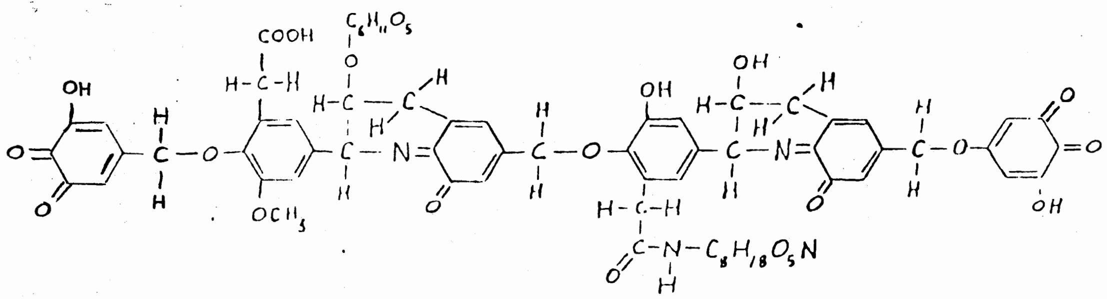


Figure 2: Earliest Proposed Structure of Humic Acid

the optimum coagulant dose for 50 percent organics removal and the raw water concentration of humic and fulvic material, with a higher coagulant dose required for fulvic acid than humic acid. The optimum pH for alum coagulation was 5-6, and for ferric coagulation a pH in the range of 3.5 to 4.5 was the optimum. They proposed that the primary method of coagulation with alum was the formation of insoluble aluminum humates or fulvates, because of specific chemical interaction between positively charged hydrolyzed aluminum species and carboxyl groups on the humic molecule. Above pH 5, the increase in the coagulant dose required for coagulation was thought to be caused by chelation of aluminum from increasing ionization of functional groups associated with the humic molecule. Hall and Packham also noted that the mechanism of color removal by Fe and Al appears to be similar. The two metals also seem to work equally well on an equivalent basis.

Albert (27) conducted a series of coagulation studies on individual organic compounds as well as on humic and hymatomelanic acids. The humic acid was extracted from Lake Constance using a technique similar to that of Hall and Packham (26), and hymatomelanic acids were concentrated from commercially available humic acid. A quartz suspension was employed to provide turbidity. Albert studied the influence of a number of operational variables on the removal of organics by coagulation, and he found that both alum and iron were effective in removing these humic substances. Much poorer removals of organic matter were observed in the coagulation of river waters than were observed with the isolated humic materials.

Mangravite et al. (28) determined the influence of humic acid concentration, alum dosage, and pH on the stability of humic acid salts. He showed that humic acid could be destabilized by soluble, hydrolyzed, polynuclear aluminum cations.

Edzwald (29) studied the effect of pH on the coagulation of humic acid with alum. He showed that high alum doses are required above pH 6. He showed that specific chemical interaction between positively charged aluminum cations and negatively charged humic acid resulting in charge neutralization and destabilization in the pH range of 4-6 takes place.

Consequently a stoichiometry between coagulant dose and humic acid concentration should exist.

Coagulation of humic substances with inorganic coagulants can be accomplished through two mechanisms of destabilization-charge neutralization or precipitation. Destabilization may be accomplished by charge neutralization resulting from a specific chemical interaction between positively charged aluminum species and negatively charged groups on the humic colloids. As described by Stumm and Morgan (30), the fixation of multivalent cations onto ionized groups on hydrophilic colloids may be caused by electrostatic or chemical interaction, reducing the charge of the particles and altering their solubility. Destabilization by this mechanism would be accomplished over the pH range of 4-6, and a stoichiometric relationship between the raw water humic concentration and the optimum coagulant dose would be observed. Humic substances can form water soluble and water insoluble complexes with metal ions. As the alum dose is increased, precipitation may occur; however, destabilization by this mechanism may incorporate humic material within $Al(OH)_3$ floc or coprecipitate it as aluminum humate.

In water treatment practice, the parameters significantly affecting the operation of a coagulation process for color-causing organics removal using Fe or Al salts include pH, coagulant dose, and raw water humics concentration. Black and Willems (31) coagulated two colored surface water with alum and ferric sulfate and showed that the optimum pH range with alum occurs at pH 5.2-5.7, while the optimum pH range using ferric sulfate is between 4-4.6. Black and Willems also noted that the flocs produced in the pH range of optimum coagulation had low values of Zeta Potential. Black et al. (32) collected six highly colored surface waters from different areas of the U.S. and examined the coagulation of these waters with ferric sulfate. They found color removal to be dependent upon pH and coagulant dose, with a stoichiometric relationship between raw water color and the optimum coagulant dose.

Magnesium has also been shown to be an effective coagulant for color removal by

Thompson et al. (33, 34). Several synthetic natural waters were utilized to develop a linear regression equation that related minimum magnesium dose to natural color, turbidity, alkalinity and hardness. Maximum reductions of 90-95 percent of the natural color were obtained through magnesium coagulation.

Coagulation of Humic Substances With Polymers

Very little information is published on the coagulation of natural organics or humic substances using polymers. Edzwald et al. (35) found that cationic polyelectrolytes can be used to destabilize humic acid. A stoichiometry was observed between the humic acid concentration and the optimum dosage of cationic polymer. Overdosing caused restabilization however. Narkis and Rebhun (36) examined the coagulation of humic and fulvic acids with a cationic polymer and found a stoichiometry between the coagulant demand and the concentration of anionic groups associated with humic or fulvic acids. They concluded that the cationic polyelectrolyte destabilizes the humics by charge neutralization involving a chemical reaction with carboxylate and phenolate groups on the humics.

An effective method to remove humics is using polymers in conjunction with alum. Bowie (37) achieved 75 to 95 percent color reduction using a cationic polyelectrolyte with alum in the coagulation several highly colored ground waters. Edzwald et al. (35) found that using high molecular weight polymers with alum is an extremely effective coagulation process for removing humic acid. An optimum polymer dosage was observed with overdosing resulting in restabilization of the humic acid. Excellent removal was reported for the coagulation of 5 mg/ℓ humic acid using 10 mg/ℓ alum and 1 mg/ℓ of a high molecular weight nonionic polymer over a pH range of 4.5 to 6.5.

Turbidity and Organics Removal

Most of the studies conducted in this area have been conducted with isolated humic and fulvic acid fractions, with clays added to provide turbidity. Hall and Packham (26) noted that the presence of fulvic acids in solution had a profound influence on optimum pH for removal of Kaolin turbidity. When kaolin and fulvic acids were coagulated with alum separately, the optimum pH value for their removal was 7.0 and 5.5, respectively. When they were combined and coagulated, the optimum pH was shifted to more acidic values. They found that higher coagulant doses were required for 50 percent turbidity removal than for 50 percent fulvic acid removal. They suggested that good organics removal would coincide with best conditions for turbidity removal.

Albert (27) studied the influence of organics on the coagulation of turbidity in river water and found that the optimum pH for turbidity removal was slightly higher than that required for optimum organics removal. In more recent studies Narkis and Rebhun (38, 39) investigated the coagulation of clay suspensions in the presence of humic and fulvic acids. In their studies, a cationic polyelectrolyte with a molecular weight of 330,000 was used as a coagulant. They found that the presence of humics in the solution or as complexed on clay inhibited coagulation.

Moore (40) examined the coagulation of fulvic acid in the presence of kaolinite, and found that the fulvic acid determines the alum dosage that causes effective coagulation. He concluded that the mechanism of coagulation consists of precipitation of an aluminum-fulvic acid compound which can physically enmesh kaolinite particles.

Semmens and Field (41) worked on real river water systems. They showed that the optimum pH for organics removal and turbidity removal from Mississippi River water are similar.

Operational Variables Affecting Coagulation

Rapid Mix

Albert (27) observed that niether the speed of addition of the flocculant nor the method of mixing had any significant impact on humic acid removal. Semmens and Field (41) observed that rapid mix time had no effect on the removal of dihydrobenzoic acid (DHBA) and resorcinol during coagulation with ferric sulfate. Bowie noted that rapid mix time has little effect on color removal (42).

Flocculation Time

Studies by Davis (43) indicated that when DHBA was added to an aged suspension of ferric hydroxide, the DHBA was completely adsorbed and the recycling process settled the sludge, suggesting some benefits from extending the flocculation time. Albert (27) investigated humic acid removals when humic acid was added to aged aluminum hydroxide and found that poorer humic acid removals were achieved with the aged suspension than with the fresh coagulant. Semmens and Field (41) found no benefit in soluble organics removal by ferric sulfate if the flocculant time was extended to 10 hours.

Order of Addition

It is reported by different researchers (44, 45) that the sequence of addition of the chemicals affects the optimum color and turbidity removal, and it varies for different waters. Kawamura (44) reported that lime should be added after or during alum coagulation for optimum turbidity and color removal. However, Jeffcoat and Singley (45) found that adding lime before alum coagulation increased turbidity removal, and they recommended this step to achieve optimum coagulation.

Coagulant Type

Hall and Packham (26) showed that both iron and alum are effective in removing fulvic and humic acids from water, they appear to have similar mechanisms, and they behave similarly on an equivalent basis. Edzwald et al. (35) found that while cationic polyelectrolytes can destabilize humic acids, a poor settling floc is produced. When they used high molecular weight polymers in conjunction with alum, they observed an effective coagulation process for the removal of humic substances, including destabilization and formation of floc readily separated by sedimentation. In this process, they added the polymer after the alum in order to bridge destabilize floc particles.

Coagulant Dosages

It has been shown that the concentration of the coagulant used is proportional to the concentration of humic and fulvic acid present in solution (26, 27, 29, 32). Other researchers showed that before turbidity can be removed, the coagulant must be added in sufficient amounts to destabilize the humic and fulvic acids (38, 39, 40).

The Influence of pH

The pH of the water during coagulation has a profound influence on the effectiveness of coagulation for organics removal. Organics removal is much better under slightly acidic conditions. For alum, the optimum pH is in the 5 to 6 range (46), whereas for Fe(III), the optimum pH range is 4 to 5 (34). The optimum pH range is influenced by the concentration of organics present in water. When the organics concentration is increased, the pH is shifted to slightly more acidic pH values.

Turbidity Removals

Albert (27) showed that the optimum pH for turbidity removal is higher than the optimum pH for organics removal in the treatment of river waters. However, some studies showed that organics are removed under the same conditions as for good turbidity removals (41).

Trihalomethanes in Drinking Waters

Since the findings of Rook (3) in 1974, and Bellar, Lichtenberg and Kroner (4) in late 1974, much research has been conducted on trihalomethanes. The major purpose of these studies was to identify their origin, the conditions under which they are formed, the influence of several variables on their formation, methods to remove them from drinking waters, and applicable rational modifications to the water treatment process.

Chloroform ($CHCl_3$) was first detected in polluted water by Novak and coworkers (47) in 1973, but they attributed its presence to contamination of the sampled water during the manipulation in the laboratory. Reports of the presence of chloroform and other trihalomethanes in finished waters occurred before 1974 elsewhere (48). Rook (3) identified four additional peaks in the chromatograms of chlorinated water, that have resulted from the chloro-bromination of naturally occurring humic substances. The four peaks corresponded to $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$. He also noted that the haloforms found after chlorination were not introduced by chlorine, but must have orginated in the water upon chlorination. Another study that called attention to the presence of trihalomethanes in finished drinking water was that done by Bellar and coworkers (4). They concluded that trihalomethanes were formed during the chlorination step of the water treatment process. In his first study, Rook (3) investigated the effect of humic substances on the formation of trihalomethanes. He suggested that the polyhydroxy benzene building blocks of the natural color molecules were responsible for the haloform reaction. In another study, Rook (49) discussed the chlorination of fulvic acid extracts from peat. Stevens et al. (12) studied the chlorination of commercially available humic acid of unknown composition. Both studies proved that significant yields of chloroform can result from chlorinating waters.

Because of those findings by the different researchers, a survey in early 1975 of 80 water utilities was initiated in the United States. Seventy nine of the 80 water utilities practiced free residual chlorination or combined residual chlorination (13). The result of the National Organics Reconnaissance Survey (NORS) showed that all of the water utilities that used free chlorination in the course of treatment had varying concentration of THMs in their finished drinking water. The THMs were formed somewhere during the treatment process (50). Another survey conducted in 1975 and 1976 (51) confirmed the earliest findings. In this survey, samples were collected from 113 locations during three different seasons and results showed that chlorination produced trihalomethanes and the problem is widespread in water treatment plants around the U.S. Since the chlorine was reacting with naturally occurring organics, trihalomethanes probably have been occurring for as long as chlorine has been in use in water treatment.

Since the discovery of trihalomethanes in 1974 in drinking water as a result of chlorination, much research has been conducted. Subjects addressed include: 1) how trihalomethanes affect the health of consumers, 2) how trihalomethanes should be measured, 3) how water quality conditions influence trihalomethane formation, 4) what treatment techniques could be used to reduce trihalomethane concentrations in distributed water, 5) what effect altering treatment procedures to control trihalomethanes will have on the bacteriologic quality of distributed water, and 6) the cost of the various treatment possibilities.

Trihalomethanes are formed when chlorine is added to the water systems as a result of a reaction that takes place between the chlorine and the precursor material present in the water (3, 4, 12, 49). The course of the traditional haloform reaction is outlined in Figure 3. The reaction consists of alternate hydrolysis and halogenation steps, with the first ionization step being the rate determining step (52). It is likely that this is also the case for halogenation of natural aquatic humus. With the exception of the mono-ketone moiety, the functional groups illustrated in Figure 1 are those that rapidly execute the first ionization step.

A general equation for the formation of trihalomethanes is:

$$\text{Free } Cl_2 + \text{Precursor Material} + Br^- \text{ and/or } I^- \rightarrow$$

$$\text{Trihalomethanes} + \text{Other Halogenated Byproducts}$$

This reaction assumes a complicated mechanism that involves the attack of the aqueous halogen on the natural aquatic humic substances (humic acids and fulvic acids), and other precursor material such as algal extracellular products (53), citric acid (54), resorcyclic acid (54), and other monomeric organics such as aminophenol, dimethylphenol, diethylaniline (11).

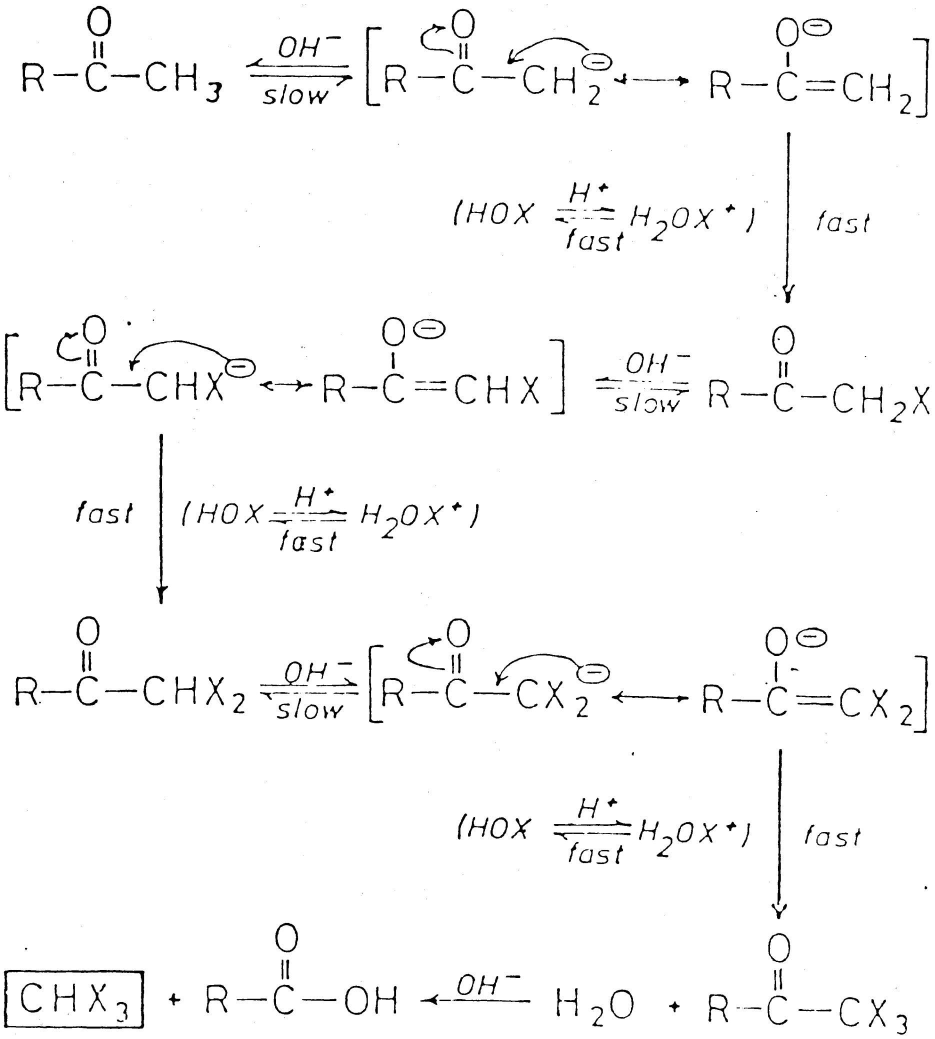


Figure 3: The Reaction Pathway of the Haloform Reaction.

Factors Affecting Trihalomethane Formation

The trihalomethane reaction is a very slow reaction. The reaction takes place over several hours, sometimes resulting in significant increases after 24 hours of contact. The rate of the trihalomethane reaction can also vary a great deal among sources of precursor material that have different chemical compositions. Several factors influence the trihalomethane levels found in drinking waters, and some of the significant ones are pH, chlorine dose, chlorine contact time, seasonal variations and bromide and iodide concentration.

pH Effects

The pH has a profound influence on the THM reaction. This effect has been discussed and illustrated by several researchers (12, 25, 55, 56). They showed that a THM reduction of well over 50% can be obtained by reducing the pH from 9 to 7. The probable explanation for this is that the higher pH results in a more efficient molar yield of trihalomethanes. THM concentrations can be reduced by maintaining low pH during disinfection and then raising the pH once a free Cl_2 residual is no longer present (after NH_3 addition). Morris and Baum (25) however, have found that THM formation occurs in the absence of a Cl_2 residual once the pH is raised. This phenomenon is attributed to formation at low pH of chlorinated intermediates that hydrolyze to form THMs once the pH is raised.

Stevens et al. (12) showed that if the reaction is given sufficient time, the yields for different pH systems may be similar. The increase of THM formation rate with pH is expected, because the classical haloform reaction is base catalyzed, but this explanation is oversimplified because of the complex structure of the humic substances that are involved in the reaction.

An alternative explanation for the effect of pH on rate and yield with humic acid precursor has been given by Christman (57). He suggested that the macromolecule may be "opening up" by mutual repulsion of the negative charges at high pH, thus increasing the availability of additional reactive sites on the molecule.

Chlorine Dose

When the free Cl_2 dose is increased beyond the demand, only a slight influence on THM formation rate or yield occurs when the precursor is kept constant (58). Work by Kajino and Yagi (59) showed that once Cl_2 demand was satisfied, increasing Cl_2 residual concentrations had little influence on chloroform yield in the 8 hours reaction time. Both similar (60, 61) and contrary (49, 62) results have been reported while conducting tests with different sources of precursor. Combined Cl_2 does not cause the formation of trihalomethanes (12).

Chlorine Contact Time

The formation of THM under natural conditions is not instantaneous. However, in some reaction conditions, the formation of THMs may be completed in less than an hour, and in other circumstances, several days are required before the maximum yield of THMs occurs. The precise effect on the kinetics of the THM reaction of various parameters influencing its formation or yield of the reaction at completion are difficult to predict because of the complexity of the reactions between aqueous free Cl_2 and the mixture of precursors of largely unknown structure (63).

Seasonal Variations

It has been reported by several researchers that the variations in THM concentration in the water depend largely on the characteristics of the watershed and the temperature (12, 64). Data taken from the Ohio River showed that when the water was chlorinated, increasing the temperature had a positive effect on THM formation (12). A corresponding seasonal variation has been shown to be largely a temperature effect at a water utility using the same source. Data collected by the Ohio River Valley Water Sanitation Commission (ORSANCO) showed that the finished water TTHM concentrations varied seasonally at several water utilities, and were lower in winter when water temperature was lower, although data was not controlled for possible variations in precursors and other treatment condition variables (65).

Bromide and Iodide Concentrations

Bromide and iodide are recognized as important precursors in the formation of some of the trihalomethanes. Bromide and iodide are oxidized by aqueous Cl_2 to species capable of participating in organic substitution reactions resulting in the formation of pure-and-mixed-halogen trihalomethanes. Br^- is oxidized to intermediates such as Br_2, HOBr, OBr^-, with some BrCl and $BrCl_5$ (66). These intermediates apparently participate in the halogenation step of the THM reaction sequence much more effectively than does Cl_2. This effect was observed by Kleopfer (67) and others (68, 69). They observed that the presence of bromide increases the yield of THMs for a given Cl_2 dose. When Bunn et al. (1) chlorinated Missouri River water in the presence of added fluoride, bromide and iodide, they observed the formation of all ten possible THMs. Symons (50) reported that bromine substitution is favoured over chlorine, even though Cl_2 is present in large excess compared with the initial bromide. In addition, he showed that the total molar yield of THMs appear to increase with increasing bromine substitution.

There is some evidence that bromide may influence the rate of the THM formation reaction as well as the THM yield. This was shown by laboratory studies conducted by Trussell and Umphres (56). They showed that the rate of THM formation reaction seemed to be higher in samples spiked with bromide.

Health Effects

Chloroform has been shown to be rapidly absorbed on oral and intraporitoneal administration and to be subsequently metabolized to carbon dioxide (CO_2), chloride ion (Cl^-), phosgene ($COCl_2$), and other unidentified metabolites. The metabolic profile of chloroform in animal species such as mice, rats and monkeys is very similar to that in humans (13).

Mammalian responses to chloroform exposure include central nervous system depression, heptatoxicity, nephrotoxicity, teratoginicity, and carcinogenicity (13). These responses are discernible in mammals after oral and inhalation exposures to high levels of chloroform ranging from 30 to 350 mg/kg of body weight, with the intensity of response being dependent upon the dose. Less toxicologic information is available for the bromine-containing trihalomethanes, but mutagenicity and carcinogenicity have been detected in some test systems. Physiological activity is suspected to be greater for the bromine-containing trihalomethanes than for chloroform (13). Harris (70) indicated that brominated organic compounds are usually much more potent as carcinogens than their chlorinated counterparts, and a few parts per billion of bromoform in drinking water may represent a far greater cancer hazard than a few hundred parts per billion of chloroform.

Human epidemiologic evidence (13) is inconclusive, although several studies have found positive associations with some cancer cases. But because of various limitations in the epidemiologic methods, difficulties with the water quality data, and problems with the individual studies, the present evidence does not lead to a firm conclusion that an association exists between contaminants in drinking water and cancer mortality or morbidity; causal relationships cannot be proven on the basis of results obtained from epidemiologic studies. However, epidemiologic studies provide sufficient evidence for maintaining the hypothesis that a health risk may be occurring and that the positive relationships may be reflecting a causal association between constituents of drinking water and cancer mortality.

On the basis of the available toxicologic data, chloroform has been shown to be a carcinogen in mice (13) and rats at high dose levels. Since its metabolic pattern in animals is very similar to that in humans, chloroform should be suspected of being a human carcinogen.

Because of the suspected health effects and risks associated with trihalomethanes, the Trihalomethane Regulation was promulgated on November 29, 1979 (2, 71).

THM Reduction by Coagulation

Morris (72) reviewed the problem of THM production from the chlorination of water supplies and has suggested several treatment steps including coagulation-filtration before chlorination for reducing the concentration of precursor organic matter. Rook (49) provided limited data on the reduction of precursor organic matter using Fe(III). He noted poor removal of color; however, the coagulation experiments were conducted at pH of 7.6-7.8, which is not a favourable pH range for color removal using inorganic salts. Stevens et al. (12) concluded that the precursor to THM production during chlorination is probably a complex mixture of humic substances and simple low molecular weight compounds containing the acetyl moiety. They were using settled Ohio River water, and they showed that conventional alum coagulation removed most precursors from raw water.

Babcock and Singer (73) examined the extent to which chloroform production is reduced when alum coagulation of humic and fulvic acids is practiced before chlorination. Chlorination of the humic acid left after coagulation yielded less chloroform and consumed less chlorine than an equivalent amount of untreated humic acid, indicating that alum coagulation selectively removes that fraction of the humic material most responsible for chloroform production. Alum coagulation of fulvic acids also showed selective removal of chloroform precursors.

Kavanaugh (74) conducted studies for the Contra Costa County water district on a modified coagulation process for improved THM precursor removal. The study indicated that the coagulant dose and pH were extremely important control parameters. The regions for optimum turbidity and THM removal were similar but not equivalent, but the solution pH was not constant during chlorination for the THM removal.

Coagulation Using Polybasic Aluminum Chloride

Little work has been reported in the literature about the use of polybasic aluminum chloride (PBAC) as a coagulant in the water treatment process. PBAC solutions can be obtained by the partial neutralization of an aluminum chloride solution. The composition and the characteristics of these solutions depend upon a number of factors (75).

