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Coagulation for Removal of Humic Materials from Groundwater

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Abstract

The use of powdered activated carbon and alum–polyelectrolyte coagulation was evaluated to determine its effectiveness in reducing the color-causing organics in a highly colored synthetic groundwater. These organics have been shown to be the precursors for trihalomethane formation in chlorinated drinking waters. Using a series of jar tests, an optimum pH range for hydroxylated aromatics removal using alum–polyelectrolyte coagulation was found to occur near a pH of 5.0. For this pH a relationship between initial hydroxylated aromatics concentration per mg/L alum added and residual hydroxylated aromatics concentration was developed. A ratio value of less than 0.05 was found to be required to reduce the hydroxylated aromatics concentration below 1 mg/L. The use of powdered activated carbon as a modification to the conventional coagulation process was found to be ineffective for this synthetic groundwater. Less than a 5% reduction in hydroxylated aromatics was realized at a powdered activated carbon dosage of 300 mg/L.

INTRODUCTION

After suspected carcinogenic compounds were found in the New Orleans, Louisiana, drinking water system in 1974, the Environmental Protection Agency (EPA) conducted a survey of the drinking water supplied of 80 cities in the United States to determine the extent of organic compounds in this nation's drinking water. The survey, called the National Organics Reconnaissance Survey, found that trihalomethanes (THM's) are widespread in chlorinated drinking water systems in this country. Since these THM's

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(chloroform, bromodichloromethane, dibromochloromethane, and bromoform) were not present in the raw waters or else were found only in very low concentrations, it was concluded that THM compounds were formed during the treatment process when chlorine added for disinfection reacted with dissolved organic material present in the water (*1*).

Although it is not exactly known at this time the health risks to humans, chloroform has been found to be carcinogenic in rodents (rats and mice) at high dosages. Because of these findings, it is suspected that this compound is a human carcinogen. Due to the possible health risks to humans, the EPA on November 29, 1979, finalized regulations for the control of THM's. A maximum limit of 0.10 mg/L for total THM's was promulgated along with monitoring requirements (*2*).

Most organic chemicals which are found in both surface and ground waters are of natural origin. Some of these compounds, specifically fulvic and humic acids, are responsible for imparting organic color and have also been identified as precursors for THM formation during the chlorination process (*3–5*).

In order for water utility systems to achieve the THM requirements set forth by the EPA, certain modifications to present day water treatment practices will have to be made. Most workers agree that there are three treatment alternatives which water utilities must explore before reaching a decision on how to obtain the newly promulgated THM levels. These are:

(1) Use a disinfectant other than chlorine which doesn't produce harmful compounds.
(2) Provide treatment to reduce THM precursors before chlorination.
(3) Provide treatment after chlorination to remove THM's after formation.

If the second alternative is selected, it is generally felt that granular activated carbon treatment will be required to achieve the THM requirements. The use of granular activated carbon (GAC) columns are quite expensive due to the fact that the carbon has to be regenerated. The frequency of regeneration is dependent on the organic loading on the carbon. Therefore, when GAC columns are used, it will be economically beneficial to reduce the organic content of water before it reaches the columns. Aluminum sulfate–polyelectrolyte coagulation has been successfully used for this purpose where surface waters are being treated. However, there has been little research involving the application of this technique to the removal of organics from groundwaters.

There are many areas in the United States, particularly in the southeastern region which have easily accessible groundwater aquifers that produce high quality waters except for high organic color. Not only is this water aesthetically unpleasing, but it contains the precursors which produce trihalomethanes during the chlorination process. The purpose of this study was twofold: (a) to evaluate the effectiveness of aluminum sulfate–polyelectrolyte coagulation in removing humic material from groundwater and (b) to investigate the feasibility of modifying the alum–polyelectrolyte coagulation process by adding small amounts of powdered activated carbon to increase humic material removal while at the same time reducing both the alum and polymer dosage required for optimum removal.

LITERATURE REVIEW

Precursors of Trihalomethane Formation

Most natural waters contain a certain amount of organic matter known as humic substances which, when present in high concentrations, impart a yellowish-brown color to the water. It was Rook (*3*) who in 1974 identified this organic matter as precursors for THM's in chlorinated water. Subsequent work by others have also identified these organic substances as precursors for THM formation (*3*–*5*).

The organic matter which is found in the soil and water consists of a combination of plant and animal products in various stages of decomposition, of substances synthesized biologically and/or chemically from the breakdown products, and of microorganisms and small animals and their decaying remains. This organic matter is usually divided into two groups: (a) nonhumic substances and (b) humic substances.

The nonhumic substances are those which are easily attacked by microorganisms and have a relatively short survival period. By far the larger part of the organic matter consists of the humic substances. These substances are resistant to microbial degradation and have the ability to form stable water-soluble and water-insoluble salts as well as soluble complexes with metal ions and hydrous oxides and to interact with clay materials and organic chemicals. The humic substances are usually divided into three main fractions based upon their solubilities in alkali and acid: (a) humic acid, which is soluble in dilute alkaline solutions but is precipitated by acidification of the alkaline extract; (b) fulvic acid, which is that humic fraction which remains in the aqueous acidified solution, i.e., soluble in both acid and base; and (c) the humic fraction that cannot be extracted by dilute base and acid, which is referred to as humin. The three humic fractions are similar to each other but have different molecular weights and functional group contents (*6*).