O'Melia and Dempsey (75) investigated the chemical active species in PBAC, and discussed the ability of PBAC to remove turbidity and humic substances with possible applications in water treatment practice. They concluded that a number of parameters determine the active species in the aluminum salt. Some of these parameters are the concentration of the stock Al solution, the type of the basic titrant, extent of mixing, temperature, and aging time of the final product. These factors can be manipulated to obtain different species of Al in water. Their results indicated that lower doses of PBAC with an OH/Al ratio equal to 1.8, than alum, are required for the destabilization of contaminants at a pH less than 6. They stated that PBAC may have advantages over alum when the water is at slightly acidic pH levels. Thebault et al. (76) investigated the mechanism underlying the removal of four micropollutants by using PBAC and $FeCl_3$. The tests were conducted on water from the Western Paris Suburb Distribution System (Le Pecq-78). The water did not contain any mineral colloids, and was artificially polluted with the micropollutants to the desired concentration. The coagulation-flocculation experiments were carried out using a standard jar test procedure. They had generally poor reduction rates of the four micropollutants, except for the case of benzopyrene. In the case of phthalates, the reduction rate increased with increasing the number of CH_2 groups in the alkyl chain. Since the water had originally no mineral colloids, they concluded that coagulation-flocculation was responsible for the removal of the micropollutants. They also observed that the removal rates are independent of the coagulant used.

Feissenger and Bersillon (77) observed that an $AlCl_3$ solution (0.1 M) that was neutralized with NaOH to OH/Al ratio (r) equal to 2.5 was more effective in removing turbidity from suspension at a pH of 7 than solutions receiving more or less neutralization with base. Similar results were reported by Bottero et al. (78), with the most effective coagulation at a pH of 7.0 observed for $AlCl_3$ solution neutralized to $r = 2.5$ and aged for 24 hours.

Albert noted that the sludge produced from PBAC was denser than the sludge produced from alum (79).

CHAPTER III

MATERIALS AND METHODS

Raw Water

Raw water from Lakes Carl Blackwell and McMurtry were the subject of this study. These lakes act as the source of drinking water for the City of Stillwater, Oklahoma. The water was withdrawn from the influent to the Oklahoma State University (O.S.U.) water treatment plant. The general characteristics of this water are listed in Table 3 (80).

Jar Test Procedure

The most common technique for evaluating the performance of a certain coagulant in a bench-scale type study is the jar test. The jar test is a traditional method that has been used for a number of years around the U.S., and has been applied to determine the efficiency of a certain coagulant under different operating conditions (81).

The jar test is a simple procedure that involves the mixing of a coagulant with water. Through this procedure, different variables can be controlled, and the desired factors can be studied individually depending on operating conditions. Jar tests have some advantages and disadvantages. The advantages are: (a) it does not involve the use of any sophisticated equipment, (b) it is easy and quick to run, and (c) it can be repeated a number of times in a short period of time and still get reproducible results within the same operating conditions and efficiency of operation. The disadvantages are: (a) it is very difficult to reproduce the existing conditions in a jar test in a full-scale type process from a hydraulic point of view, (b) it is very hard to determine the nature of the flocs if they are to be determined visually, and (c) the characteristics of water in a full-scale process are always subject to changes during operation, while in a jar test the characteristics of water are

TABLE III

WATER TREATMENT PLANT, OKLAHOMA STATE UNIVERSITY, STATISTICAL ANALYSIS OF RAW WATER QUALITY JANUARY 1974 THROUGH NOVEMBER 1979 (80)

Parameter	Percent Less Than or Equal to Probability of Occurrence	
	50%	95%
Turbidity (NTU)	24	46
Total Hardness (mg/ℓ)	156	192
Total Alkalinity (mg/ℓ)	108	142
pH	7.9	8.3

constant in one single jar.

Overall, jar testing is a good quick method for the evaluation of different operating variables in the laboratory. In this particular study, jar tests were performed on the raw water using alum and polybasic aluminum chloride.

All jar tests were performed in sets of 6 jars each, and were conducted on a Phipps and Bird multiple lab stirrer, using one liter beakers. The volume of the sample in each beaker was 1000 ml. Mixing paddles had a surface area of three square inches (three inches wide and one inch high), and were placed one inch above the bottom of the beakers. The jar test procedure consisted of a rapid-mix step at 100 rpm, that was controlled over a period of 30 seconds. A second step of slow-mixing (flocculation) at 30 rpm followed the rapid-mix step, and this was done over a period of 20 minutes. Finally, the solution was allowed to sit quiescently for at least 30 minutes to allow the particle aggregates to settle from the suspension. All coagulants were added at their predetermined doses to the beakers prior to the rapid-mixing step. Samples for analyses were withdrawn from 2-3 cm below the surface of the water in the different jars.

Aluminum Sulfate

Aluminum sulfate (alum) was one of the coagulants used in this study. It was obtained from the O.S.U. water treatment plant, Stillwater, Oklahoma. A stock solution of 4 g/l was freshly prepared prior to the jar tests. Different doses of the stock solution were added to the different jars depending on the desired concentration. One jar served as the control in each set. Each set consisted of the following concentrations: 0, 10, 20, 30, 40 and 80 mg/l of coagulant.

Polybasic Aluminum Chloride

Polybasic Aluminum Chloride (PBAC) solution was prepared in the lab according to Fiessenger and Bersillon (77). An $AlCl_3$ solution was partially neutralized through the addition of NaOH. The 0.5 N NaOH solution was added to the 0.5 M $AlCl_3$ solution at a rate of 2.1 ml/min with the mixture being constantly mixed at a high speed using a magnetic stirrer bar. When addition of NaOH was complete, mixing was stopped, and the solution was diluted with distilled water to 250 ml. After dilution, the solution was mixed thoroughly and allowed to sit for one hour before use in the jar test (77).

PBAC was prepared with two different neutralization ratios $(\frac{OH}{Al})$. The two ratios (r) values were 2.5 and 1.8. PBAC solutions with the two r values were applied to the jar test in the same manner and at the same concentration as alum.

Chlorine Solution

The chlorine stock solution used in this study was prepared from $Ca(OCl)_2$ obtained from Aldrich Chemical Company. The solution concentration was 4 g/ℓ to give a Cl_2 concentration of 2.5 g/ℓ. This was prepared fresh prior to each jar test run, and was used in both pre- and post-chlorinating the water under investigation. In case of pre-chlorination, the Cl_2 solution was added after the addition of the coagulant, with the concentration being 4mg/ℓ as Cl_2. The post-chlorination dose was chosen to be 1 mg/ℓ, and was added right after the period of 20 minutes of flocculation.

Turbidity

Residual turbidity was determined with a Hach Ratio Turbidity Meter model 2100 A located at the O.S.U. water treatment plant. Turbidity was recorded as Nephelometric Turbidity Units (NTU). The turbidimeter was calibrated daily using an 18 NTU calibration standard that is commercially prepared by Hach Chemical Co.

Trihalomethane Analysis

Samples for THM analysis were collected from the jars after the water had been allowed to settle for at least 30 minutes. Samples were collected in 40 ml glass vials with plastic screw-on caps containing a teflon sealing liner. No air bubbles were allowed in the vials. Samples for instantaneous THM analysis were taken in vials containing excess sodium thiosulfate to stop the THM formation after Cl_2 had been added. Samples were then stored at 5 °C until analysis. Samples for terminal THM analysis were incubated at 20 °C for 72 hours, after which period they were quenched by adding excess sodium thiosulfate.

A great deal of precaution was taken during the procedure of collecting the samples to prevent any contamination of glassware and the teflon accessories. All glassware, teflon seals and caps were washed with a detergent and rinsed with activated carbon water. The caps were then submerged with the teflon seals in activated carbon water for a period of 24 hours prior to use. Caps were placed afterwards in a 45 °C oven for few hours to dry. All glassware (vials, test tubes and pipettes) was placed in chromic acid for at least 24 hours. After it was removed from the acid, it was washed with tap water, then rinsed at least three times with distilled water and activated carbon water respectively. All glassware was then placed in a 200 °C oven for a period of at least 8 hours. Glassware was then removed, allowed to cool to room temperature, and was used immediately to avoid any contamination.

Standard solutions of the trihalomethanes were prepared gravimetrically by syringing the trihalomethane standards into methanol. Methanol was obtained from Fisher Scientific Company. Chloroform, dichlorobromomethane, dibromochloromethane, and bromoform were obtained from Aldrich Chemical Company. The procedure for preparing the stock standard solution of each trihalomethane is as follows:

1. A 10 ml volumetric flask with a glass stopper was filled approximately with 9.8 ml of methanol.

2. The flask was allowed to stand for a period of 10 minutes unstopped to evaporate the alcohol from the wetted surfaces.

3. The flask was weighed unstoppered.

4. Two drops of the referenced standard were added immediately to the flask using a 10 μl syringe (Hamilton 710-N). Care was taken to make sure that the drops fell directly into the methanol.

5. The flask was reweighed again.

6. Methanol was added to complete the volume to 10 ml.

7. The stopper was placed, and the solution was mixed thoroughly.

The same procedure was carried out to prepare all 4 different stock standard solutions. After preparing a single standard solution of each trihalomethane, a solution containing all four trihalomethanes was prepared. This was prepared by micropipeting 100 μl of each standard into a fifth 10 ml volumetric flask containing methanol. Methanol was then filled up to the 10 ml mark. The solution was then mixed and all 5 solutions were stored at 5 °C until time of use. Aqueous calibration standards were freshly prepared prior to each analysis by micropipeting various volumes of the combined standard solution into 100 ml volumetric flasks which contained activated carbon water. A series of dilutions were then prepared in different test tubes using again activated carbon water. A calibration curve was obtained for each trihalomethane covering a range of 10 to 100 ppb. This was done to insure that all results could be read on the calibration curve.

A liquid-liquid extraction method (82) was applied to analyze THM on the dilution series and the unknowns. A 10 ml volume of all samples were transferred into 15 ml glass test tubes, and 1 ml of pentane was added using a gas tight syringe (Hamilton #1001). The pentane was obtained from Supelco, Inc., and was distilled in glass, and further treated with sodium metal. The glass test tubes were then capped with teflon lined screwed caps, and shaken vigorously and uniformly for a period of 1 minute to insure complete extraction of the haloforms by the pentane. Then they were allowed to sit for at least two minutes to allow complete separation of the pentane layer from the water layer. A 3 μl aliquot of the pentane layer was then withdrawn using a syringe (Hamilton #701) and injected into gas chromatograph.

A Hewlett Packard Gas Chromatograph Model 7626A equipped with a Ni^{63} electron capture detector Model was used for the analysis of the trihalomethanes. A 6 foot x ¼ inch glass column packed with 4 percent SE-30 and 6 percent OV-210 on 80-100 mesh gas chrom Q support was used to perform the separation. The carrier gas was 5% methane + 95% argon.

The instrumental conditions for the gas chromatographic analysis were as follows:

Carrier Gas Flow Rate	40 cc/min.
Oven Temperature	70 °C isothermal
Inlet Temperature	210 °C
Detector Temperature	175 °C
Attenuation	10^2
Pulse	50

All analyses were quantitative and were done by using respective peak areas calculated by Hewlett Packard Integrator Model 3380A. After analysis on each set of samples were done, the temperature on the detector, oven and inlet was raised by 50 °C, and left for at least 6 hours to insure removal of all impurities before the next set of analysis was carried out.

Total Organic Carbon Analysis

All samples collected for total organic carbon (TOC) analysis were acidified to a pH of 2.0 to eliminate any interference from inorganic carbon compounds. Samples were acidified by addition of a 1 N solution of H_2SO_4, and were preserved at 5 °C. Standard solutions for the analysis were prepared according to Standard Methods (83). All samples were first analyzed for total carbon content then for inorganic carbon content. In the first operation, a 20 μl sample was syringe-injected into the furnace, and swept into a Hastelloy catalytic combustion tube containing cobalt oxide impregnated in asbestos fibers as the packing material. The source of the carrier gas was oxygen. The combustion tube was thermostatically controlled at 950 °C. After injection, the sample is carried by the oxidant into the combustion tube, where all the water is vaporized and the carbonaceous material (inorganics + organics) are oxidized to CO_2 and steam. The carrier flow carries the cloud of CO_2 and steam out of the furnace where the steam is condensed and removed. The CO_2 is swept into the I.R. analyzer where it is measured. The CO_2 content is recorded on a strip chart recorder interfaced with the I.R. detector. The CO_2 content is recorded on the chart as a peak. The peak height is a measure of the CO_2 present, which is directly proportional to the concentration of total carbon in the sample being injected. By using the standard solutions, the chart was calibrated in mg total carbon per liter of sample. In the second operation, a similar-sized sample is also syringe-injected into a flowing stream of carrier/oxidant and swept into a second glass combustion tube which contains quartz chips wetted with 85% H_3PO_4. The tube temperature is maintained at 150°C. The acid-treated tube causes the release of the CO_2 from the inorganics present in the water. In the same manner as before, the CO_2 is then carried by the carrier gas along with the water vapor, which is condensed and removed. The CO_2 is swept into the I.R. analyzer. The amount of CO_2 is recorded on the strip chart recorder as a transient peak. The peak height corresponds to the amount of CO_2 being present, which is proportional to the inorganic carbon present in the sample being injected. By using standard solutions, the chart was calibrated in mg of inorganic carbon per liter of solution. The amount of inorganic carbon calculated was then subtracted from the amount of total carbon calculated, to get the total organic carbon in mg of T.O.C. per liter of sample. All analysis was performed on a Beckman 915 Total Organic Carbon Analyzer.

Electrophoretic Mobility

Electrophoretic Mobility (E.M.) was measured with a Zeta Meter manufactured by Zeta Meter Incorporated. Particle charge was evaluated for raw water treated with PBAC at different pH values to try to assist in determining the mechanism by which PBAC acts as a coagulant. A sample volume of 20 ± 5 ml of the settled water was withdrawn from the jars at a depth of 2-3 cm below the water level. Particle charge and migration velocity were determined under the microscope, and the electrophoretic mobility was determined using the following equation (84).

$$\text{Absolute E.M.} = \frac{\mu.\ \text{cm}}{\text{v. sec.}}$$

where:

μ = the distance the particle travels in microns.
cm = 10 (distance between ends of electrophoresis cells).
v = voltage applied.
sec = average time required for one particle to travel over one division of electrophoresis cell.

The calculated value was then multiplied by 13.5 to obtain Zeta Potential (Z.P.) value in m.v. (85).

Molecular Weight Analysis

Raw water samples treated with optimum doses of alum and PBAC at four different pH values of 6.0, 7.0, 8.0 and 8.5 were chosen for molecular analysis. Samples of 500 mls each were concentrated by lyophilization which was conducted at the Biochemistry Department of O.S.U. Lyophilization took place over a period of at least 24 hours. The concentrated samples were then stored at 5 °C.

A G-75 Sephadex column was used in this study for the molecular weight analysis. The G-75 Sephadex dextran gel was manufactured by Pharmacia Fine Chemicals of Uppsala, Sweden. The gel preparation and packing procedure was done as described in Gel Filtration Theory and Practice Manual (86). The buffer solution used to swell Sephadex gels contained a 0.01M solution of K_2HPO_4 and KH_2PO_4, and 0.02 percent concentration of sodium azide, which acts as a bacteriacide. The pH of the buffer solution was 7.9 - 8.0.

The column used was a 3500 HPLC series column. The physical dimensions were 1.5 cm inside diameter, 100 cm in length, and had a volume of 170 ml. The column was made of glass with teflon end plates, bed supports and tubing.

The column was operated in the down flow mode. The flow rate was adjusted to 30 ml/hour. The elutrant was collected in 2.5 ml fractions in 80 glass tubes by a Gilson FC-80 micro-fractionator, operating in a drop counting mode.

The glass tubes were washed with chromic acid first then with activated carbon water, and then placed in a 200 °C oven for at least 8 hours before they were used to collect the elutrant from the column. The column was calibrated using different compounds of known molecular weights. The different compounds are listed in Table IV. The marker compounds were dissolved in activated carbon water in sufficient concentration to insure that their organic content (u.v. absorbance) could be determined. Samples of 1 ml were then injected individually using a syringe onto the top of the column, with the column outlet valve being closed. The outlet valve was then opened so that the sample would be allowed to travel through the column carried by the buffer solution. After injecting the marker solution, the organic content of the elutrant was determined using a Hitachi Ultraviolet Spectrophotometer Model 800A with the u.v. absorbance being measured at a wavelength of 254mm in 1 cm quartz cell.

Pilot Plant Features

A pilot plant was constructed in the laboratory (87) to simulate the features of the O.S.U. water treatment plant at Stillwater. All units of the pilot plant were constructed out of ¼ " thick plexiglass sheets. The raw water was pumped from the intake structure of the O.S.U. water treatment plant to a constant head holding tank which had a capacity of 13.2 gallons. Pumping to the tank was at a rate of approximately 1.5 gallons per minute. Water was then allowed to flow to a rapid mixing unit with dimensions of 7.0"(L) x 7.0"(W) x 24.0"(D). The influent line was ½ " in diameter and was located one inch above the bottom of the unit, so discharge was close to the mixer blades. The mixer had a power of 1/50 H.P. and was controlled by a voltage regulator. Two pumps manufactured by Cole-Palmer Co. were used to pump the coagulant and the Cl_2 solution to the rapid mixing tank. The tank had a detention time of 90 seconds. The water then flowed out of the rapid-mix tank to a flocculation tank by gravity through a ½ " plexiglass tubing. The flocculation tank dimensions were 12.5"(W) x 24.5"(L) x 18.0"(D). Three baffles were located in the unit, one in the center of the unit, and one each at about one inch in front of the influent and port discharge weir. The baffles were used to prevent short circuiting in the flocculation unit. Hydraulic

Table IV

Molecular Weight Markers

Compound	Molecular Weight
Blue Dextran 2000	2,000,000
Ovalbumin	43,500
Trypsinogin	23,560
Bacitracin	1,430
Raffinose	595

detention time in the flocculation tank was 12 minutes. Two mixers of 1/50 H.P. were used and were controlled again by a voltage regulator.

The effluent from the flocculation tank was directed into a sedimentation tank through a ½″ plexiglass tubing. The sedimentation tank was 17.5″(L) x 17.5″(W) x 51.0″(D), with a detention time of 85 minutes. The water flowed from the flocculation tank to the sedimentation tank by gravity.

The effluent from the sedimentation tank was directed into a plastic Y tube that allowed the water to flow to two dual media filters of equal dimensions. The filters were constructed of plexiglass columns that had a length of 72″. The filters were 4″ in diameter. The two media in each filter were sand and coal, with coal sitting on top. The effective size of sand was 0.4-0.5 mm, with a uniformity coefficient of 1.5. The effective size of coal was 0.8-1.0 mm, with a uniformity coefficient of 1.2. The sand occupied a depth of 6″, while coal had a depth of 12″. The hydraulic loading on the filters was 3.5 gpm/ft^2. The filters were backwashed with tap water for at least 15 minutes at a rate of 15 gpm/ft^2 before each pilot plant run. The pilot plant features are shown in Figure 4.

During the pilot plant operation, a constant flow through the entire system was regulated by the filter effluent control valve. The manual monitoring flow meter was manufactured by Fisher Scientific Co. A constant detention time was maintained in the rapid-mix unit, the flocculation unit, and the sedimentation tank. The intensities of mixing in the rapid-mix and the flocculation tanks were regulated by means of the voltage regulator. The whole system was allowed to run for at least two hours before any samples are collected to assure stabilization.

All samples were collected from each unit in 40 ml glass vials which were precleaned with chromic acid and washed with activated carbon water, and then were oven-dried for at least 8 hours. Samples collected from each unit were then stored at 5 °C until time of analysis. All samples were analyzed for turbidity, organic content (u.v. absorbance and T.O.C.) and trihalomethanes.

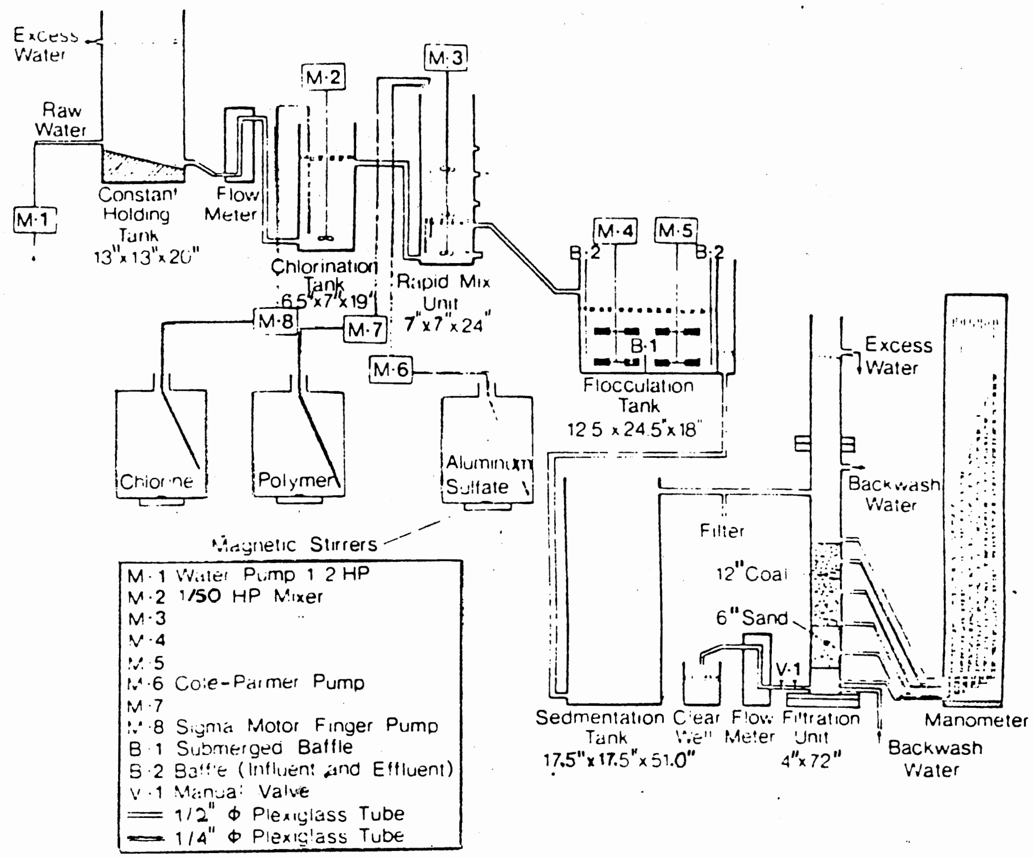


Figure 4: Pilot Plant Features

CHAPTER IV

RESULTS

All jar testing were conducted on the raw water using alum and PBAC as the sole coagulants. PBAC solution was prepared with two different neutralization ratios (r) of 1.8 and 2.5, and the performance of the two solutions was compared to alum. Jar testing was performed in sets, with each set consisting of 6 jars. The first jar in each set served as a control, i.e., no coagulant was added. The concentrations in jars 2, 3, 4, 5 and 6 were 10, 20, 30, 40 and 80 mg/ℓ respectively. Cl_2 solution was added to all 6 jars after the addition of the desired dose of the coagulant. pH adjustments to the desired values were done prior to the addition of the coagulant and the Cl_2 solution.

Turbidity

Jar tests using the two types of PBAC solution were conducted on various types of raw water. The original raw water had an approximate turbidity of 25 NTU and a TOC of 10 mg/ℓ. By raising the turbidity to about 50 NTU and the TOC to 26 mg/ℓ, four different combinations of raw water were obtained. Three pH values of 5.0, 7.0 and 8.0 were selected for jar tests. Turbidity values are recorded in Table V and all possible combinations are plotted in Figures 5 through 10 for the ambient pH value of 8.0. Figures 5 and 6 were plotted for a neutralization ratio (r) of 1.8 and 2.5 respectively, with the four possible combinations of turbidity and TOC values. Figures 7 and 8 were plotted for the TOC values of 10 and 26 mg/ℓ respectively, with the four possible combinations of r and turbidity values. Figures 9 and 10 were plotted for the turbidity values of 25 and 50 NTU respectively, with the four possible combinations of r and TOC values. This was done for the ease of comparison between all 3 variables. Figures 5 through 10 are plotted on a percent remaining turbidity basis.

Table V

Comparison of Turbidity Values using four different combinations of Turbidity and TOC at two PBAC ratios.

r = 2.5, Turbidity = 24 NTU, TOC = 10 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	23	8.5	4.3	4.0	3.4	2.5
7.0	24	9.4	7.1	6.5	5.8	4.5
8.0	24	10.5	9.0	8.2	7.0	5.3

r = 1.8, Turbidity = 24 NTU, TOC = 10 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	24	11.5	7.5	6.6	6.1	5.8
7.0	24	10.3	9.1	8.0	7.1	6.3
8.0	24	12.5	10.7	8.0	7.5	6.8

r = 2.5, Turbidity = 24 NTU, TOC = 26 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	25	9.2	5.0	4.5	4.0	3.0
7.0	25	9.9	8.5	7.6	6.5	5.1
8.0	25	11.4	10.5	9.4	8.0	6.9

r = 1.8, Turbidity = 24 NTU, TOC = 26 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	25	12.5	8.7	7.7	6.8	6.1
7.0	25	14.0	12.3	10.4	11.5	7.7
8.0	25	13.4	13.0	12.2	8.3	7.9

r = 2.5, Turbidity = 52 NTU, TOC = 10 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	51	23	10.5	8.1	6.0	2.5
7.0	51	25	13.4	8.6	7.5	4.4
8.0	51	24	14.1	9.3	8.0	6.1

r = 1.8, Turbidity = 52 NTU, TOC = 10 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	51	23	11.4	9.1	6.9	4.3
7.0	51	28.6	19.6	13.2	10.0	7.7
8.0	51	31	17.5	12.3	11.9	6.8

r = 2.5, Turbidity = 52 NTU, TOC = 26 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	53	25	11.5	7.2	5.9	2.8
7.0	52	29	14.5	9.3	7.7	5.1
8.0	52	31	19.5	11.3	8.1	5.5

r = 1.8, Turbidity = 52 NTU, TOC = 26 mg/ℓ

pH Value \ Concentration mg/ℓ	0	10	20	30	40	80
5.0	53	29	14	9.5	7.2	6.0
7.0	54	33	30	12.4	8.9	6.5
8.0	53	35	23	15.6	10.3	6.9

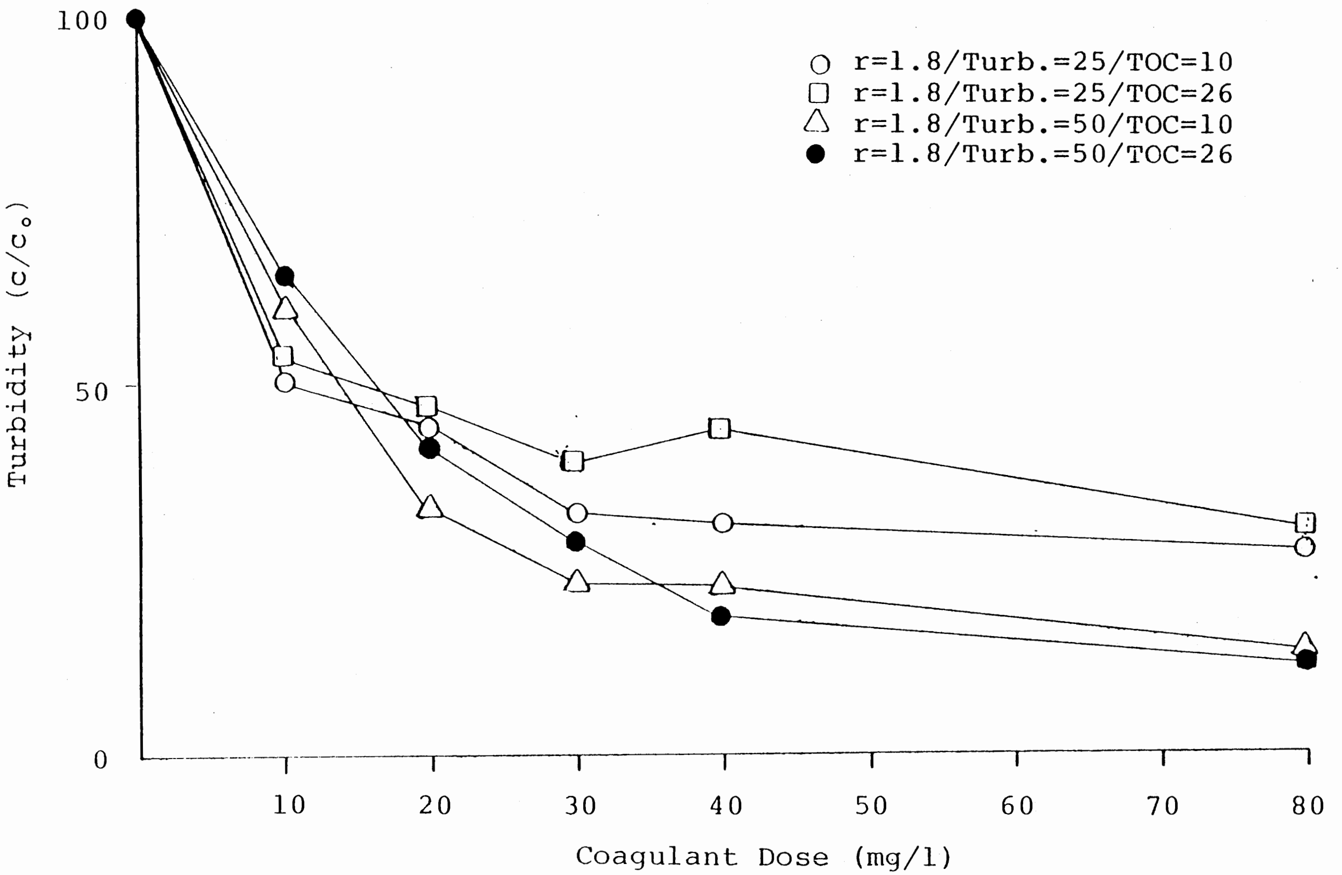


Figure 5: Turbidity Versus Dosage for a PBAC (r=1.8) Using Low and High Turbidity and Low and High TOC Waters.

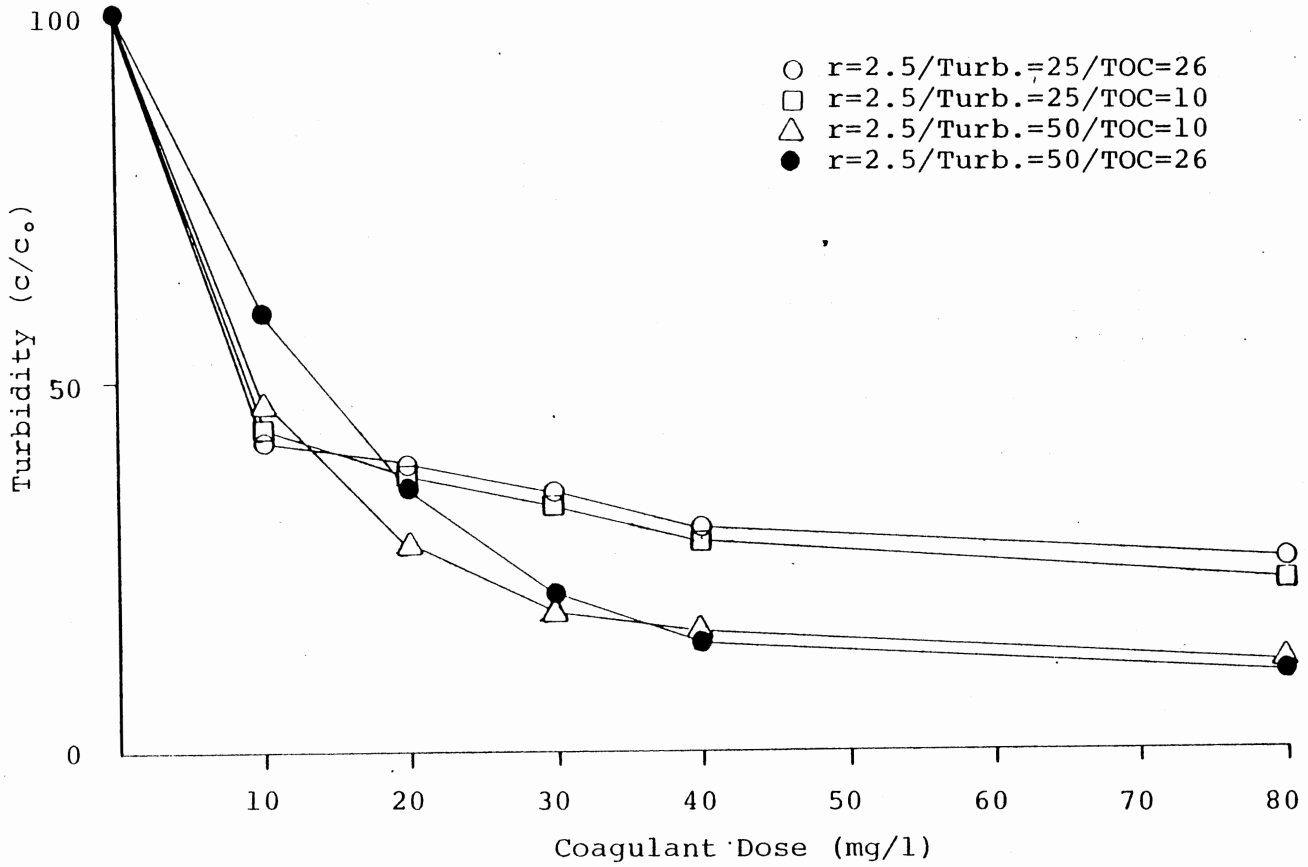


Figure 6: Turbidity Versus Dosage for a PBAC (r=2.5) Using Low and High Turbidity and Low and High TOC Waters.

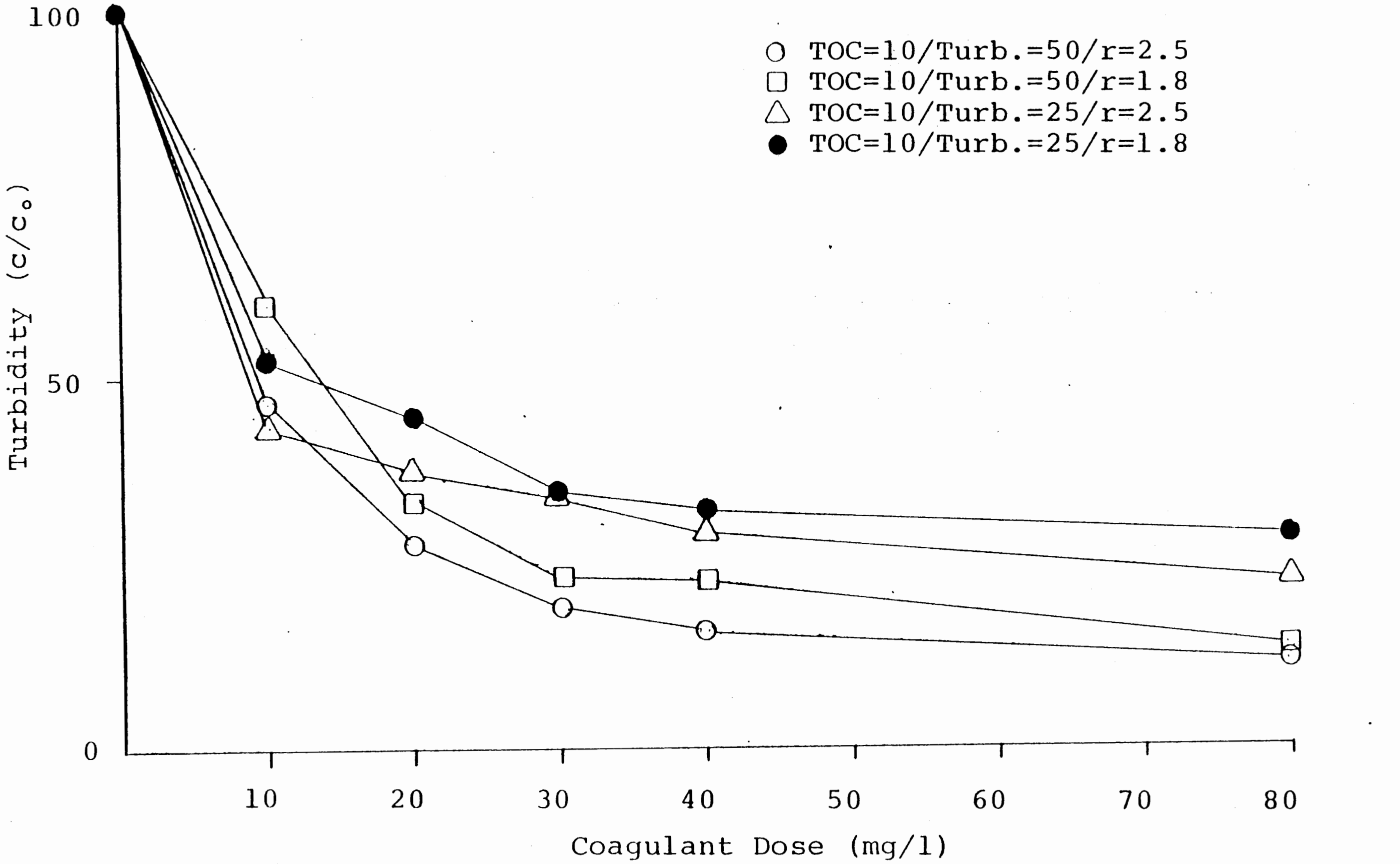


Figure 7: Turbidity Versus Dosage for Two PBACs (r=1.8,r=2.5) Using Low TOC, and High and Low Turbidity Waters.

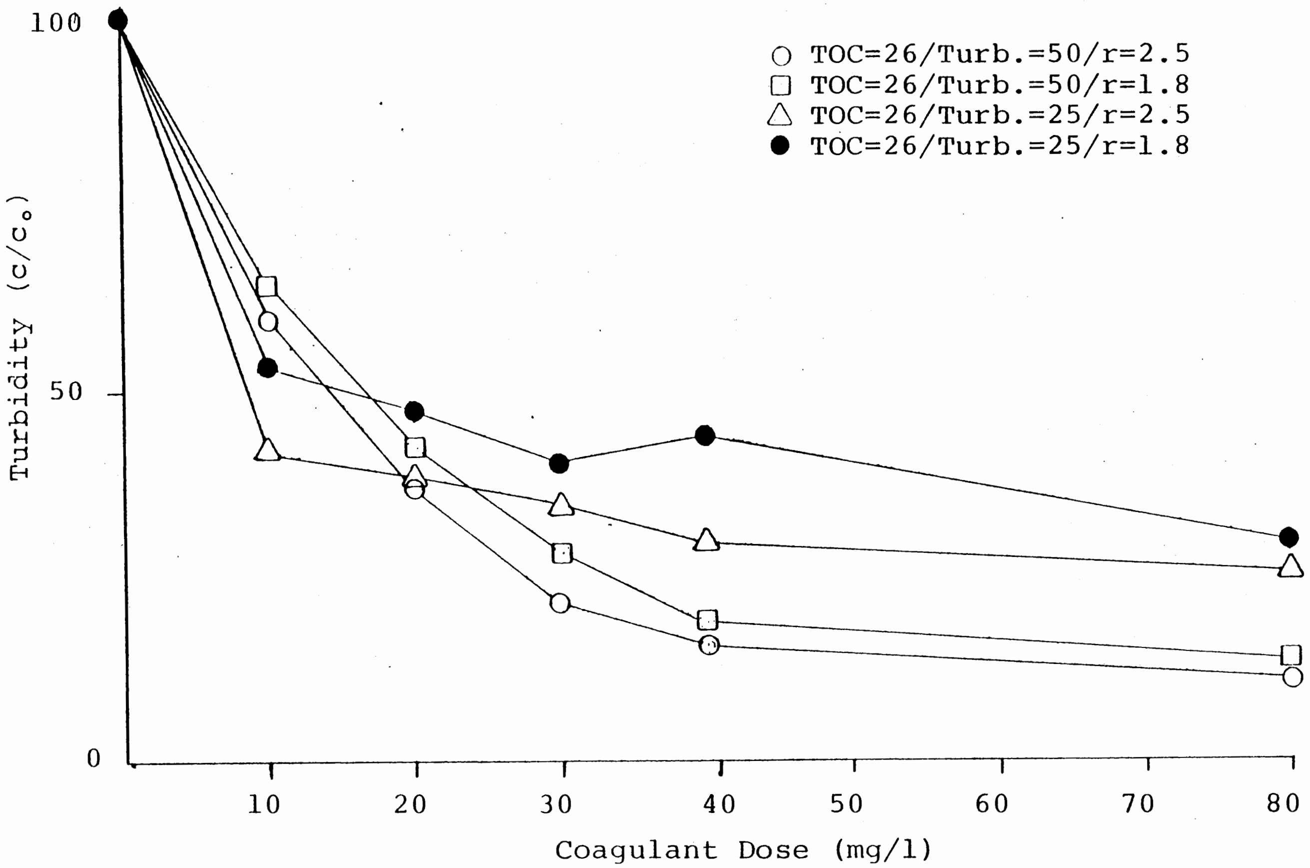


Figure 8: Turbidity Versus Dosage for Two PBACs (r=1.8,r=2.5) Using High TOC, and Low and High Turbidity Waters.

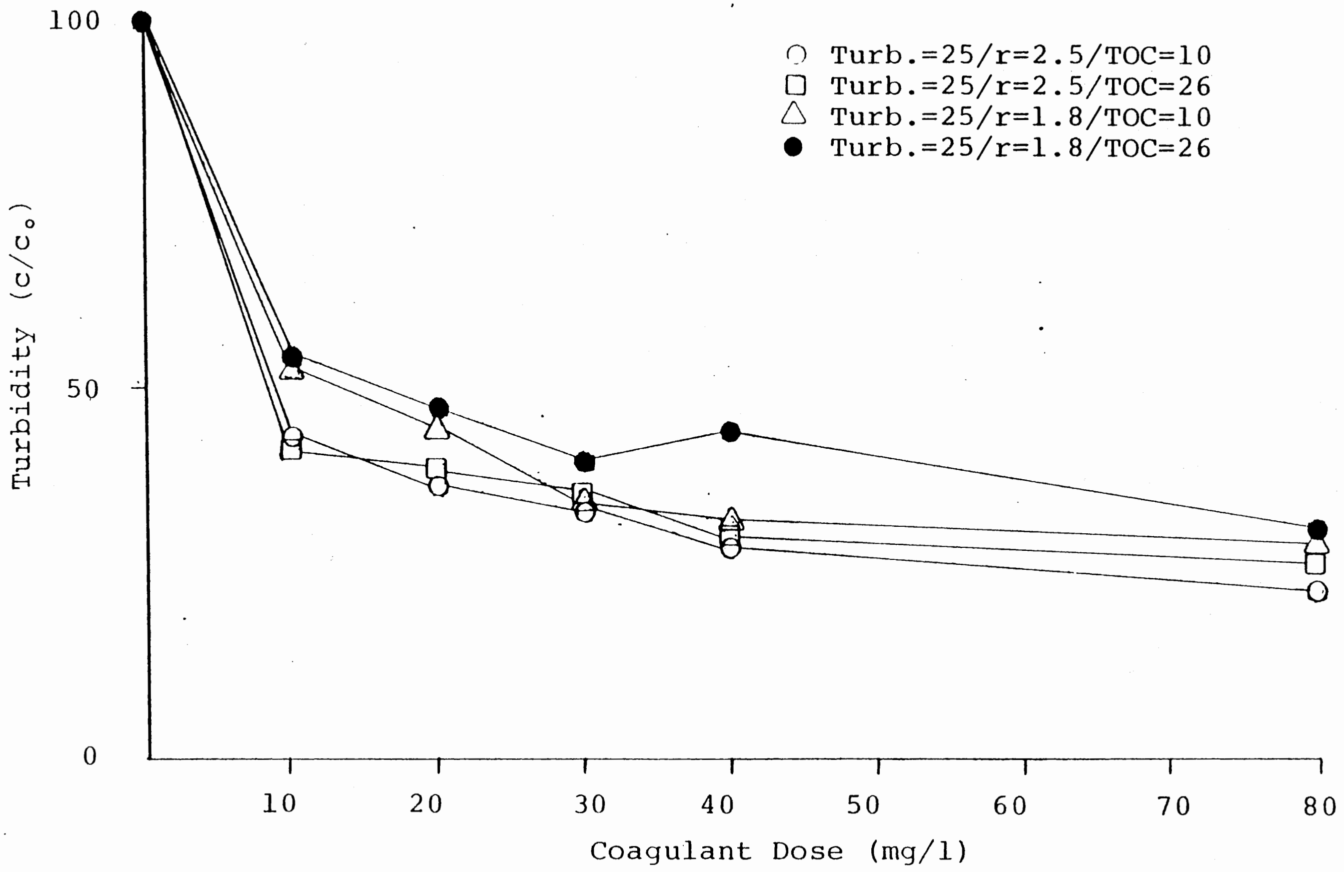


Figure 9: Turbidity Versus Dosage for Two PBACs (r=1.8,r=2.5)
Using Low Turbidity, and Low and High TOC Waters.

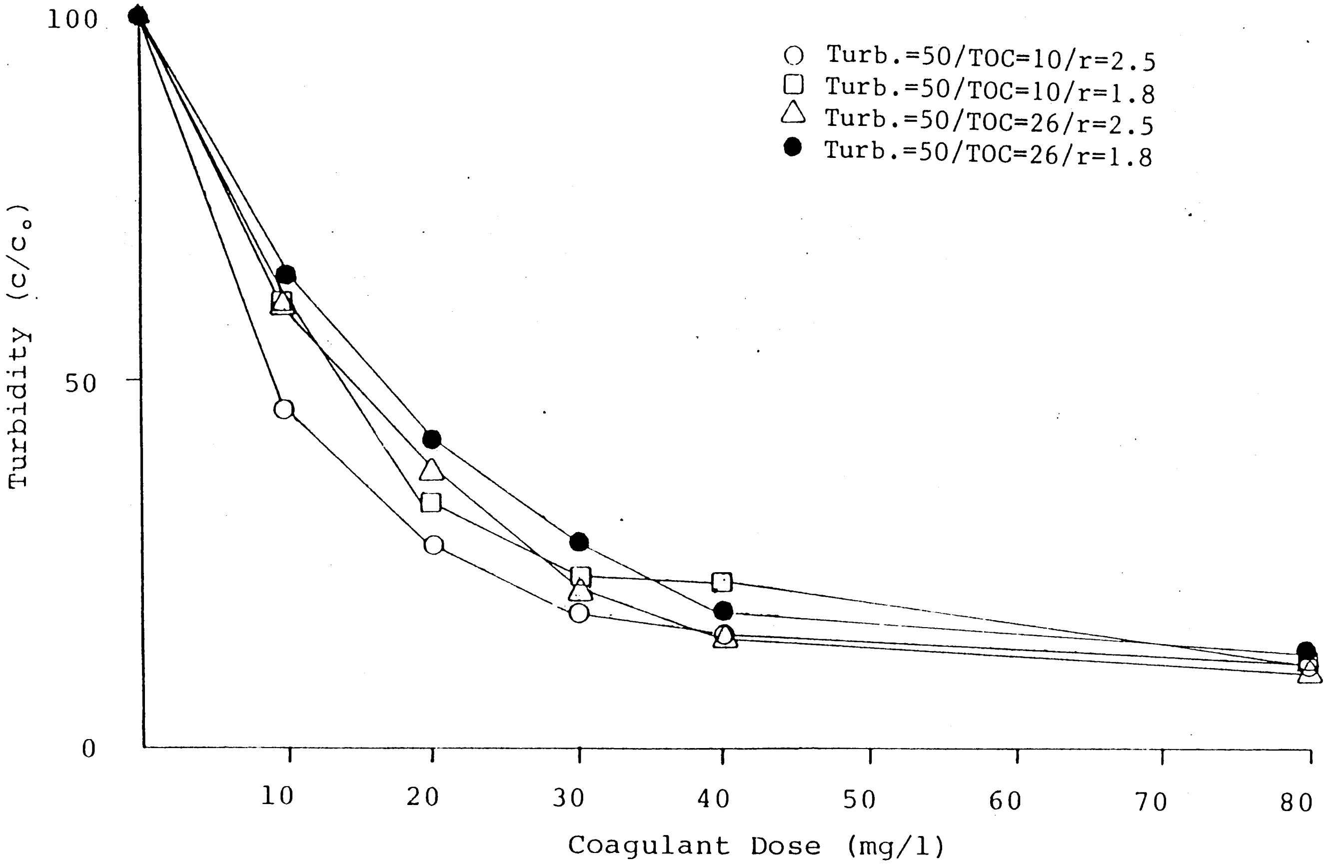


Figure 10: Turbidity Versus Dosage for Two PBACs (r=1.8,r=2.5) Using High Turbidity, and Low and High TOC Waters.

By looking at the six figures, the following facts can be observed:

1. Better turbidity removals were achieved when PBAC was applied to high turbidity water, except at very low doses. This is demonstrated in Figures 5, 6, 7 and 8.

2. The effect of TOC on the removal of turbidity was minimal. This was observed at a PBAC neutralization ratio of 2.5, and at both high and low turbidity. Figure 6 demonstrates this fact. At a neutralization ratio of 1.8, turbidity removals were almost the same using the low and the high turbidity water, and TOC was considered to have almost no effect on turbidity removal within the experimental error. This is illustrated in Figure 5.

3. The performance with respect to turbidity removal of PBAC with a neutralization ratio (r) of 2.5 was found to be superior to that of PBAC with a neutralization ratio of 1.8. This was observed in all six figures. It can be seen from Table V that turbidity removals were higher using PBAC with an r value of 2.5 at all pH values for the different combinations of the water.

On the basis of the results shown above, PBAC with a neutralization ratio of 2.5 was chosen to compare its performance with alum. All jar tests were done accordingly.

Representative results portraying coagulation of the raw water with alum and PBAC (r = 2.5) for removal of turbidity are presented in Table VI, and are shown in Figures 11, 12, 13, or 14. For ease of comparison between the performances of both coagulants, Figures 11, 12, 13, and 14 were plotted on a percent turbidity remaining basis. Table VI shows the actual turbidity values. As revealed by these figures, turbidity removals were higher using alum doses between 20 and 40 mg/ℓ, with the best removals achieved using a dose of 30 mg/ℓ of alum. It can also be seen from these figures that turbidity removals using alum were better at low doses, whereas PBAC seemed to be a better coagulant than alum at higher doses. Very good turbidity removals were achieved using PBAC at a dose of 80 mg/ℓ. Since this dose was thought to be very high to achieve maximum removal of turbidity, further work was done using 5 mg/ℓ increments of PBAC in the range of 0 to 40 mg/ℓ. The observed results are shown in Figure 15.