The AWWA Research Committee on Coagulation (*7*) define humic substances in the following manner:

> Humic substances are amorphous, acidic, predominantly aromatic, hydrophilic, chemically complex polyelectrolytes that range in molecular weight from a few hundred to tens of thousands. Humic materials are negatively charged macromolecules under the pH conditions of most natural waters. Although these macromolecules may be truly dissolved, they can be classified as colloids because of their colloidal dimensions.

The specific chemical structure of humic substances is still unresolved; however, it is known that they contain the following functional groups in varying quantities: carboxyl, phenolic, alcoholic, ketonic, quinonoid, and methoxyl.

The formation of humic substances is dependent on factors such as vegetation, population, and activity of microorganisms as well as on the hydrothermal conditions. The physical and chemical properties of the soil are also of great importance as they significantly affect both the rate of the humification process and the composition of the humus products (*8*). It is thought that the majority of aquatic humus exists in natural waters as the fulvic acid fraction while the humic acid fraction is insignificant. Gjessing (*8*) explains that moist conditions such as swampy areas promote the formation of smaller molecular weight humic substances (fulvic acids) because these conditions interfere with the molecular condensation reactions, which are the key steps in forming the macromolecules of the humic fraction.

Removal of THM Precursors

An option for reducing THM concentrations in drinking water is to remove THM precursors before chlorine addition. A review of the published literature concerning precursor removal indicates that most of this work has been in the areas of coagulation, carbon adsorption, and, to a lesser extent, ion exchange.

Coagulation

Inorganic salts such as aluminum sulfate and ferric sulfate have been widely used for many years in water treatment to remove colloidal particles which are responsible for imparting color and turbidity to natural waters. The mechanisms responsible for the destabilization of inorganic clay particles are well understood. However, in the past few years there has been considerable interest in determining the effectiveness of coagulation in removing THM precursors and elucidating the mechanisms responsible for the destabilization of these substances.

The coagulation of humic substances with a coagulant occurs by the mechanisms of charge neutralization or precipitation or a combination of both (*7*). Destabilization may be accomplished by charge neutralization resulting from a specific chemical interaction between positively charged aluminum species and the negatively charged groups on the humic colloid. As described by Stumm and Morgan (*9*), the fixation of multivalent cations onto ionized groups on hydrophilic colloids may be due to electrostatic or chemical interaction. Such an interaction causes a reduction in the net charge of the particles as well as an alteration of their solubility. Destabilization by this mechanism would probably occur within the pH range of 4 to 6, and a stoichiometric relationship between the raw water humic concentration and the optimum coagulant dosage would be observed. At large alum dosages precipitation may occur, since humic substances are capable of forming both water-soluble and water-insoluble complexes with metal ions. Coagulation via this mechanism may result from the incorporation of humic material with aluminim hydroxide floc or coprecipitation as aluminum humate or both.

Hall and Packham (*10*) studied the coagulation of organic color using humic substances that had been isolated from river water. They found that organic color and clay turbidity were removed by entirely different mechanisms in the coagulation process. These workers suggest that the removal or organic color with alum is a chemical process in which a partially hydrolyzed aluminum ion of empirical formula $Al(OH)_{2.5}$ interacts with ionic groups such as the carboxyl group on the humic acid colloid. Such a response results in the precipitation of an insoluble humate or fulvate. At pH values greater than 5, larger coagulant dosages were required. This was thought to result from the ionization of a second type of functional group such as the phenolic group. The presence of such a group could cause the formation of a soluble chelate with aluminum. They found a stoichiometric relation between the optimum coagulant dosage for 50% organic removal and the raw water concentration of humic acid and fulvic acid. The optimum pH range for alum coagulation was found to be 5–6.

Mangravite et al. (*11*) investigated the stability of the humic acid sol as a function of coagulant concentration, pH, coagulant-anion type, and sol concentration. Figure 1 is a stability diagram for humic acid taken from this work. It serves to illustrate the various destabilization mechanisms as a function of pH and alum dose. In Regions 1 and 5 the humic acid sols are stable. In Region 6 the sols are stable but exhibit turbidities higher than the uncoagulated humic acid. Aluminum hydroxide precipitates in the areas