As shown in Figure 15, maximum turbidity removal was observed at a PBAC dose of 25 mg/ℓ with restabilization occurring at a dose of 30 mg/ℓ. Destabilization of particulate

Table VI

Turbidity Values for Alum and PBAC
at Various pH Values

pH Value	Concentration mg/ℓ	0	10	20	30	40	80
6.0	Alum	26	6.0	1.5	1.1	1.0	1.3
	PBAC	25	8.5	4.5	3.5	2.5	1.5
7.0	Alum	24	14.5	7.2	5.8	6.5	12.5
	PBAC	25	14.0	10.5	7.0	4.0	2.0
8.0	Alum	22	16	9.5	7	7.5	14
	PBAC	25	21	11	7	5.5	3.5
8.5	Alum	20	7	2.5	1.0	1.8	4.5
	PBAC	25	24	15	9.5	6.0	2.5

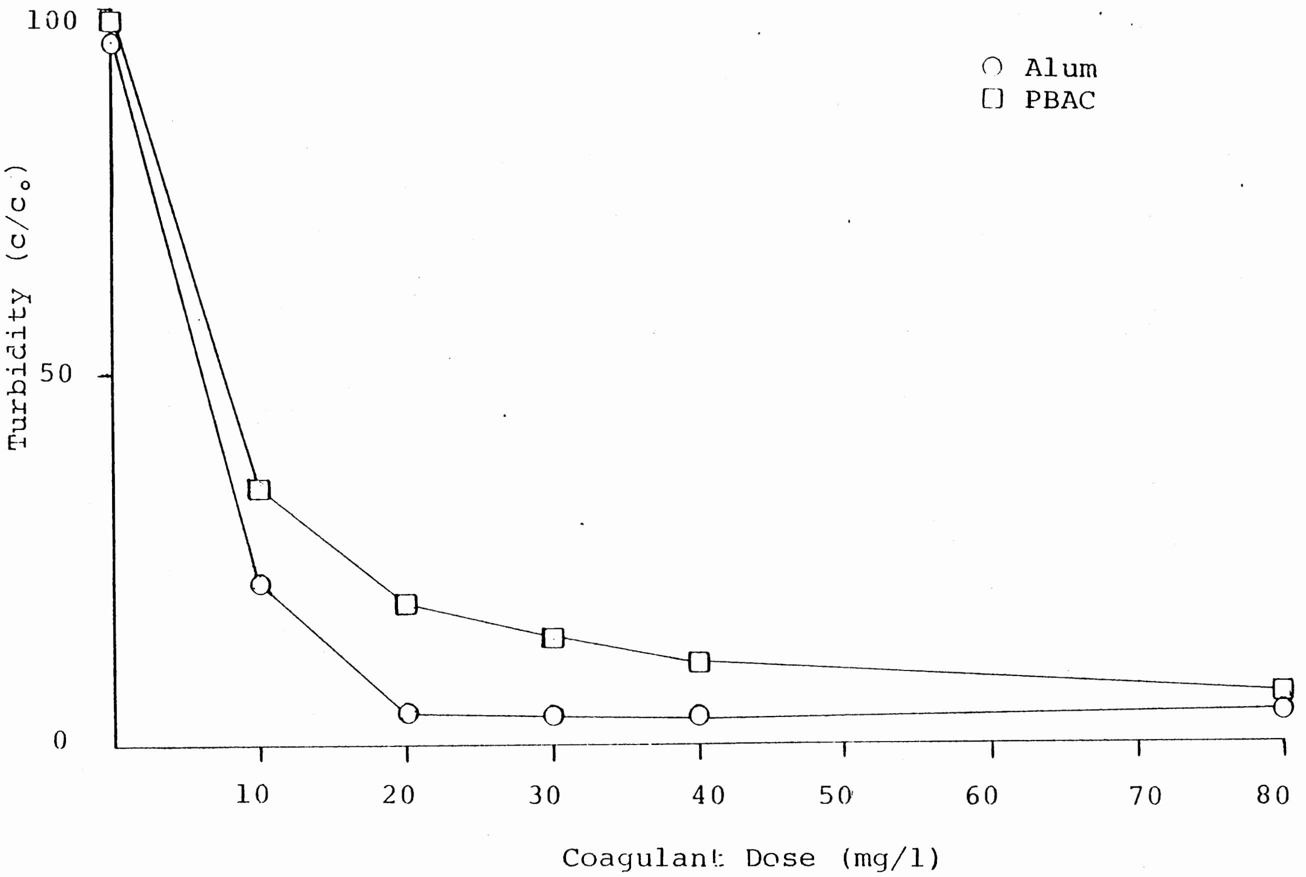


Figure 11: Turbidity Values Comparing Alum and PBAC (r=2.5) at pH 6.0.

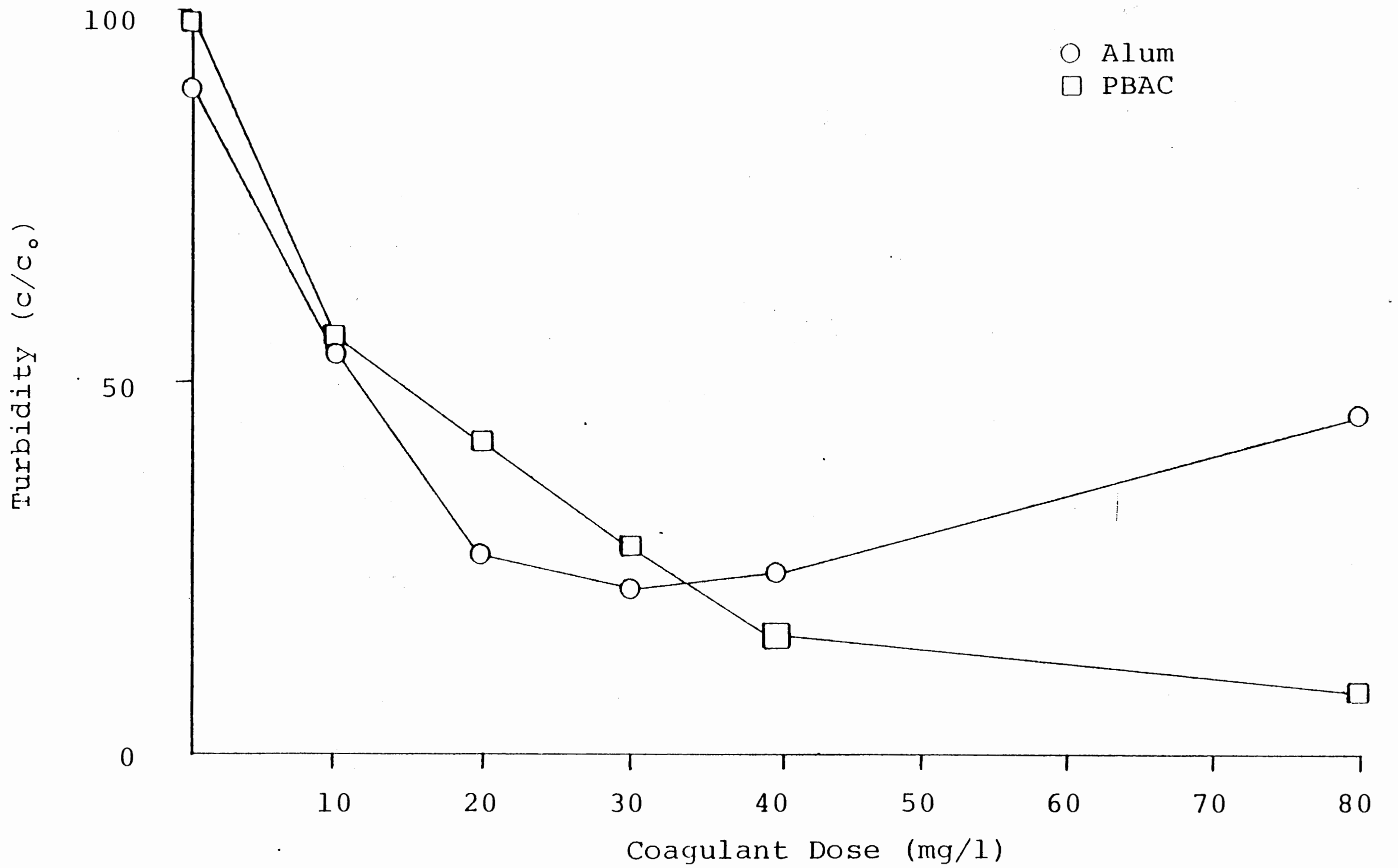


Figure 12: Turbidity Values Comparing Alum and PBAC (r=2.5) at pH 7.0.

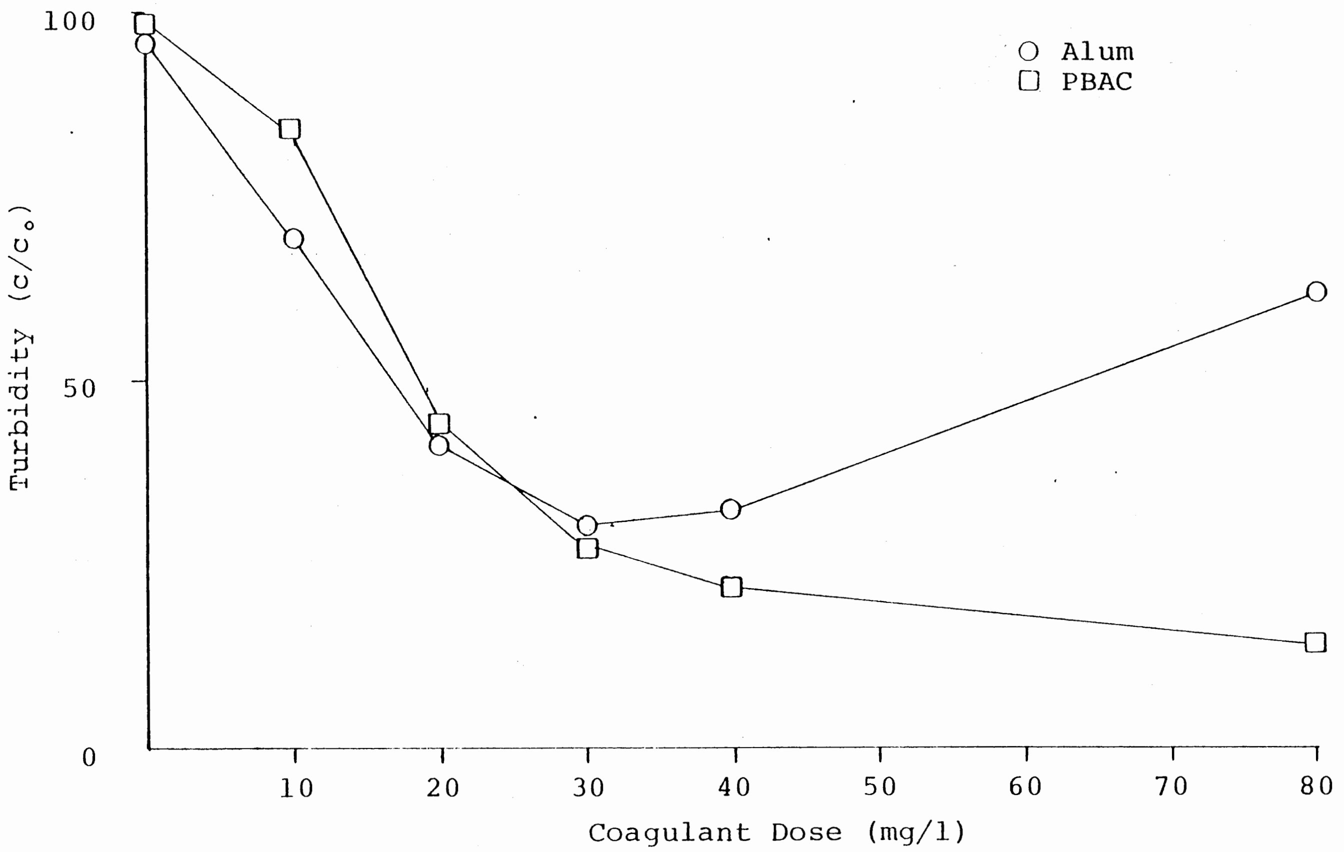


Figure 13: Turbidity Values Comparing Alum and PBAC (r=2.5) at pH 8.0.

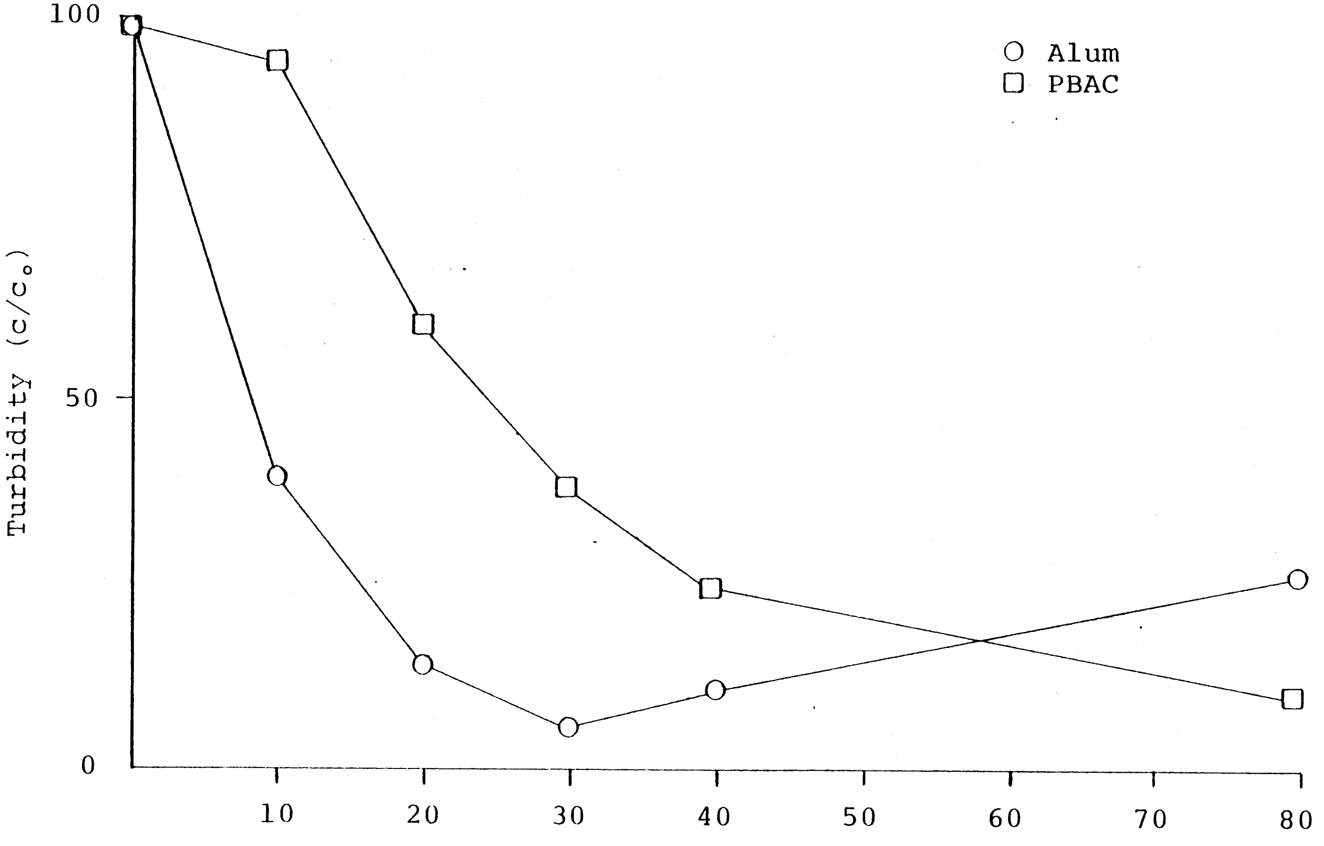


Figure 14: Turbidity Values Comparing Alum and PBAC (r=2.5) at pH 8.5.

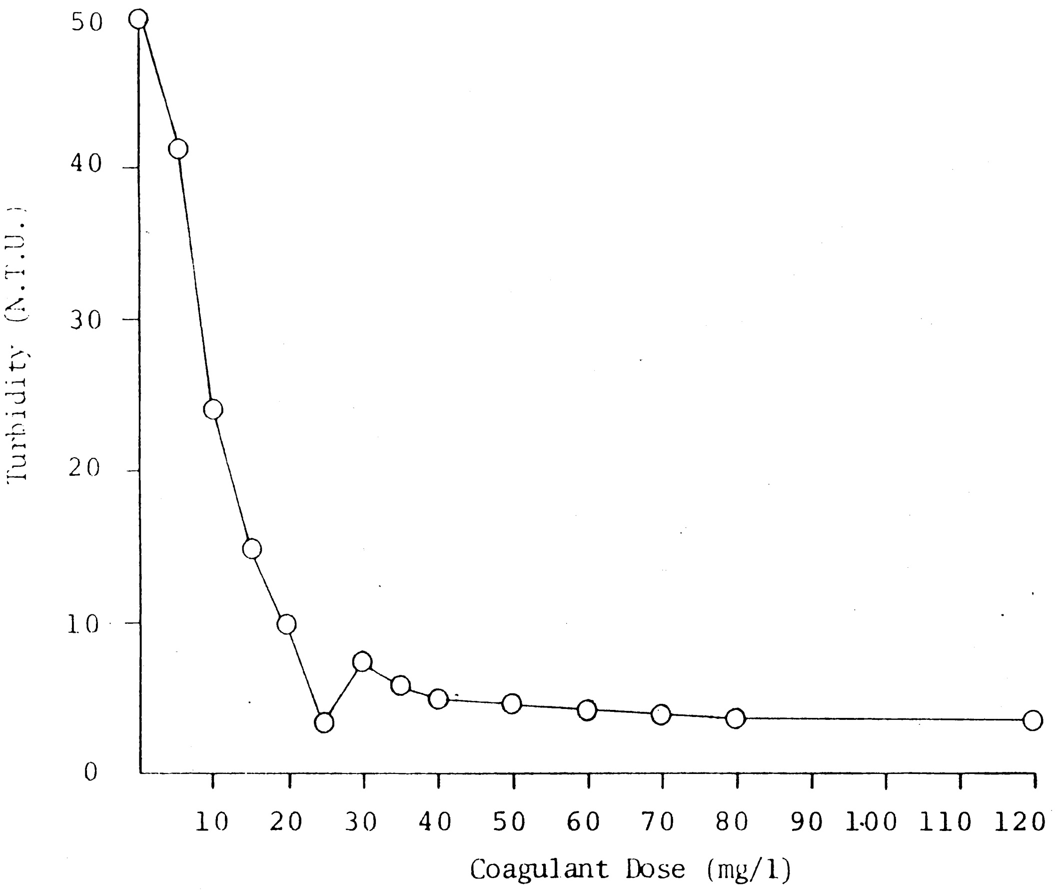


Figure 15: Residual Turbidity Values Using 5mg/l Increments of PBAC (r=2.5) at pH 8.0.

matter took place again when applying higher doses of PBAC. The repeatability of this test using 5 mg/ℓ increments of PBAC showed that the optimum dose for turbidity removal using PBAC ($r = 2.5$) is 25 mg/ℓ. Alum run in 5 mg/ℓ increments showed an optimum between 25 and 30 mg/ℓ with the optimum favoring 30 mg/ℓ.

Table VI also demonstrates another fact. Effluent turbidity values were observed to be lowest at lower pH values. At a PBAC dose of 10 mg/ℓ and a pH value of 8.5, almost no removal was observed, whereas at a pH of 6.0, a removal of 77% was observed using the same dose. At a PBAC dose of 40 mg/ℓ and a pH of 8.5, a turbidity removal of 76% was observed, whereas when the same dose was applied at a pH value of 6.0, turbidity was reduced by 90%.

The same type of results were obtained using alum coagulation for removal of turbidity. At an alum dose of 10 mg/ℓ and a pH of 8.0, turbidity was removed by 27%, whereas at a pH of 6.0, a removal of 77% was observed using the same dose. At a pH of 8.5, alum reduced turbidity by 91% using a dose of 40 mg/ℓ, while turbidity removals were 96% using the same dose of alum at a pH of 6.0. Based on the criterion of maximum turbidity removal, pH of 6.0 was found to be the optimum pH for turbidity removal using both alum and PBAC.

Organics and Precursor Removal

Organic removal tests were conducted using TOC and U.V. analysis. TOC and U.V. were monitored on all jar tests performed under the various pH conditions using both alum and PBAC with a neutralization ratio (r) of 2.5. On a comparable dosage basis at low pH values of 6.0 and 7.0, alum was generally found to be more effective than PBAC in reducing the TOC and U.V. of the raw water. At a pH value of 6.0, alum achieved a maximum TOC removal of around 92% using 80 mg/ℓ of coagulant, while PBAC achieved a maximum TOC removal of 84% using the same dose. At higher pH values of 8.0 and 8.5, PBAC had better removal of TOC than alum. PBAC at a dose of 80 mg/ℓ was able to achieve a TOC removal of 55% and 41% at pH values of 8.0 and 8.5 respectively, while using alum at the same dose, TOC removals were only 33% and 37% at the same two pH values respectively. This data is shown in Table VII, and illustrated in Figures 16 through 19, where each Figure gives a comparison between alum and PBAC at one pH value.

Additional representative data is given in Table VIII portraying the U.V. values for alum and PBAC at the various pH values. This data is plotted in Figures 20 through 23, where each figure represents a comparison between the two coagulants at the various pH values. At a pH of 6.0, alum achieved a maximum U.V. reduction of 70% at a dose of 40 mg/ℓ, while PBAC achieved maximum U.V. reduction of 51% using a dose of 80 mg/ℓ. At a higher pH value of 8.5, alum removed 58% of the U.V. originally measured for untreated water, using a dose of 30 mg/ℓ, while PBAC was able to remove 67.5% of the original U.V. value using a dose of 80 mg/ℓ. Overall, alum achieved maximum reductions in U.V. ranging from 53% to 70%, while results using PBAC ranged from 51% to 67.5%. Although these reductions are almost the same, doses of PBAC were greater than alum to accomplish the same reduction. Organics reductions at optimum doses and otimum pH of 6.0 using TOC and U.V. absorbance were in the range of 50 to 60 percent.

Part of this study was conducted with both alum and PBAC (r = 2.5) to compare their performance in removing selective molecular weights of humic and fulvic material present in the raw water. Jar tests were performed in the same manner mentioned earlier in this study, with the exception that no initial Cl_2 was added. The Cl_2 solution was added after the flocculation step, and was allowed to react during the sedimentation period. Samples withdrawn from the jars were then concentrated by lyophilization, fractionated on a G-75 Sephadex column, and analyzed for U.V. absorbance. The results are presented in Figures 24 through 28, with Figure 24 showing the original amount of humic and fulvic material present in the raw water (untreated with coagulant). Figure 24 indicates that fulvic acids predominated in the raw water. Reductions of the fulvic acids were observed using both coagulants at the various pH values. Figures 25 through 28 indicate that PBAC had a higher efficiency in removing the precursor material than alum at all pH values, with the efficiency of removal decreasing at higher pH values for both alum and PBAC. All removals were in the apparent

Table VII

T.O.C. Values for Alum and PBAC at Various pH Values

pH Value	Concentration mg/ℓ	0	10	20	30	40	80
6.0	Alum	13	10	8	7	4	1
	PBAC	25	19	11	15	10	4
7.0	Alum	18	15	10	8	14.5	4
	PBAC	17	16	8	10	13	7
8.0	Alum	15	12	10	11	26	13
	PBAC	20	16	18	16	15	9
8.5	Alum	35	32	24	26	22	22
	PBAC	34	33	43	30	24	20

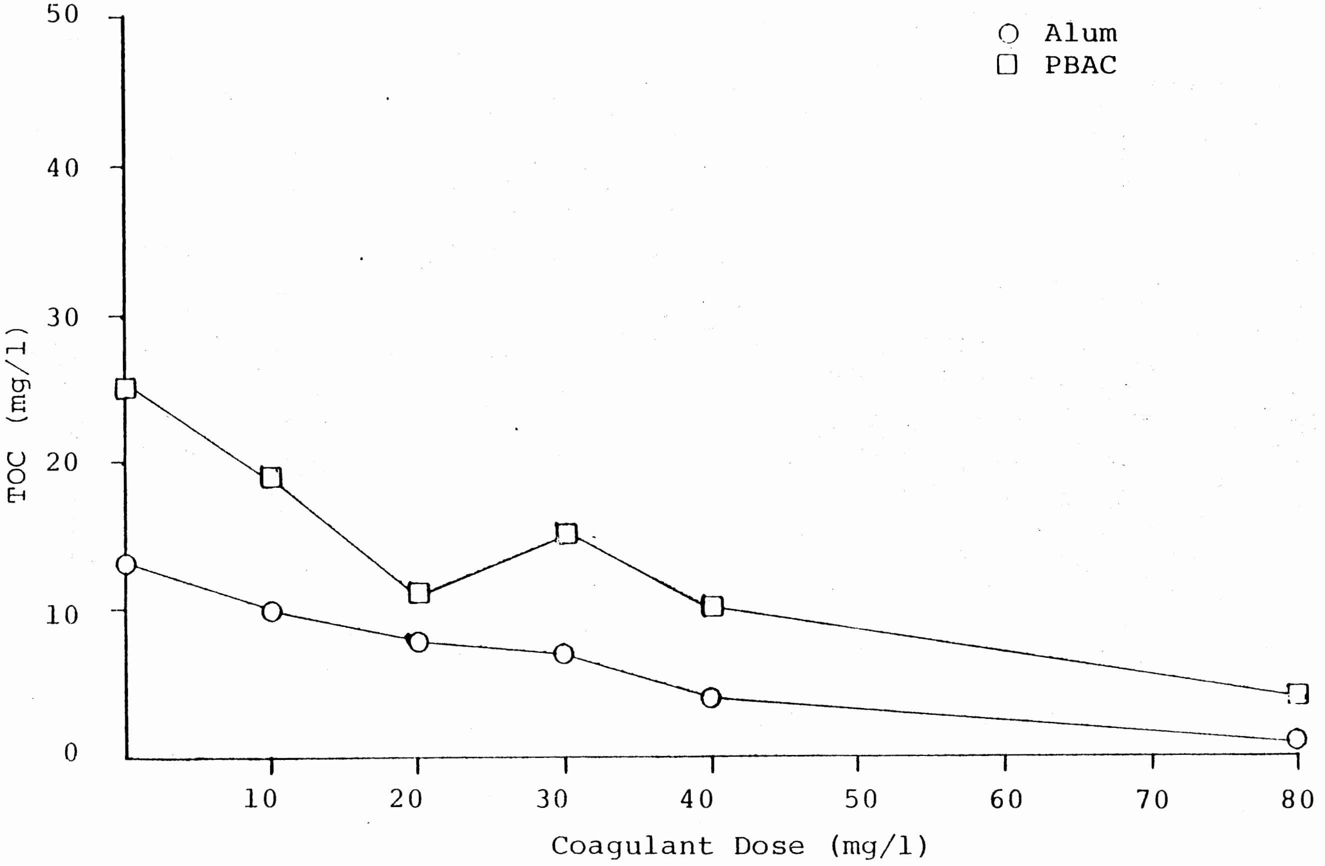


Figure 16: TOC Values Comparing Alum and PBAC (r=2.5) at pH 6.0.

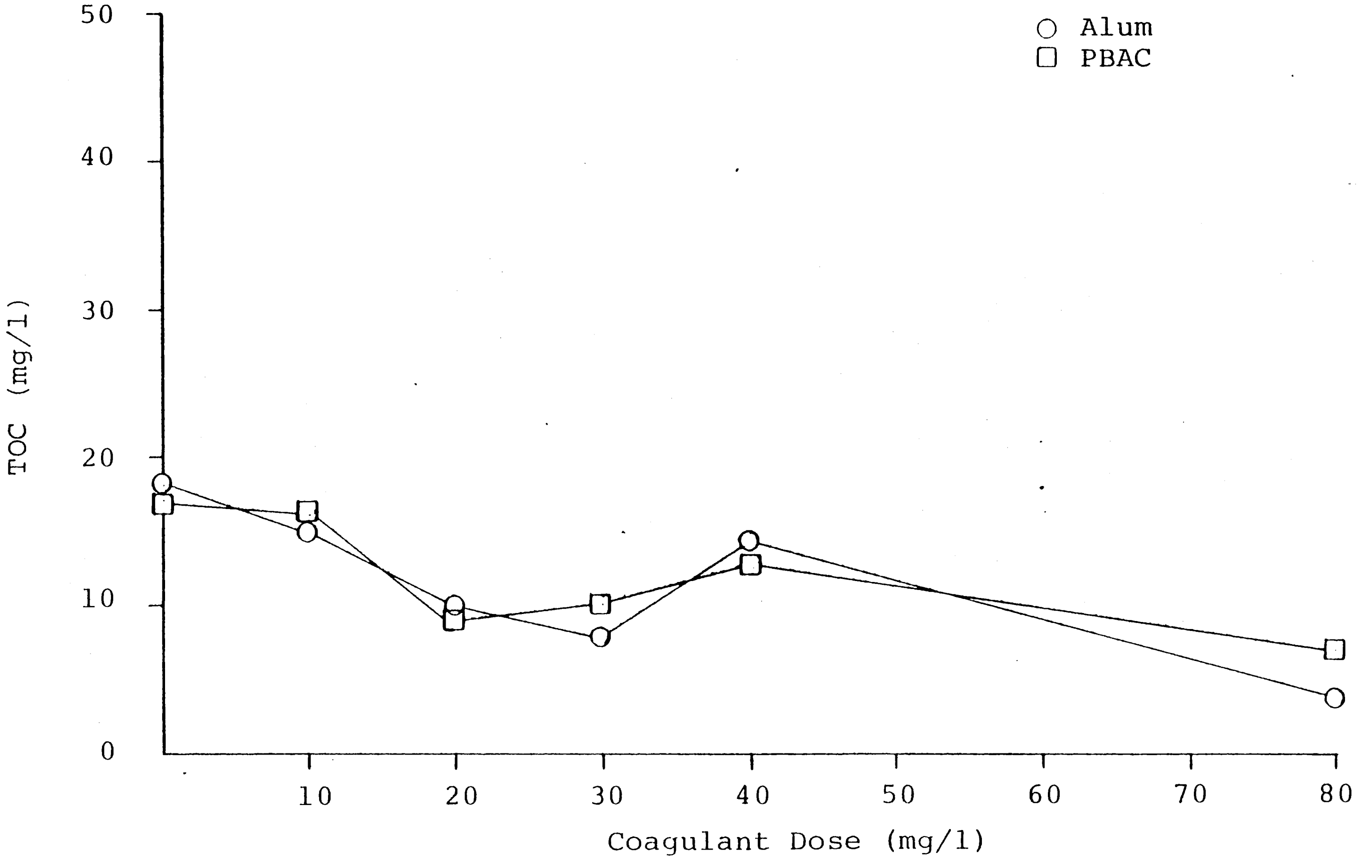


Figure 17: TOC Values Comparing Alum and PBAC (r=2.5)
at pH 7.0.

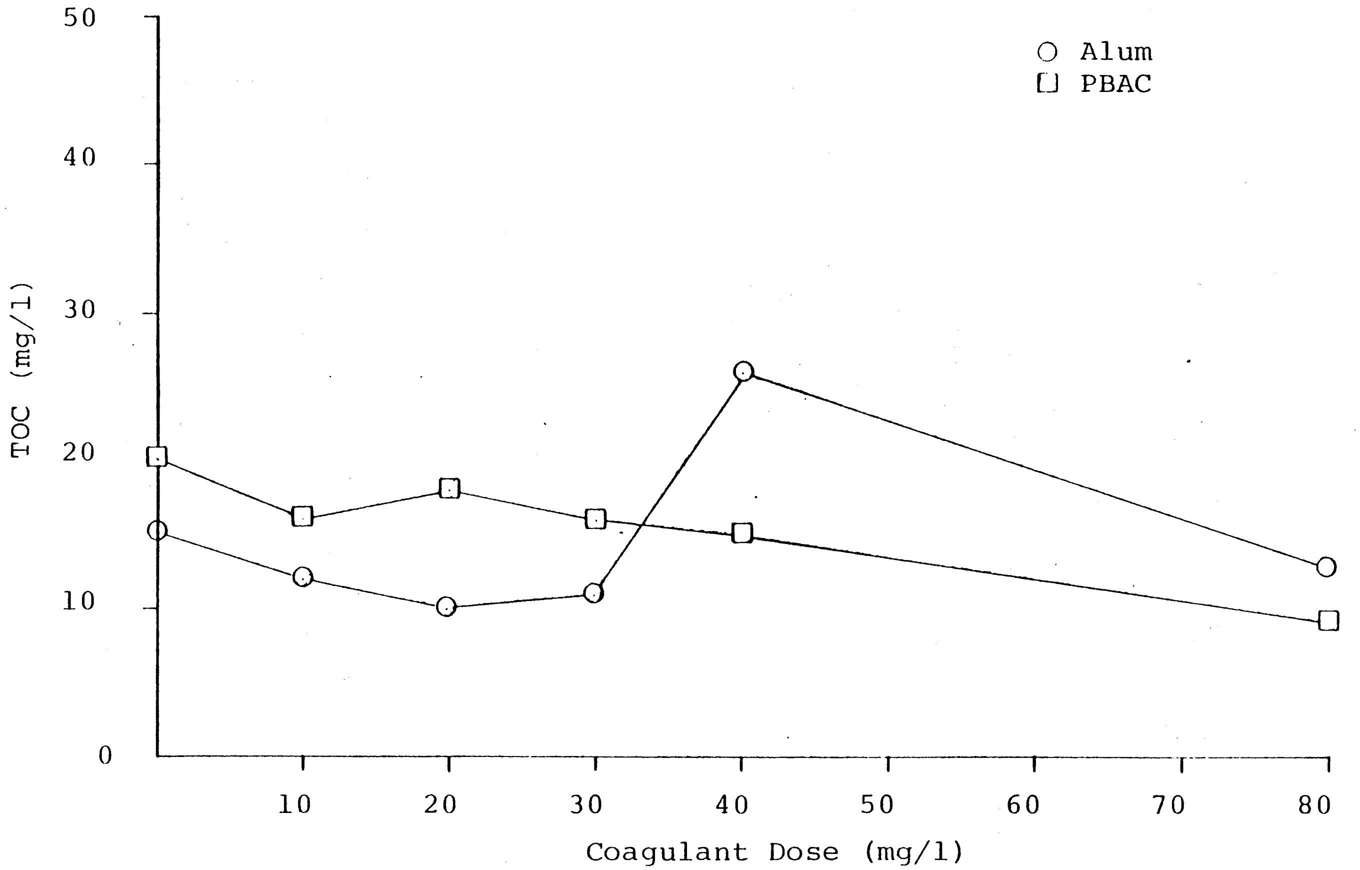


Figure 18: TOC Values Comparing Alum and PBAC (r=2.5) at pH 8.0.

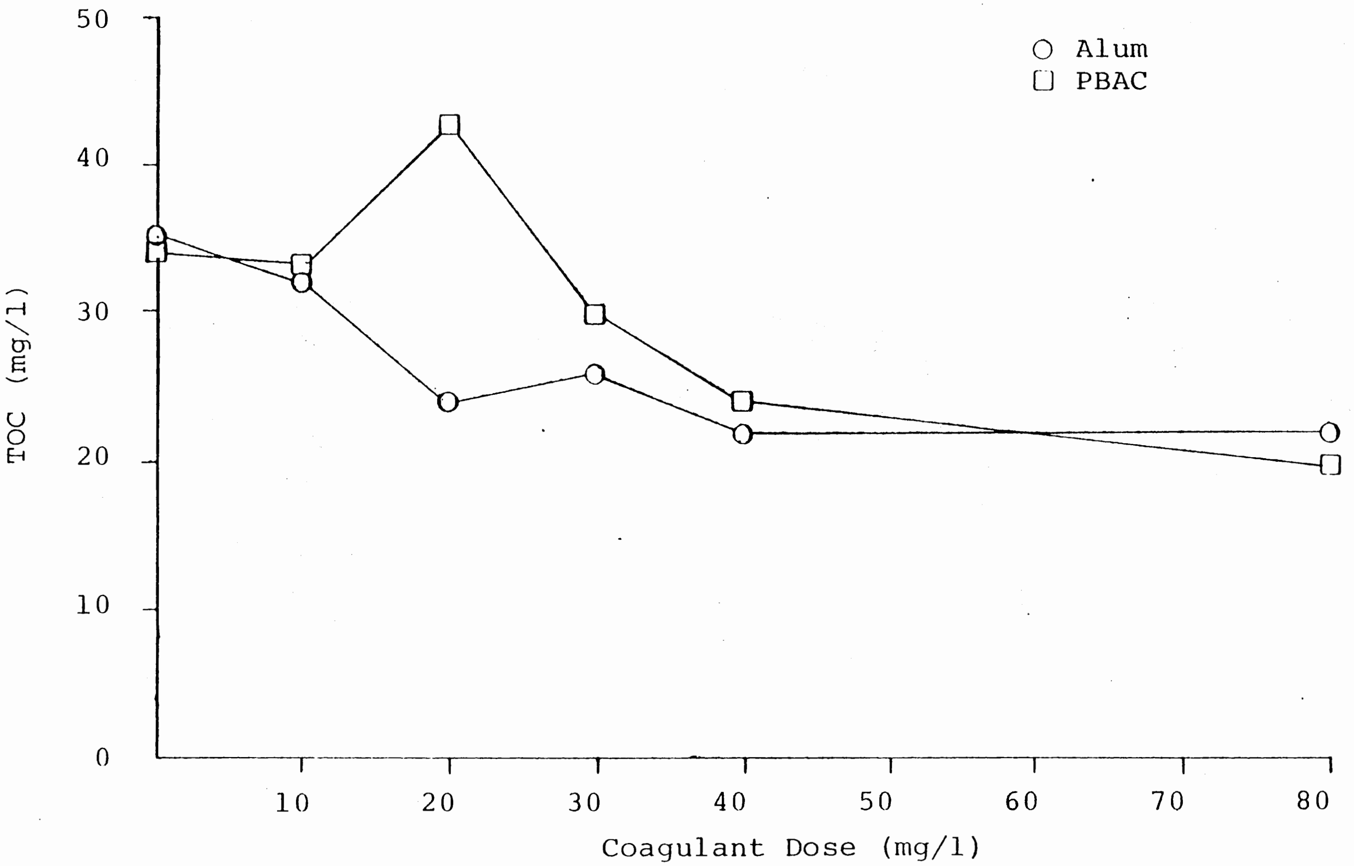


Figure 19: TOC Values Comparing Alum and PBAC (r=2.5) at pH 8.5.

Table VIII

U.V. Values for Alum and PBAC at Various pH Values

pH Value	Concentration mg/ℓ	0	10	20	30	40	80
6.0	Alum	0.135	0.112	0.045	0.042	0.040	0.056
	PBAC	0.134	0.120	0.103	0.100	0.075	0.066
7.0	Alum	0.157	0.130	0.092	0.074	0.076	0.096
	PBAC	0.147	0.135	0.100	0.083	0.078	0.063
8.0	Alum	0.134	0.098	0.093	0.073	0.062	0.065
	PBAC	0.173	0.139	0.118	0.085	0.073	0.061
8.5	Alum	0.123	0.097	0.082	0.052	0.068	0.078
	PBAC	0.133	0.128	0.109	0.084	0.054	0.043

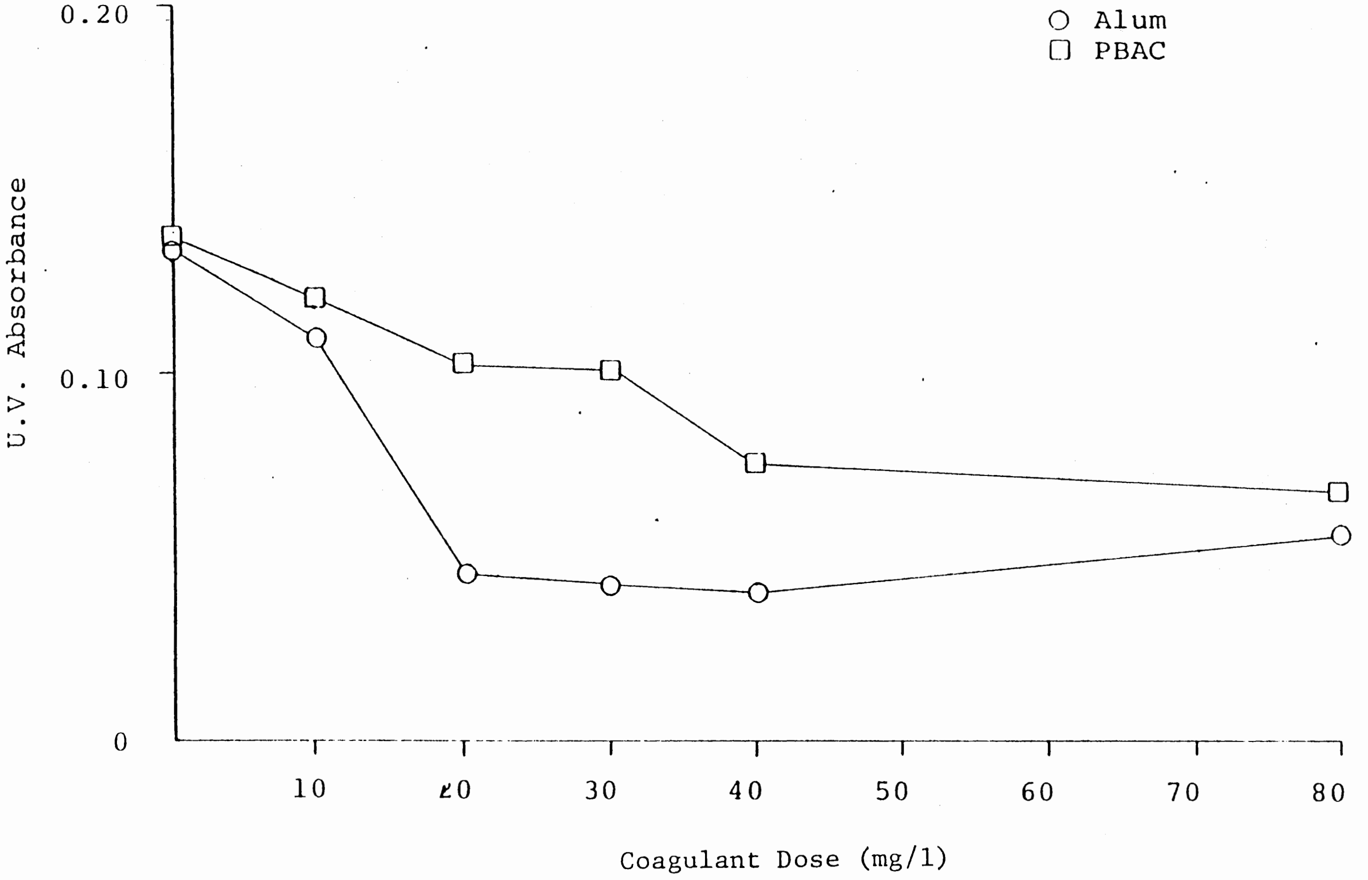


Figure 20: U.V. Absorbance Values Comparing Alum and PBAC (r=2.5) at pH 6.0.

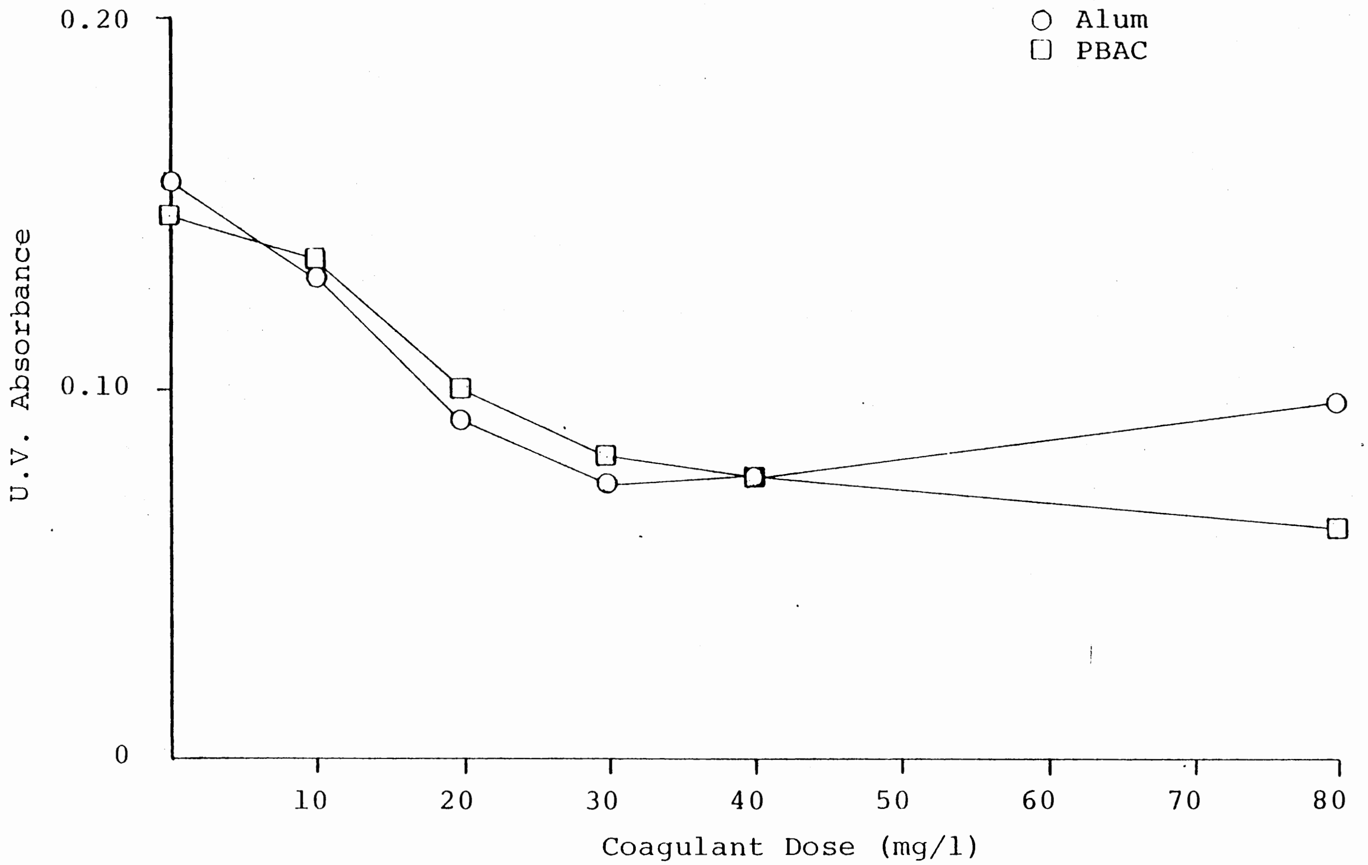


Figure 21: U.V. Absorbance Values Comparing Alum and PBAC (r=2.5) at pH 7.0.

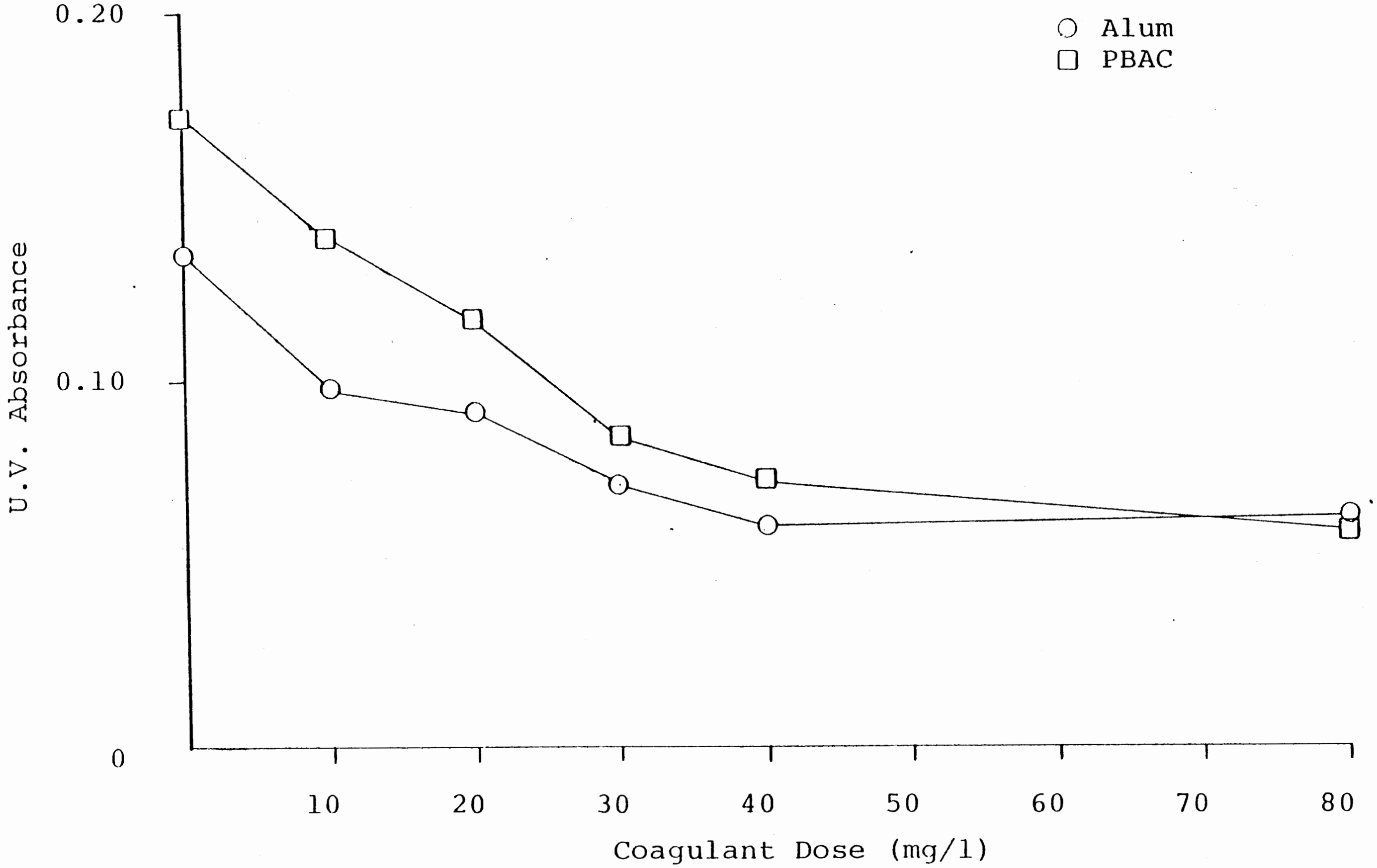


Figure 22: U.V. Absorbance Values Comparing Alum and PBAC (r=2.5) at pH 8.0.

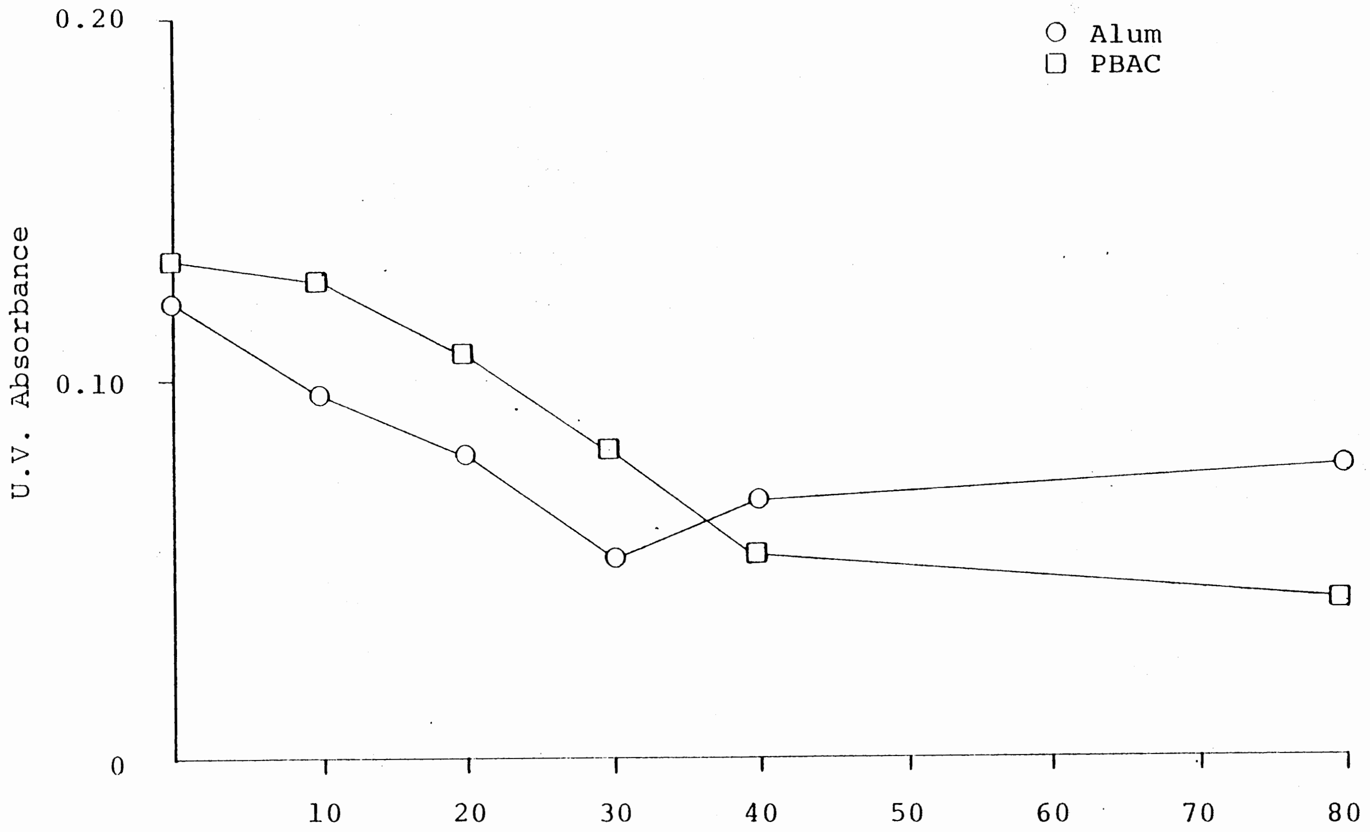
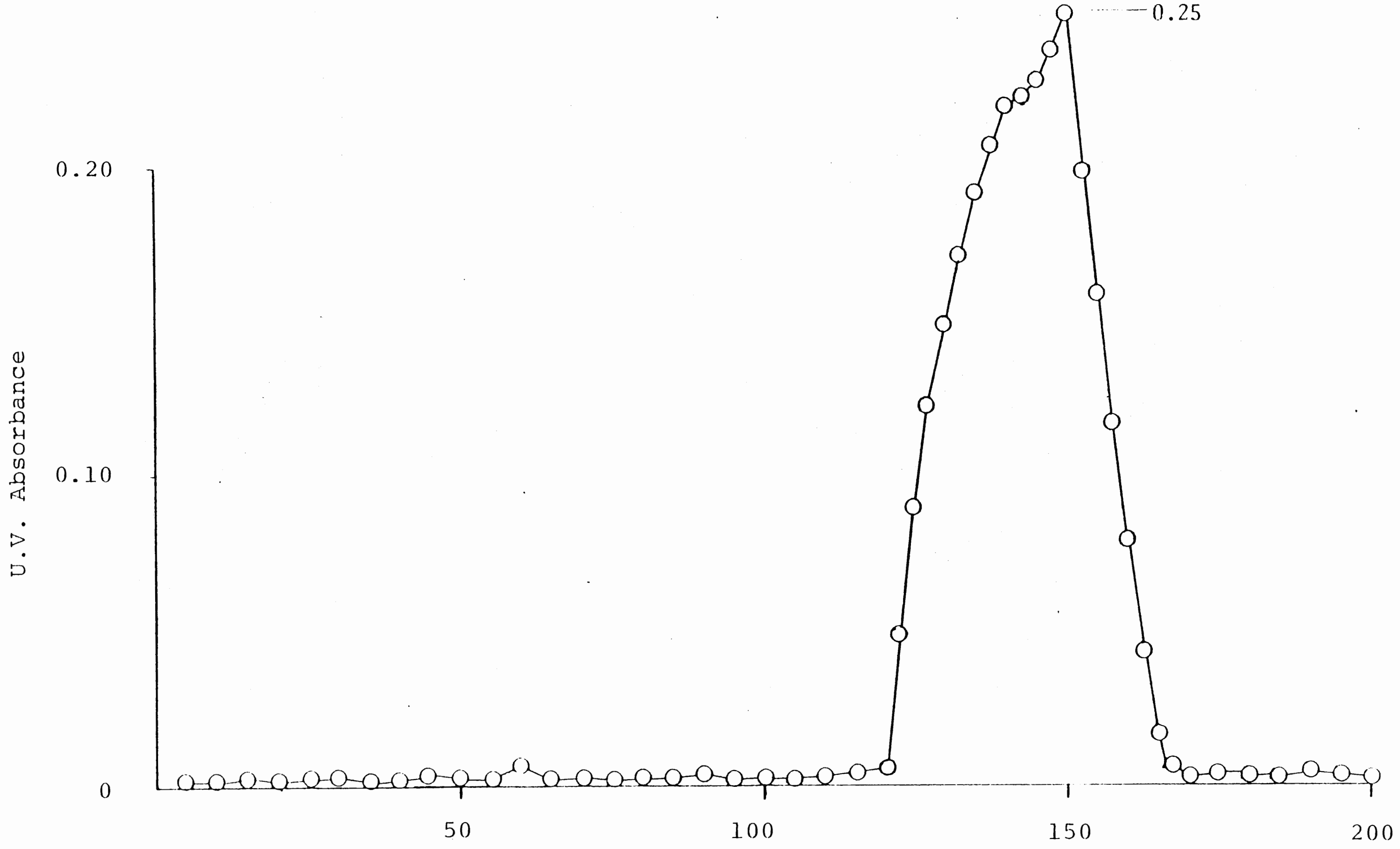


Figure 23: U.V. Absorbance Values Comparing Alum and PBAC (r=2.5) at pH 8.5.



Elution Volume (ml.)

Figure 24: U.V. Absorbance Versus Elution Volume for Raw Water at pH 8.0.

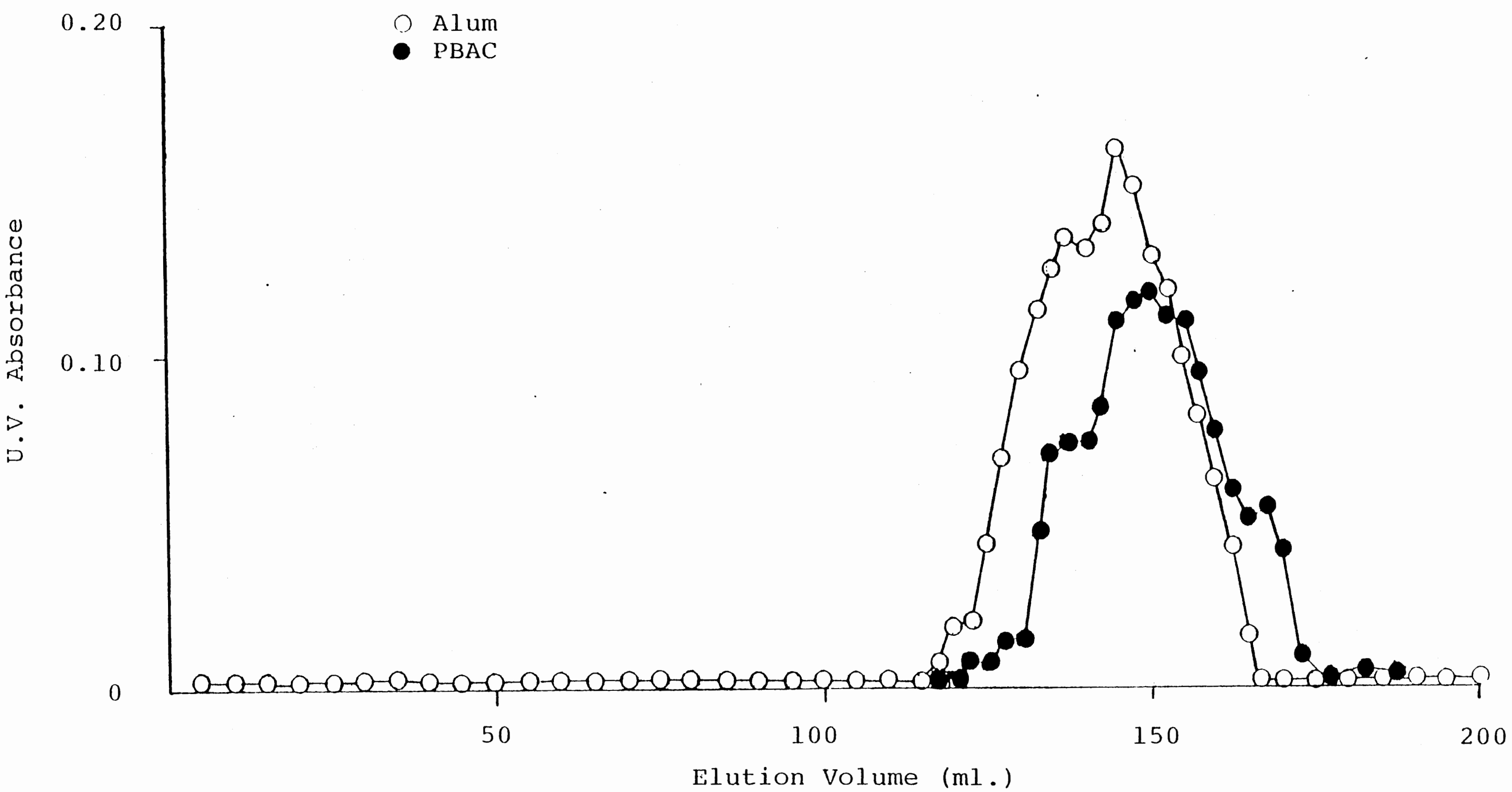


Figure 25: U.V. Absorbance Versus Elution Volume for Waters Treated with Optimum Doses of Alum and PBAC (r=2.5) at pH 6.0.

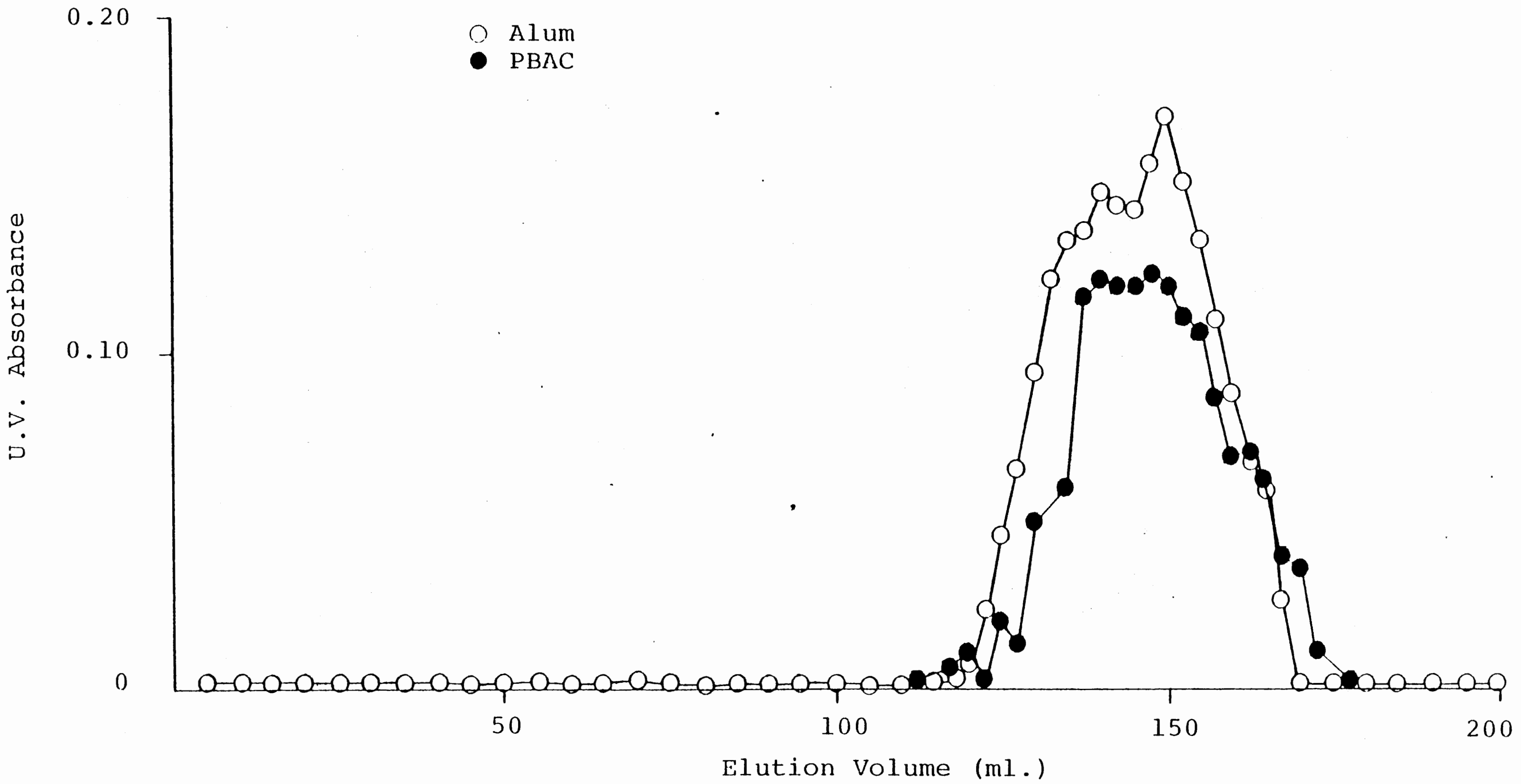


Figure 26: U.V. Absorbance Versus Elution Volume for Waters Treated with Optimum Doses of Alum and PBAC (r=2.5) at pH 7.0.

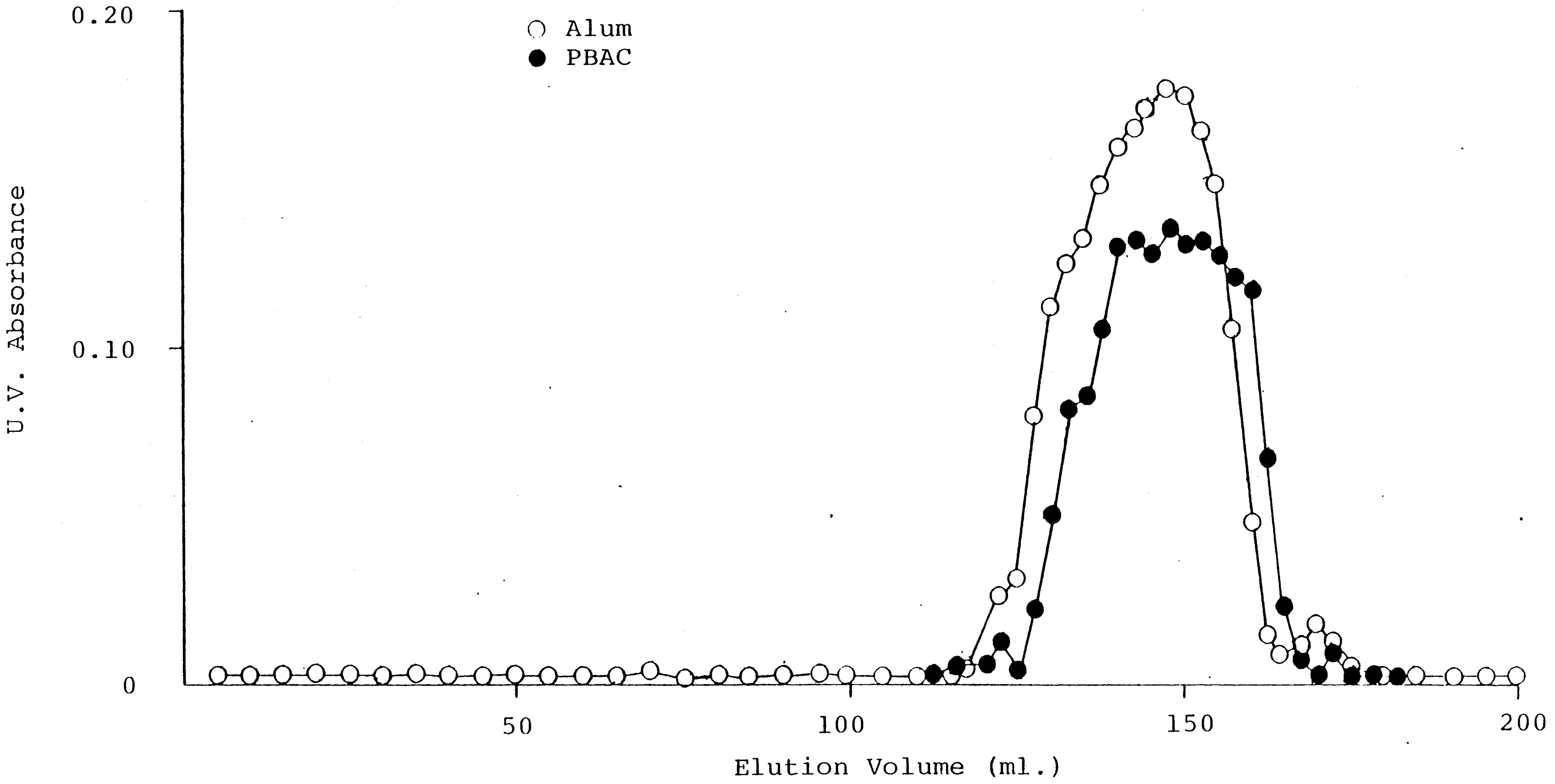


Figure 27: U.V. Absorbance Versus Elution Volume for Waters Treated with Optimum Doses of Alum and PBAC (r=2.5) at pH 8.0.

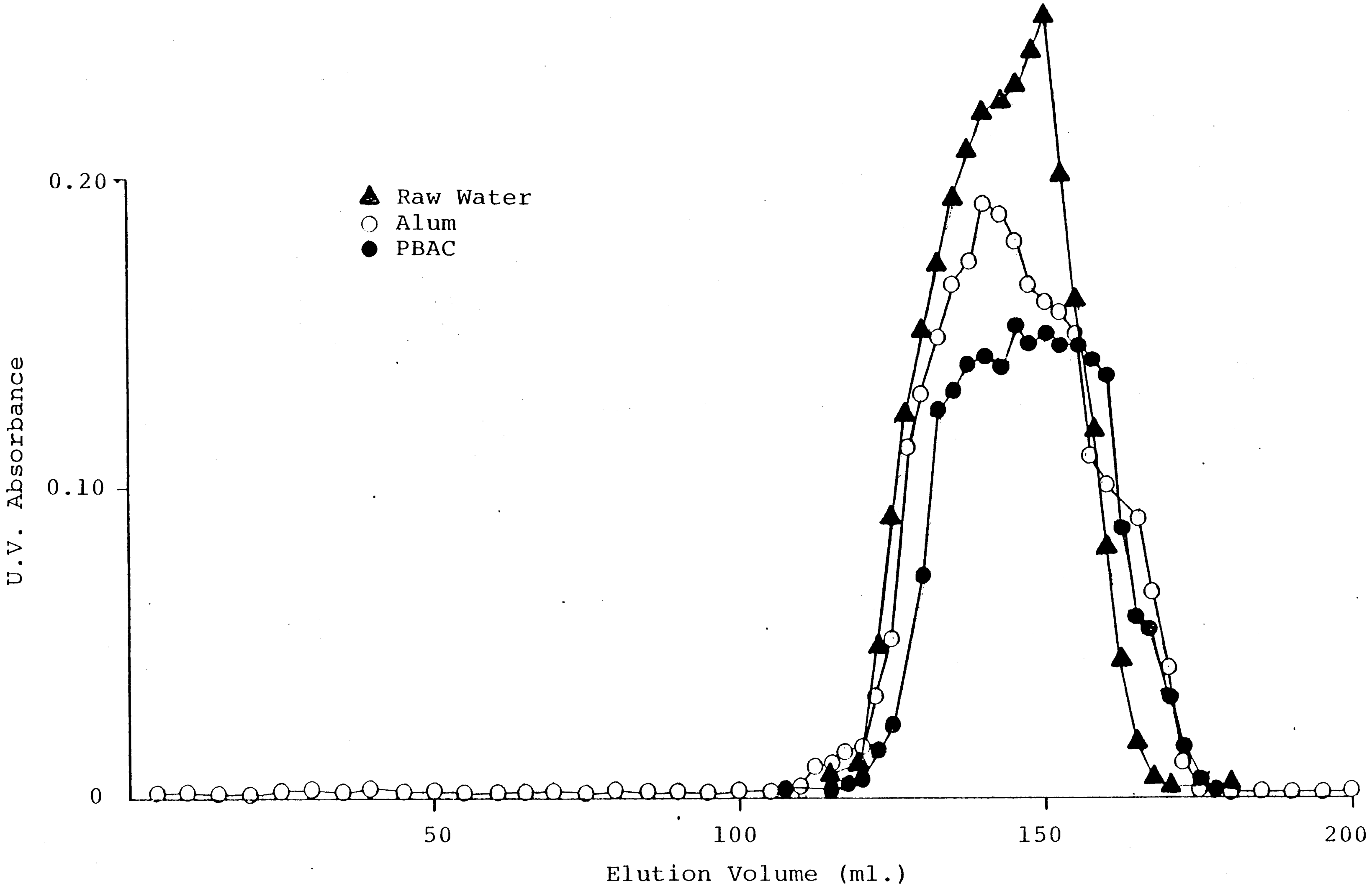


Figure 28: U.V. Absorbance Versus Elution Volume for Raw Water and Waters Treated with Optimum Doses of Alum and PBAC (r=2.5) at pH 8.5.

M.W. range of 12,000 to 1000. By manipulating the U.V. values from figures 25 and 27 in a different manner, figure 29 was obtained for pH values of 6.0 and 8.0. This bar diagram provides a comparison between alum and PBAC on the basis of selective molecular weight removals in the ranges of 12,000 to 5,500, 5,500 to 2,500, and 2,500 to 1,000. Figure 29 indicated that PBAC had a higher efficiency in removing the precursor material than alum at these two pH values, but only in the molecular weight range of 12,000 to 2,500. In the molecular weight range of 2,500 to 1,000, the situation was reversed, and alum seemed to be a better coagulant than PBAC for removing that particular M.W. range of precursor material.

Zeta Potential

Electrophoretic mobility measurements and correspondingly zeta potentials were performed on all jar tests using both alum and PBAC. The observed data is presented in Figure 30, where each data point represents an average of 10 readings on the zeta meter. Figure 30 portrays the Z.P. for alum at a pH of 8.0 and PBAC at pH of 6.0 and 8.0. Results obtained at other pH values resembled the ones shown in Figure 30. The raw water had a Z.P. value of around -20 m.v., and applying increasing alum doses had a significant effect on lowering the Z.P. values to around -4.0 m.v. Overall, the higher the alum dose, the lower the Z.P. value measured.

Applying PBAC to the raw water at a dose of 5 mg/ℓ lowered the Z.P. to around -10 m.v. Increasing the applied doses to 20 mg/ℓ tended to lower the Z.P., with some variations in the values obtained at different pH's. However, when even higher doses up to 80 mg/ℓ were applied, the Z.P. kept increasing to around -15 m.v. The same type of graph shown in Figure 30 for PBAC was obtained at other pH values considered in this study.

Trihalomethanes

Trihalomethane analyses were conducted on raw water treated with various doses of

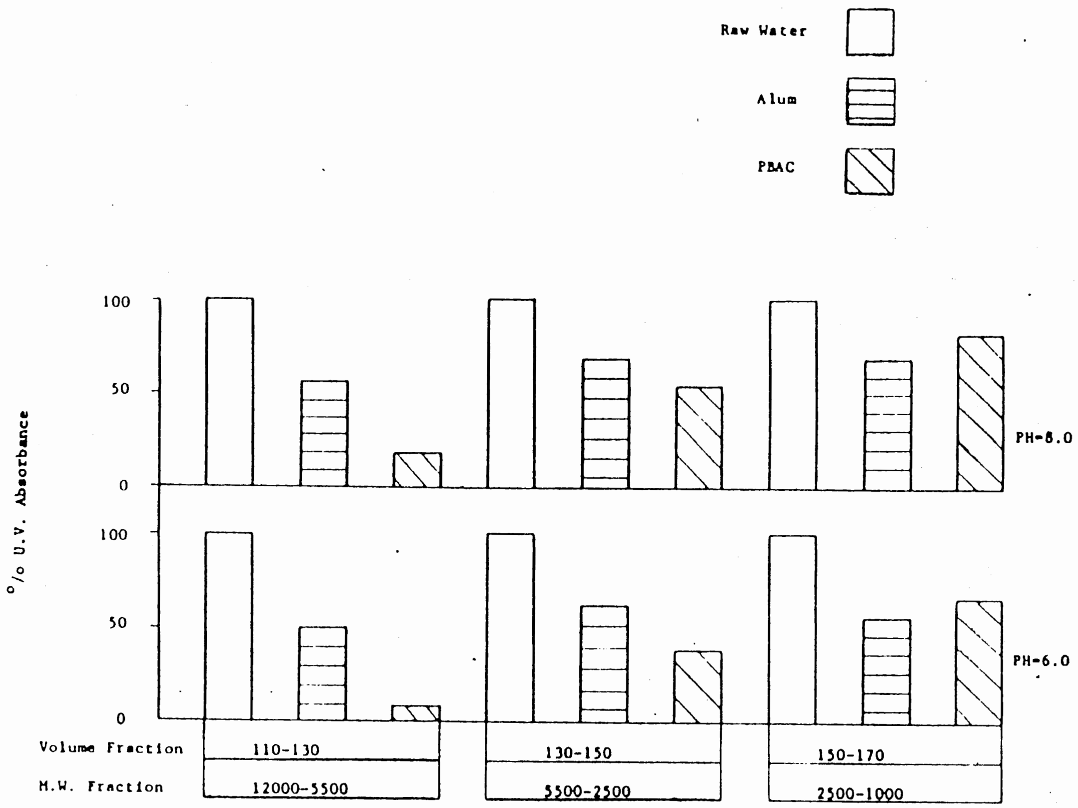


Figure 29: Organics Removal Measured by U.V. Absorbance for Selected M.W. Ranges at pH 6.0 and 8.0 for Raw Water and Waters Treated with the Optimum Dose of Alum and PBAC (r=2.5).

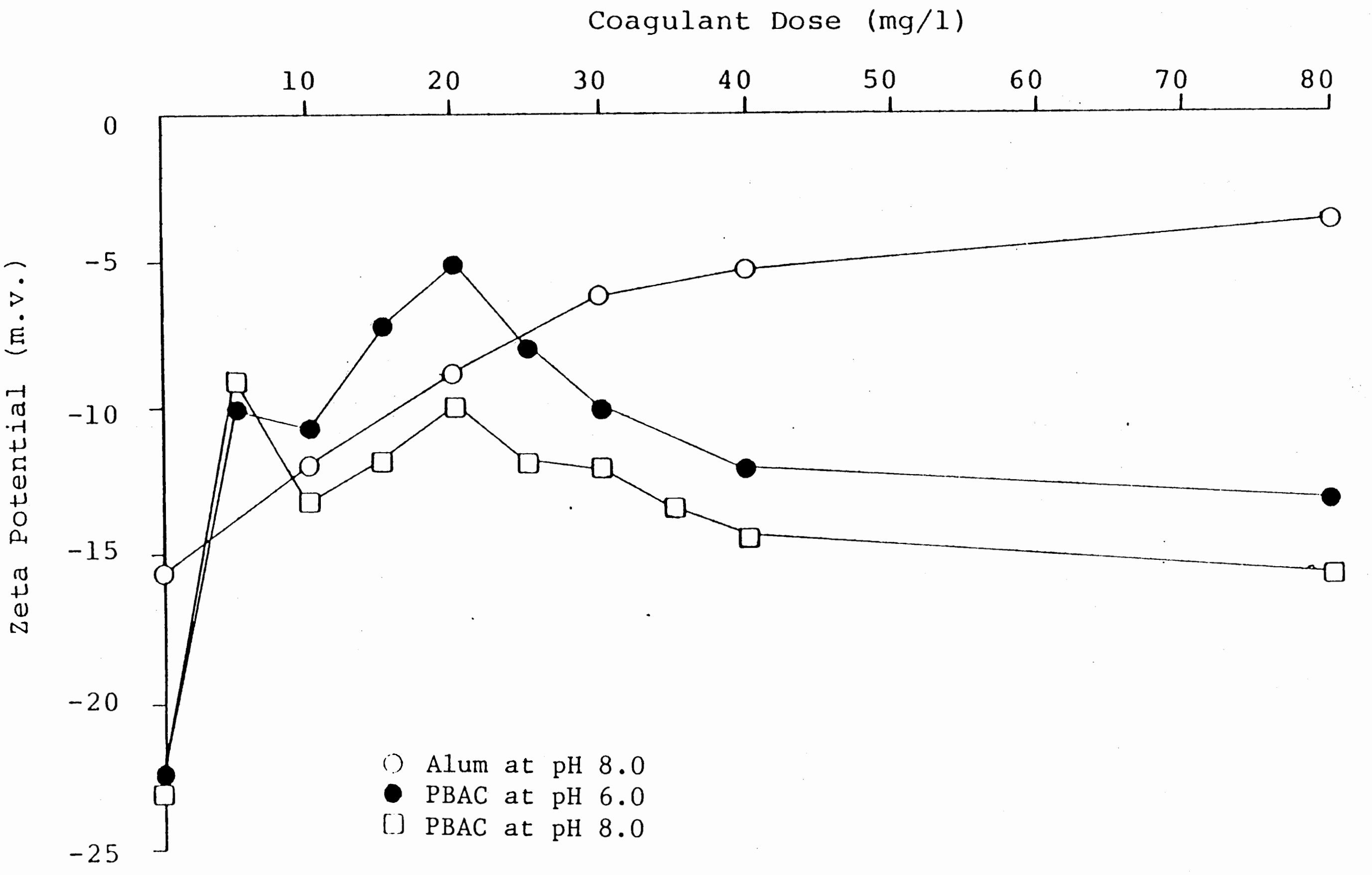


Figure 30: Zeta Potentials Versus Dosage for Alum at pH 8.0 and PBAC (r=2.5) at pH 6.0 and 8.0.

both alum and PBAC. Analyses were done at pH values of 6.0 and 8.0, since pH 6.0 was found to be the optimum for turbidity removal, and pH 8.0 is the natural pH of the water system used in this study. Results are presented in Figures 31 and 32, and reported as Trihalomethane Formation Potential (THMFP). Figure 31 provides a comparison between THMFP values using PBAC and alum at a pH of 8.0, while Figure 32 shows THMFP values for PBAC at both pH values of 6.0 and 8.0

As revealed by Figure 31, THMFP values obtained by using alum were lower than those obtained by using PBAC. THMFP values using PBAC at pH 8.0 were slightly lower than those obtained at pH 6.0 as shown in Figure 32. Overall, increasing doses of both coagulants at both pH values reduced the THMFP values by around 50%.

Pilot Plant Results

The pilot plant was operated in the same fashion as the O.S.U. water treatment plant, using both alum and PBAC individually. Results from the O.S.U. water treatment plant that was using alum at a dose of 22 mg/ℓ are presented here for the sake of comparison, and are shown in Table IX. This table also presents results obtained from the pilot plant using alum and PBAC individually. Results from the O.S.U. water treatment plant show that a turbidity below 1.0 NTU was obtained using conventional treatment (coagulation, flocculation, sedimentation, filtration). The pilot plant was operated using an alum dose of 30 mg/ℓ as this dose was found to be the optimum while running the jar tests. Turbidity values of around 0.7 NTU were achieved, and a significant reduction of organic materials was obtained. When the pilot plant was operated using PBAC with a dose of 25 mg/ℓ, results obtained were not much different from the ones using alum. PBAC was able to reduce turbidity to around 0.6 NTU, while organics removal was almost equal for both coagulants. The pilot plant was operated twice using each coagulant, and the data shown in Table IX was reproducible for both alum and PBAC.

THM analysis was conducted on samples obtained from the plant and the pilot plant.

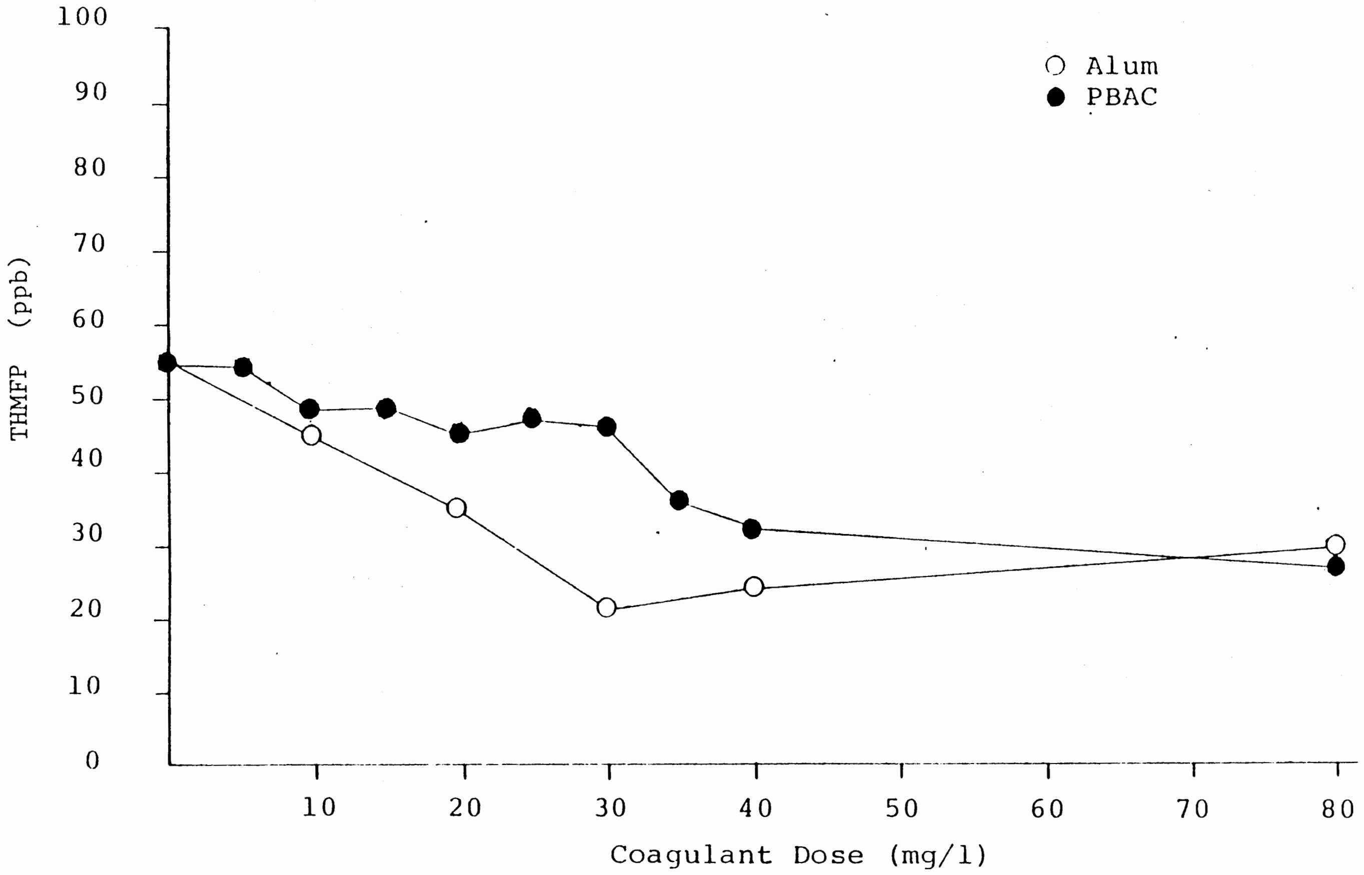


Figure 31: Trihalomethane Formation Potential (THMFP) Versus Dosage Comparing Alum and PBAC (r=2.5) at pH 8.0.

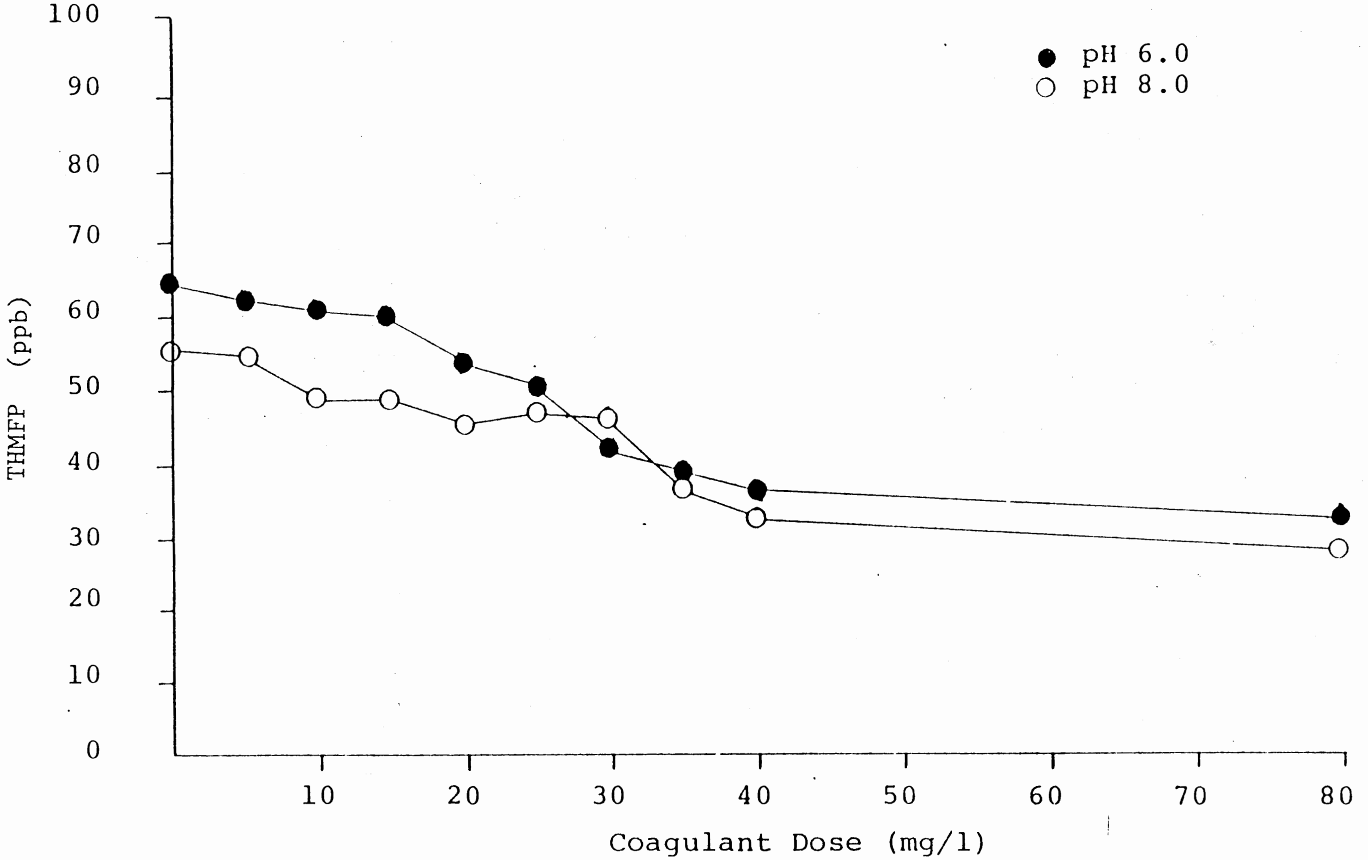


Figure 32: Trihalomethane Formation Potential (THMFP) Versus Dosage for PBAC (r=2.5) at pH 6.0 and pH 8.0.

Results are presented as THMFP and shown in Table IX. Results indicate that there was not much difference between the plant and the pilot plant operation using alum except values obtained from the pilot plant were a little higher. Pilot plant operations using alum and PBAC show that THMFP values are comparable through the various units.

Table IX

Representative Data Comparing O.S.U. Water Treatment Plant and Pilot Plant Operations Using Alum and PBAC

Location	Variable \ Sampling Point	Raw Water	Rapid Mix	Floccu-lation	Sedimen-tation	Filter Effluent
O.S.U. Treatment Plant	Turbidity	27	28	31	4.0	0.8
	T.O.C.	15	14	12	13	12
	U.V.	0.309	0.311	0.320	0.152	0.031
	T.H.M.F.P.	160	140	130	110	60
Pilot Plant Using Alum	Turbidity	25	27	32	5.0	0.7
	T.O.C.	15	15	13	14	13
	U.V.	0.327	0.342	0.289	0.122	0.024
	T.H.M.F.P.	160	145	135	115	100
Pilot Plant Using P.B.A.C.	Turbidity	27	28	30	4.5	0.6
	T.O.C.	15	16	15	14	12
	U.V.	0.305	0.314	0.309	0.153	0.037
	T.H.M.F.P.	160	149	142	117	110

CHAPTER V

DISCUSSION

Turbidity Removals

PBAC (r = 2.5) vs. PBAC (r = 1.8)

Two PBAC solutions with neutralization ratios of OH/Al = 1.8 and OH/Al = 2.5 were compared on the basis of maximum turbidity removal at 3 different pH values, using the different combinations of the raw waters. Results of such comparison were presented in Table V, and illustrated in Figures 7 and 8 for a pH value of 8.0. It is readily apparent from those results that the PBAC solution with a neutralization ration (r) of 2.5 was superior to the PBAC solution with a neutralization ratio of 1.8 in the removal of turbidity from the different combinations of the raw waters at all pH values. Similar results were obtained by Bottero and coworkers (78) where they performed coagulation-flocculation studies on bentonite suspensions using various types of PBAC solutions. They indicated that minimal residual turbidities were obtained when using PBAC solution with an r value of 2.5. They also indicated that flocculation was brought about faster when r values go from zero to 2.5, which was observed in this study.

In another study, similar results were obtained by Fiessinger and Bersillon (77). They observed that an $AlCl_3$ solution that was neutralized with NaOH to obtain a neutralization ratio of $\frac{OH}{Al} = 2.5$ was more effective in removing turbidity from suspension at pH = 7.0, than other $AlCl_3$ solutions receiving more or less neutralization with base.

O'Melia and Dempsey (75) in a coagulation study using PBAC, mentioned that the effectiveness of the PBAC solution coagulant depends on the aging time with the most efficient being aged for 1 hour, and the least effective being aged for a month. However, Bottero and his coworkers mentioned that the most effective PBAC solution was the one aged for 24 hours.

Since PBAC is a fairly new coagulant, not enough work has been done on PBAC solutions to determine the nature of the active species involved in the coagulation-flocculation process. In their attempt to identify the actual species present in a hydrolyzed PBAC solution with $r = 2.5$, Bottero and coworkers (78) identified the presence of 12 different aluminum ions in an octahedral coordination of the polymer Al_{13}, and the Al ions were bound to the non-settleable colloidal gel. This might provide an explanation for the superior performance of PBAC with an r value equal to 2.5 over PBAC with $r = 1.8$. At a neutralization ratio of 2.5, the solution may contain more colloidal $Al(OH)_3$ particles that will provide sticky targets for the flocculation of particulate matter in low and high turbidity waters. Table V reveals the fact that turbidity values using the two PBAC solutions ($r = 1.8$, $r = 2.5$) were lowest at a pH of 5.0. Increasing the pH of the different raw waters to pH 7.0 and 8.0 caused an increase in the residual turbidity measured. This agreed with results obtained by O'Melia and Dempsey (75), where they stated that PBAC should be effective at a pH of 6.5 or lower. It should be expected from the previous discussion that the performance of PBAC solutions neutralized to a certain degree should be more efficient at higher pH values, since there is a higher potential for formation of different aluminum hydroxide species. However, it should be noted that other factors such as hydrogen bonding play a role in the complexed solution structure, and these factors tend to pull the hydroxide ions closer together, thus decreasing the total area of active sticky sites where particles could be attached to during flocculation. Since in this study the pH range selected was not broad enough to draw any conclusions, the above discussion cannot be generalized and the performance of a PBAC solution should be carefully studied on a broader pH range to determine the effect of different negative and positive ions present in solution on its performance for the removal of turbidity from different waters.

Effect of Turbidity and TOC

Figures 5 through 8 demonstrate the efficiency of PBAC solutions in removing turbidity from low and high turbidity waters. When a PBAC solution with r = 2.5 was used, the lowest turbidity residuals were observed for the highest turbidity water at doses of 30 mg/ℓ and above, whereas at lower doses of coagulant, turbidity removals from the high and the low turbidity waters were almost equal. This is illustrated in Figure 6. The same kind of results were observed when the neutralization ratio value of the PBAC solution was 1.8. It seems that PBAC solutions with the two neutralization ratios seem to have higher efficiency of removal of turbidity from higher turbidity waters compared to waters with lower turbidity. By examining Figures 7 and 8, the same thing could be observed where removals were better from the high turbidity water than from the lower turbidity water. In the low turbidity water, doses of PBAC of 80 mg/ℓ were able to achieve the same degree of removal as 20 to 30 mg/ℓ of PBAC coagulant in the highly turbid water. This type of results was reproducible at all pH values selected, with better removals achieved at lower pH values. These results are consistent with observations made by other researchers in the past. In highly turbid water, only low doses of coagulant are required to achieve good removals, whereas in low turbidity waters more coagulant is always required. In low turbidity waters, the active species present in the solution coats the colloids with a gelatinous and sticky sheath. It also provides additional targets for the original solids to "hit" in the flocculation process, thereby accelerating the flocculation of these particles into large aggregates. These targets would be necessary when the water being coagulated is of low turbidity nature. This type of mechanism has been termed "sweep coagulation", or "enmeshment in a precipitate" since it really involves the entrapment of the colloidal particles by the active species providing the sticky sites in the solution.

On the other hand, in highly turbid waters, lower doses of coagulants are required, since the predominant mechanism of removal would be adsorption of the soluble active hydrolysis species on the colloidal particles and destabilization. This was observed in Figure 7 where removals were almost indifferent at the doses of 30 and 80 mg/ℓ. Doses of 80 mg/ℓ were able to achieve almost the same degree of turbidity removal from highly turbid water as the 30 mg/ℓ dose, which shows that excessive amounts of coagulant for this type of water is unnecessary. On the other hand, higher doses of the coagulant for the low turbidity water could be justified to achieve the same degree of removal as compared to the highly turbid water. This argument holds true for alum and other metal coagulants as well as for PBAC.

Comparison of Figures 9 and 10 show that TOC does not have a profound influence on turbidity removals using either PBAC solutions. This is clearly demonstrated when the PBAC solution had a neutralization ratio of 2.5 (Figure 6). Results obtained were almost the same when the PBAC neutralization ratio was equal to 1.8, except for some deviation noticed at a dose of 40 mg/ℓ, which is probably associated with some experimental error (Figures5 and 9). Overall results show that turbidity removals were almost the same from the low and the high TOC raw water, and it seems from the previous results that the effect of TOC on the removal of turbidity from the low and the high turbidity waters is minimal.

PBAC (r = 2.5) vs Alum

Since it was shown from the previous results and discussion that the performance of the PBAC with an r value of 2.5 was superior to that with an r value of 1.8 for the removal of turbidity, the PBAC with a neutralization ratio of 2.5 was chosen to compare its performance with alum throughout the remainder of this study. From Table VI and Figures 11, 12, 13 and 14, it is apparent that turbidity removals were higher using alum doses between 20 and 40 mg/ℓ, with best removals achieved at an alum dose of 30 mg/ℓ. At this same range of dose between 20 and 40 mg/ℓ, PBAC seemed to have poorer turbidity removals. Further investigations showed that the optimum dose of PBAC for turbidity removal was 25 mg/ℓ. This was not observed earlier since the doses chosen for this study were running at 10 mg/ℓ increments. It can be seen from Figure 15 that the PBAC optimum dose for turbidity removal was 25 mg/ℓ, with restabilization occurring at 30 mg/ℓ. It was observed that PBAC was able to destabilize particulate matter one more time at higher doses achieving the same degree of removal at a dose of 80 mg/ℓ as compared to 25 mg/ℓ. Restabilization started to take place at a dose of 40 mg/ℓ using alum. For the particular raw water used in this study it seems that a PBAC dose of 25 mg/ℓ is required to achieve optimal removal of turbidity, while a dose of 30 mg/ℓ using alum is required to achieve optimal removal. Optimal removals were achieved at a pH of 6.0.

Destabilization using alum may be accomplished by charge neutralization. Positively charged aluminum species present in solution are adsorbed on negatively charged particles, neutralizing their charge, and permitting effective aggregation when sufficient contact opportunities (flocculation) are provided. This mechanism works best at a pH range of 4.0 to 6.0 (29). At increasing concentrations of turbidity increasing amounts of coagulant are required and destabilization occurs by precipitation.

At lower turbidity concentrations, the mechanism is somewhat different. $Al(OH)_3$ precipitate is formed and the sticky precipitate can interact with the particles causing turbidity. The solid precipitate also increases contact opportunities and speeds physical flocculation kinetics. Increasing amounts of turbidity will require fewer targets for flocculation, so that the coagulant requirements can decrease slightly. Since the original turbidity of the raw water used in this study was around 25 NTU, the predominant mechanism is charge neutralization. This was verified by Zeta Potential measurements for alum, shown in Figure 30.

PBAC seems to act in a different fashion, and results are quite different. The observed optimum dose for turbidity removal was 25 mg/ℓ, with restabilization taking place when applying the next higher dose (30 mg/ℓ). At even higher doses, PBAC tends to destabilize the particulate matter achieving almost the same degree of removal at doses of 25 and 80 mg/ℓ. Since the active species involved in the hydrolysis-flocculation reaction was not identified, it is very hard to comment on the actual mechanism by which PBAC acts in removing turbidity from water, especially since the Zeta Potential data did not provide enough information on whether PBAC works by charge neutralization or precipitation. The complete behavior of PBAC as a coagulant for turbidity removal is not fully understood, and more research work should be conducted regarding this aspect.

Zeta Potential

As shown in Figure 30, the zeta potential values for alum were consistent with other data found in the literature. The behavior of alum was confirmed through this data, that it works predominantly by charge-neutralizing the particulate matter. As alum doses kept increasing, zeta potential values kept approaching zero, which indicates that the negative charges present on the particulate matter are becoming more and more neutralized by the addition of more alum.

As observed from the data in Figure 30, the Z.P. values for PBAC kept decreasing up to an applied dose of 20 mg/ℓ, with some variation at a dose of 10 mg/ℓ. This agrees with results obtained by Bottero and coworkers (78) and O'Melia and Dempsey (75) where they applied very small increments of low doses of the coagulant. Z.P. values however started increasing when the applied dose increased from 20 mg/ℓ to 80 mg/ℓ. These results can be explained up to an applied dose of 20 mg/ℓ if charge neutralization is to be considered as the predominant mechanism in that range of applied concentration. When PBAC was applied at increasing doses, Z.P. values increased, which means that an increase in the negative charge took place. Considering the fact that turbidity, TOC and U.V. measurements kept decreasing with increasing doses of PBAC, yet the negative charge kept increasing, this could mean that the hydroxide ion may have a major role in the coagulation-flocculation process using PBAC as one of its constituents. It could be that the hydroxide ion may be forming some kind of a sheet around the floc particles that are approaching neutralization when doses of PBAC increase above 20 mg/ℓ. It also appears that the electrostatic forces in the solution are not alone responsible for the flocculation process. Other forces such as hydrogen bonding interactions may intervene.

Based on this behavior shown by PBAC, the mechanism by which it removes particulate matter can not be fully explained. Further work is required using very small increments of PBAC concentrations, with the zeta potential measurements to be monitored throughout the range selected.

Organics and Precursors Removal

Results presented earlier in this study indicate that alum has a better removal of organics (original humic and fulvic acids that have been chlorinated) based on TOC and U.V. values obtained from treated raw water than PBAC at all pH values selected. However, this behavior was sometimes reversed at high dosages applied, especially at higher pH values. These results agree with results obtained for turbidity removals. Results obtained from the study conducted on the precursor material (unchlorinated organics) show that PBAC removes humic substances to a better degree than alum does at all pH values. This was shown solely by using U.V. absorbance measurements, which were conducted on lyophilized samples obtained from jar tests being run using only optimum doses of coagulants.

The bar diagram in Figure 29 reveals the fact that a selective M.W. removal exists for both alum and PBAC in the M.W. range of 12,000 to 1,000 with PBAC being more effective in the range of 12,000 to 2,500. Alum at both pH values of 6.0 and 8.0, showed to be a better coagulant than PBAC for the removal of precursor material in the range of 2,500 to 1,000.

Even though coagulation is traditionally considered a pretreatment process for particle removal, it is also instrumental in reducing the organic content of treated waters. Very little is known about the type of organic compounds that may be removed during the coagulation process. Many specific compounds in natural water systems do not exist as entirely free species, but rather they show some association with the humic substances and other colloidal material in the water. The degree of association will depend on the nature of the organic compound, the characteristics of the colloidal material in suspension, and the water quality.

Alum seemed to be better than PBAC in removing those organics (those that have been chlorinated). It could be seen from results presented earlier that an optimum dose exists for organics removal using both alum and PBAC, and the optimum dose is between 30 and 40 mg/ℓ. It was shown previously in this study that the optimum doses for turbidity removal using alum and PBAC were 30 and 25 mg/ℓ respectively.

It is readily apparent that the optimum dose for organics removal is slightly higher than that for turbidity removal using alum. The optimum dose for organics removal is around 15 mg/ℓ higher than the optimum dose for turbidity removal using PBAC. In the case of alum, it seems that the hydrolysis species present in solution tend to remove turbidity particulates preferentially over the organic material present, with the optimum dose being slightly shifted to a higher dose. In the case of PBAC, the active species present in solution removes preferentially turbidity at a lower dose than alum, but the requirements for optimal removal of organics are higher. Some of the earlier studies disagree with the results presented here. Field (41) conducted studies on the coagulation of Mississippi River waters and indicated that the optimum conditions for removal of turbidity and organics are identical. However, some studies show that this was not always the case, and it appears that the best conditions for organics removal in a natural water may or may not coincide with the conditions required for good turbidity removal. Using either PBAC or alum, it seems that if the coagulant doses are sufficiently high, good removals of turbidity may be achieved and the optimum pH may be selected for the best organics removal. At lower coagulant doses, the best operating pH must be determined by comparing the benefits of improved turbidity removal against the benefits of improved organics removal.

The coagulation study conducted on precursor material (unchlorinated organics) indicate that PBAC had better removals of precursors than alum at all operating pH values. Figures 25 through 28 show that PBAC reduced the amount of humic substances present in the raw water significantly, with reduction efficiency increasing at lower pH values. The bar diagram in Figure 29 also confirms this fact in the M.W. range of 12,000 to 2,500. On the basis of these results, it could be hypothesized that if PBAC is to be used as the sole coagulant, pre-chlorination of the raw water is not recommended since Cl_2 will destroy the humic structure of the precursors, thus forming open-chain type organics which are not removed as efficiently as the ring-type humic materials. Since the actual organic content of the raw water is unknown, and the nature of the active PBAC species in solution is unidentified, this hypothesis needs to be more investigated, and a more detailed study on synthetic water would be recommended.

Overall, comparison of results obtained from both alum and PBAC show that PBAC is a better coagulant for turbidity removals and organics removal if applied at sufficient concentrations, and if pre-chlorination is not applied. Alum would require a little higher concentration for turbidity removal than PBAC (5 mg/ℓ), and since its optimal dose for turbidity and organics removal coincide, alum might not be as efficient as PBAC in the coagulation-flocculation process.

Trihalomethanes

Trihalomethane concentrations were measured for the raw water treated with both coagulants applied at various doses at pH values of 6.0 and 8.0. The results presented in Figure 31 show that trihalomethane concentrations reported as THMFP using alum were lower than those using PBAC. However, applying sufficient concentrations of both coagulants, the yields were almost equal. The apparent higher yield of trihalomethanes obtained using PBAC may be interpreted and explained by the quantitative behavior of organics removals observed earlier in this study. PBAC has been shown to be a less effective coagulant than alum in removing chlorinated organics, thus a higher chance for THM formation is likely to occur. The fact that the yields were almost equal using 80 mg/ℓ of both coagulants can then be expected, since alum and PBAC had almost equal removal of organics when applied at this high dose.

Trihalomethane formation potential values at a pH of 6.0 were slightly higher than those at a pH of 8.0 as shown in Figure 32. This can be explained considering the facts that the THM formation reaction is base catalyzed, and given sufficient time, the yields for two pH systems are almost equal. Results obtained earlier showed that the Instantaneous THM values at pH 6.0 were lower than those at pH 8.0, but were not presented in this study. If the Terminal THM at pH 6.0 and 8.0 were considered to be equal, and the Instantaneous THM concentration at pH 6.0 was lower than that at pH 8.0, then the formation potential (Terminal - Instantaneous) would be higher at pH 6.0, which was observed in this experiment. This explanation is likely to be oversimplified where rather complex humic acid structures are involved, and the nature of the actual active species in the PBAC structure is unknown.

Alum vs. PBAC in the Pilot Plant Operation

Pilot plant results indicate that PBAC performance was comparable with that of alum on the basis of turbidity and organics removals. PBAC was applied at a dose of 25 mg/ℓ, and alum was applied at a dose of 30 mg/ℓ, as these doses were found to be the optimum for turbidity removal during the jar testing. The pilot plant was operated at the ambient pH of 7.9 - 8.0. Results indicate that the efficiency of PBAC in removing turbidity and organics was the same as that when alum was applied. Filter effluent from the pilot plant using both alum and PBAC had a turbidity of around 0.6 NTU, and organics removals were almost the same as can be seen from the results shown in Table IX.

It could be be revealed from these results that the lower dose of PBAC achieved the same degree of turbidity and organics removals as the alum being applied at a higher dose than PBAC. According to this, PBAC could be considered as a substitute for alum in actual water treatment practice since lower doses are required to meet effluent standards.

CHAPTER VI

CONCLUSIONS

This study has presented a comparison between the performance of PBAC and alum for the coagulation of raw water. A brief review of the theory of coagulation has been addressed, particularly adsorption-destabilization and sweep coagulation. The comparison between both coagulants has been conducted at four different pH values, and figures showing the performance of both coagulants were provided at each pH value for the ease of comparison.

From the results of this study the following conclusions can be drawn:

1. PBAC with a neutralization ratio (OH/Al) of 2.5 and aging time of 1 hour is a better coagulant for removal of turbidity than PBAC aged to the same length of time, and neutralized to an r value of 1.8.

2. PBAC with a neutralization ratio of 2.5 has an equal performance to alum for the removal of turbidity and colloidal particles from the raw water in the optimum dose range of 25 to 30 mg/ℓ.

3. Coagulation of raw water with PBAC ($r = 2.5$) results in a selective removal of turbidity over organics.

4. It has been shown by the use of surrogate parameters such as TOC and U.V. absorbance that PBAC ($r = 2.5$) and alum do not work equally well for the removal of organics from the raw water, even though their optimum conditions were almost the same. Alum is a better coagulant for the removal of organics (originally chlorinated) from raw waters.

5. For raw water where post-chlorination only has been applied, PBAC ($r = 2.5$) has been shown by U.V. absorbance to be a better coagulant for the removal of precursor material (unchlorinated) over the pH range selected for this study.

6. Since PBAC is less efficient than alum in removing chlorinated organics, trihalomethane concentrations were higher when PBAC was applied to the raw water.

7. In water treatment practice where the pilot plant study has been conducted, PBAC ($r = 2.5$) can substitute alum for the coagulation process, since good turbidity and organics removals were achieved using lower doses of PBAC.

8. The mechanism underlying turbidity and organics removal using PBAC ($r = 2.5$) was not completely understood since the active species involved in the hydrolysis-coagulation process was not identified, and the results obtained in this study did not provide enough information on the nature of the mechanism. The identification of the active species involved in the hydrolysis-coagulation process was not the subject of this study.

As an overall result of the work presented in this study, it should be possible to use PBAC in an effective and rational manner as a coagulant in water treatment. More investigation is required to determine the efficiency of PBAC over other conventional coagulants.

CHAPTER VII

RECOMMENDATIONS FOR FUTURE RESEARCH

The following recommendations should be considered in future research:

1. Much of the knowledge concerning organics removal during coagulation has been gained from studies conducted with isolated humic and fulvic acids. Additional coagulation studies are essential for characterizing the behavior of the real organic content of drinking water sources.

2. Fundamental studies are needed to examine the influence of natural organic material on the stability and coagulation of turbidity. Different waters should be optimized for turbidity and organics removals for a wide pH range.

3. Additional studies are needed to demonstrate the reduction of trihalomethanes that may be achieved by the coagulation of precursors. These studies should be conducted with natural waters, paying attention to the nature of the organic content of these waters. Identification of the precursors removed by coagulation should be given high priority.

4. Extensive amount of research should be conducted on PBAC. Parameters such as aluminum concentration, the type of basic titrant, neutralization ratio (OH/Al), extent of mixing, aging time, temperature, are all determinants of speciation of the PBAC in solution. These parameters can be manipulated to obtain different species of Al in water. Both theoretical and empirical information is needed and must be used as guides for such manipulation.

5. Additional studies conducted on PBAC should be oriented towards identifying the actual active species present in solution, and once this is done, work should be considered to determine the actual mechanism by which the active species present work in the coagulation process.

6. PBAC products should be further studied on laboratory, pilot plant, and plant scales. When studying PBAC products for application to water treatment, it is important that conditions such as Al concentration be representative of water treatment technology.

7. PBAC should be evaluated for different types of water, and compared to other conventional coagulants used in the field, especially since the PBAC technology is gaining a lot of importance in countries such as France and Japan.

LIST OF REFERENCES

(1) Bunn, W. W., Haas, B. B., Deane, E. R. and Kleopfer, R. D. "Formation of Trihalomethanes by Chlorination of Surface Water." Environmental Letters, 10:3:205 (1975). U.S. Environmental Protection Agency, Region VII, Kansas City, Kansas.

(2) Federal Register 44, No. 231, 68524-68704. Nov. 29, 1979.

(3) Rook, J. J., "Formation of Haloforms During Chlorination of Natural Water." Water Treatment and Examination, 23:234 (1979), Part 2.

(4) Bellar, T. A., Lichtenberg, J. J. and Kroner, R. C. "The Occurrence of Organohalides in Chlorinated Drinking Water." Jour. AWWA, 66:12:703 (1974).

(5) Oden, S. "Humic Acids." Kolloidchem. 11:75 (1919).

(6) Ramann, E. "Soil Science". Berlin (3rd edition, 1911).

(7) Page, H. J., Dutroit, M. M. S. "The Formation of Natural Humic Matter." Jour. Agr. Sci. 20:478 (1930).

(8) Black, A. P., and Christman, R. F. "Chemical Characteristics of Fulvic Acids". Jour. AWWA, 55:7 897 (1963).

(9) Weber, J. H., and Wilson, S. A. "The Isolation and Characterization of Fulvic Acids and Humic Acids From River Water." Wtr. Res. 9:1079 (1975).

(10) Black, A. P. and Christman, R. F. "Characteristics of Colored Surface Water." Jour. AWWA, 6:753 (1963).

(11) Jy, S. W., Moyers, M. and Duggins, J. "Removal of Organic Precursors by Coagulation", 1981 Annual Meeting of the N.C. Section of AWWA and WPCF.

(12) Stevens, A. A., Slocum, C. J., Seeger, D. R. and Robeck, G. G. "Chlorination of Organics in Drinking Water." Jour. AWWA, 68:11:615 (1976).

(13) "Treatment Techniques for Controlling Trihalomethanes in Drinking Water". EPA-600/2-81-156. MERL, Office of Research and Development, U.S. EPA, Cincinnati, OH, September 1981.

(14) Symond, J. M. et al., "Interim Treatment Guide for Control of Chloroform and Other Trihalomethanes". EPA, Wtr. Sply. Res. Div. 6(1976).

(15) "Control of Organic Chemical Contaminants in Drinking Water"--Part 2--Federal Register--USEPA (Feb. 9, 1978).

(16) Kispert, F. C. "Plant Modifications to Minimize Chloroform Formation at Cincinnati". Presented at the 96th AWWA Annual Conference, New Orleans, LA 6(1976.)

(17) Young, J. S. and Singer, P. C. "Chloroform Formation in Public Water Supplies; A Case Study Presented at 97th AWWA Ann. Conf., Anaheim, CA 6(1977).

(18) Packham, R. F. "Studies of Organic Color in Natural Water". Proc. Sec. for Wtr. Trtmt. and Exam, 13:4:316 (1964).

(19) Ghassemi, M. and Christman, R. F. "Properties of Yellow Organic Acids of Natural Waters". Limn. Oceanog. 13:583 (1968).

(20) Gjessing, E. and Lee, G. F. "Fractionation of Organic Matter in Natural Waters on Sephadex Columns." E. S. and T., 1:8:631 (1967).

(21) Dragunov, S. "Soil Organic Matter" (M. M. Kononova, Editor). Pergamon, New York 65 (1961).

(22) Christman, R. F. and Ghassemi, M. "Chemical Nature of Organic Color in Water". Jour. AWWA, 58:723 (1966).

(23) Kleinhempel, D. Albrecht Thaer Arch; 14:3 (1970).

(24) Rook, J. J. "Chlorination Reactions of Fulvic Acids in Natural Waters." E. S. and T., 11:478 (1977).

(25) Morris, J. and Baum, B. "Precursors and Mechanisms of Haloform Formation in the Chlorination of Water Supplies." Presented at Gaslinberg Conf. (1977).

(26) Hall, E. S. and Packham, R. F. "Coagulation of Organic Color With Hydrolyzing Coagulants". Jour. AWWA, 57:1149 (1965).

(27) Albert, G. "Influence of Dissolved Organic Compounds on Flocculation". Heft 9. Engler-Bunke Inst; University of Karlsruhe, Karlsruhe, Germany (1975).

(28) Mangravite, F. J. et al. "Removal of Humic Acid by Coagulation and Microflocculation". Jour. AWWA, 67:2:88 (1975).

(29) Edzwald, J. K., "Coagulation of Humic Substances". Presented at AICHE. Mtg., Atlanta. GA (1978).

(30) Stumm, W. and Morgan, J. "Chemical Aspects of Coagulation". Jour. AWWA, 54:8:971 (1962).

(31) Black, A. P. and Willems, D. G. "Electrophoretic Studies of Coagulation for Removal of Organic Color". Jour. AWWA, 53:4:438 (1961).

(32) Black, A. P. et al. "Stoichiometry of the Coagulation of Color-Causing Compounds With Ferric Sulphate". Jour. AWWA 55:10:1347 (1963).

(33) Thompson, C. G., Singley, J. E. and Black, A. P. "Magnesium Carbonate: A Recycled Coagulant, Part 1". Jour. AWWA, 64:1:11 (1972).

(34) Thompson, C. G., Singley, J. E. and Black, A. P. "Magnesium Carbonate: A Recycled Coagulant, Part 2". Jour. AWWA, 64:2:93 (1972).

(35) Edzwald, J. K., Haft, J. D. and Book, J. W. "Polymer Coagulation of Humic Acid Waters". Jour. Envir. Engrg., Div. ASCE 103:989 (1979).

(36) Narkis, N. and Rebhun, M. "Stoichiometric Relationship Between Humic and Fulvic Acids." Jour. AWWA, 69:6:325 (1977).

(37) Bowie, J. E. "A Comparison of Aluminum Sulphate and Activated Carbon for Organic Color Removal From Ground Waters." Master's Thesis, Mississippi State University, State College, MS (1975).

(38) Narkis, N., Rebhun, M. and Sperbex, H. "Flocculation of Clay Suspensions in the Presence of Humic and Fulvic Acids." Israel, Jour. Chem., 6:295 (1968).

(39) Narkis, N. and Rebhun, M. "The Mechanism of Flocculation Processes in the Presence of Humic Substances". Jour. AWWA, 67:2:101 (1975).

(40) Moore, G. N. "Interactions of Fulvic Acids and Kaolinite During Coagulation." Proc. AWWA 97th Ann. Conf.; Anaheim, CA (1977).

(41) Semmens, M and Field, T. "Factors Affecting the Removal of Organics From Mississippi River Water by Coagulation With Alum." Unpublished Paper.

(42) Bowie, J. and Band, M. T. "Chemical Precipitation—Coagulation for Organics Removal From Ground Waters." Wtr. Res. Bull. 13:6:1269 (1977).

(43) Davis, J. Personal Communications.

(44) Kawamura, S. "Considerations on Improving Coagulation". Jour. AWWA, 68:6:328 (1976).

(45) Jeffcoat, W. B. and Singley, J. E. "The Effect of Alum Concentration and Chemical Addition Times on Coagulation". Jour. AWWA, 67:4:177 (1975).

(46) Albert, G. "The Elimination of Organic Materials by Flocculation". Heft a, Engler-Bunte Inst. of the University of Karlsruhe, Germany (1975).

(47) Novok, J., Zluticky, J., Kubella, V. and Mostecky, J. "Analysis of Organic Constituents Present in Drinking Water." Jour. of Chrom. 76:45 (1973).

(48) "Industrial Pollution of the Lower Mississippi River in Louisiana". Surveillance and Analysis Division, USEPA, Region VI, Dallas, TX.

(49) Rook, J. J. "Haloforms in Drinking Water." Jour. AWWA, 68:3:168 (1976).

(50) Symons, J. M. et al. "National Organics Reconnaissance Survey of Halogenated Organics", Jour. AWWA, 67:11:634 (1975).

(51) "Region V Joint Federal/State Survey of Organics and Inorganics in Selected Water Supplies." USEPA, Chicago, IL 6 (1975).

(52) Morrison, R. and Boyd, R. "Organic Chemistry", Allyn and Bacon, Inc., Boston (1973).

(53) Briley, K. F. "THM Production From Algal Precursors". Water Chlorination: Environmental Impact and Health Effect. 3:117 (1980).

(54) Larson, R. A. and Rockwell, A. L. "Chloroform and Chlorophenol Production by Decarboxylation of Natural Acids During Aqueous Chlorination", E. S. and T. 13:325 (1979).

(55) Rook, J. J. "Formation and Occurrence of Haloforms in Drinking Waters." Proc. 95th Ann. AWWA Conf.: Paper 32-4, June (1975).

(56) Trussell, R. R. and Umphres, M. D. "The Formation of Trihalomethanes". Jour. AWWA, 70:604 (1978).

(57) Christman, R. F. University of North Carolina, Chapel Hill (1977). Personal communications.

(58) Stevens, A. A. "Formation of Nonpolar Organochloro Coumpounds as Byproducts of Chlorination." Proc. Oxidation Tech. in Drinking Water Treatment, Sept. 11-13 (1978), Karlsruhe, F.R.G.

(59) Kajino, M. and Yagi, M. "Formation of THM During Chlorination and Determination of Halogenated Hydrocarbons in Drinking Water". In: Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment. Afghan, B. K. and MacKay, D. Eds., Plenum Publishing Co. 491 (1980).

(60) Lange, A. A. and Kawczynski, E. "Controlling Organics—The Carbon Costa County Water District Experience." Jour. AWWA, 70:11:653 (1978).

(61) Trussell, R. R. "Factors Influencing the Formation of THMs and Organics in Domestic Water Supplies." Proc. Calif. Nevada Section Forum Jour. AWWA, Palo Alto, CA 4(1978).

(62) Kavanaugh, M. C., Trussell, R. R., Cromer, J. and Trussell, A. R. "An Empirical Kinetic Model of THM Formation: Application to meet the THM proposed standard", Jour. AWWA, 78:10:578 (1980).

(63) Stevens, A. A. and Symons, J. M. "Formation and Measurement of Trihalomethanes in Drinking Water." Proc. Control of Organic Chemical Contaminations in Drinking Water (1979), USEPA, Washington, D. C. (In press).

(64) Veenstra, J. N. and Schnoor, J. L. "Seasonal Variations in THM Levels in an Iowa River Water Supply", Jour. AWWA 72 (1980).

(65) Ohio River Valley Water Sanitation Commission. "Water Treatment and Process Modification for THM Control and Organic Substances in the Ohio River." EPA-600/2-80-028, USEPA, Cincinnati, OH 3 (1980), NTIS, Accession No. P13 81-301222.

(66) Carpenter, J. and MaCalady, D. "Water Chlorination: Environmental Impact and Health Effects", Ann. Arbor Science, Ann Arbor (1978).

(67) Kleopfer, R. "Analysis of Drinking Water for Organic Compounds. Identification and Analysis of Organic Pollutants in Water". (L. Leith, Editor), Ann. Arbor Science, Ann Arbor (1976).

(68) Lange, A. and Kawczynski, E. "Experiences of Contra Costa County Water District". Presented at Calif. Nevad Sect. of AWWA, Water Treatment Forum No. VIII, 4 (1978).

(69) Stevens, A. A. EPA Wtr. Sply. Res. Div., Cincinnati, Telecom 3 (1978).

(70) Harris, R. H. "Regulation of Carcinogens in Drinking Water Under the Safe Drinking Water Act". Proceedings of 5th Annual AWWA Water Quality Technology Conference. Kansas City, MO, Dec. 1977.

(71) Federal Register 45, No. 49, 15542-15547. Mar-11-1980.

(72) Morris, J. C. "Formation of Halogenated Organics by Chlorination of Water Supplies". EPA-600/1-75-002 (Mar-1975).

(73) Babcock, D. B. and Singer, D. C. "Chlorination and Coagulation of Humic and Fulvic Acids." Jour. AWWA, 71:3:149 (1979).

(74) Kavanaugh, M. C. "Modified Coagulation for Improved Removal of Trihalomethane Precursors". Proc. AWWA 98th Ann. Conf. Atlantic City, N.J. (1978).

(75) O'Melia, C. R. and Dempsey, B. A. "Coagulation Using Polyaluminum Chloride".

(76) Thebault, P., Cases, J. M. and Fiessenger, F. "Mechanism Underlying the Removal of Organic Micropollutants During Flocculation by an Aluminum or Iron Salt". Water Research. 15:183.

(77) Fiessenger, F. and Bersillon, J. L. "Prepolymerisation de L'hydroxyde D'aluminum Pour La Coagulation des Eaux". SEBEDEAU-BECEWA, 399:52 (1977).

(78) Bottero, J. Y., Poirier, J. E. and Fiessenger, F. "Study of Partially Neutralized Aqueous Aluminum Chloride Solutions: Identification of Aluminum Species and Relation Between the Composition of the Solutions and Their Efficiency as a Coagulant". Progr. in Water Technol., 12:601 (1980).

(79) Albert, G. "The Influence of Dissolved Organic Compounds on Flocculation." Translation of Reports on Special Problems of Water Technology, 9, Adsorption. H. Santheimer, ed. USEPA 35 (1975).

(80) Williams Brothers Engineering Co. "Water Treatment Plant Study." Prepared for Stillwater Utilities Authority, Stillwater, OK. 3 (1980).

(81) Ockerhausen, R. W. "Coagulation Symposium I". Water Works Waste Engr., 2:53 (1965)

(82) Richard, J. J. and Junk, G. A. "Liquid Extraction for the Rapid Determination of Halomethanes in Water". Jour. AWWA, 69:1:62 (1977).

(83) "Standard Methods for the Examination of Water and Wastewater." 14th edition, 532 (1975).

(84) Riddick, T. M. "Control of Colloidal Stability Through Zeta Potential." Vol. 1, (1968).

(85) "Zeta Meter Manual." Zeta Meter Incorporated. 1720 First Avenue, New York, N.Y., 10023.

(86) "Gel Filtration Theory and Practice." Pharmacia Fine Chemicals. AB, Box 175-5-751-04, Uppsala 1, Sweden. 4 (1979).

(87) Khan, P. A. "Interaction of Polymers, Natural Organics, and Chlorine in the Direct Filtration System." Ph.D. Thesis, Oklahoma State University, July 1983.

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