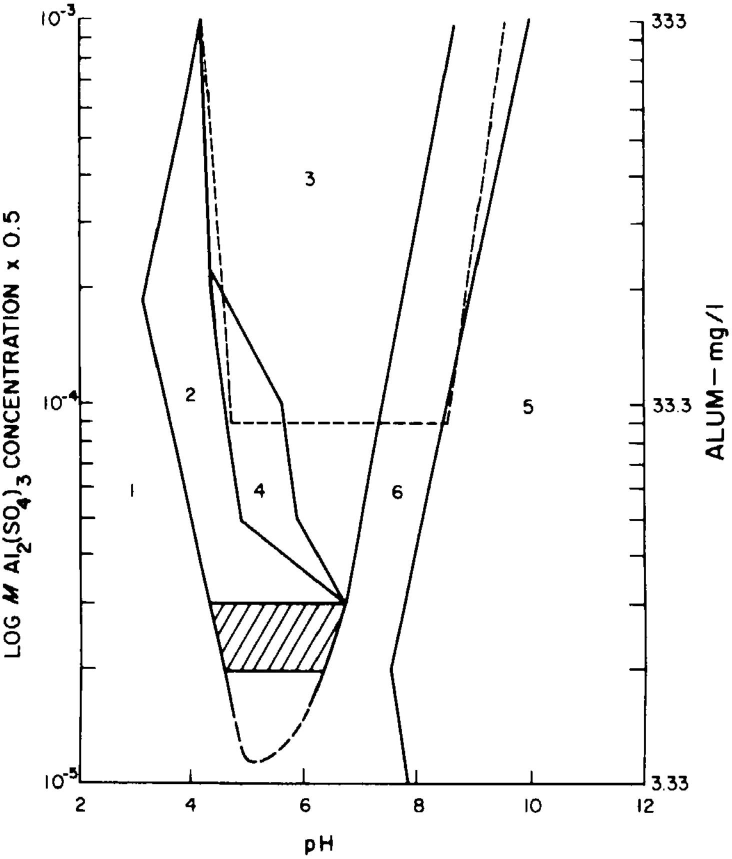


FIG. 1. Aluminum sulfate–pH stability diagram for 5 mg/L humic acid. [Reprinted from *Journal of the American Water Works Association*, *67*(2), (1975), by permission. Copyright 1975, the American Water Works Association.]

outlined with the dashed lines. In Regions 5 and 6 some aluminate anions do not chemically interact with the negatively charged humic acid. In Region 2 the humic acid is destabilized by soluble, hydrolyzed, polynuclear aluminum cations. The humic acid is destabilized in Region 3 where, in the absence of humic acid, aluminum hydroxide precipitation is expected. Mangravite states that for Region 4 the humic acid sols are aggregated (high turbidity) but stable.

Edzwald (*12*) performed studies using polymer coagulation of humic and fulvic acids. He found a stoichiometric relation between the acid concentration and the required dosage. It was observed that a smaller dosage of the polymer was required to destabilize humic acid than an equal weight concentration of fulvic acid. This was thought to be due to the lower molecular weight and therefore greater charge density of the fulvic acids. He proposed the following model for destabilization and aggregation by cationic polymers: Destabilization by charge neutralization followed by aggregation as a result of a specific chemical interaction between the acid macromolecules and the cationic polymer. This interaction involves cross-linking such that alternative layers of polyelectrolytes and acid are interwoven and attached to each other.

Edzwald (*12*) found good removal of humic acid using alum with high molecular weight polymers in the pH range of 4.5 to 6.5. Reductions of 90% and greater for humic acid were obtained at a pH of 6 using the following dosages: 10 mg/L of alum and 0.5 mg/L of a cationic polymer, 10 mg/L of alum and 1 mg/L of a nonionic polymer. According to Edzwald, destabilization was accomplished by charge neutralization resulting from adsorption of soluble cationic aluminum species. This was followed by interparticle bridging with polymers. Restabilization was observed when the system was overdosed with polymer. This was attributed to the unavailability of reaction sites on the surface of the colloidal acid particle.

In conducting coagulation studies of Durham and Chapel Hill, North Carolina, drinking water supplies, Young and Singer (*13*) found that a typical alum dose of 25 mg/L was effective in chloroform precursor removals. Upon chlorination, the coagulated water had a 60% chloroform reduction compared to the chlorination of the raw water. More interesting was the fact that the coagulant was more selective in removing the chloroform precursors than other organic matter. This was evidenced by the fact that a 60% chloroform reduction was observed and only a 40% reduction in TOC was obtained. It was suggested that changing the point of chlorination to a point after coagulation could result in a significant decrease in finished water chloroform concentration.

Activated Carbon

The ability of carbon to remove certain organic compounds in water which cause odor and taste or impart color or which may be toxic has been recognized for many years. Carbon is usually applied either in a granular or powdered form. Powdered activated carbon (PAC) has been widely used in water treatment to remove taste and odors and has been used to some extent in the wastewater treatment field to remove dissolved organics. Granular activated carbon (GAC) which is usually utilized in a bed or column can be placed at various points in the treatment process to remove dissolved organics, biodegradable organics, and suspended solids and colloidal materials.

PAC is finely divided (325 mesh) with a highly developed pore structure and a large specific surface area. These factors all contribute to its low particle density and its extremely low settling velocity. As a result of these characteristics, a problem encountered with PAC systems has been carbon removal from the system. Therefore, it is necessary to use some type of coagulant aid or polymer to enhance the clarification process. Davies and Kaplan (*14*) found that dosages of 0.5 to 0.75 mg/L of a nonionic polyacrylamide polymer enhanced flocculation.

The kinetics or rate of adsorption is an important characteristic of any carbon system. There are essentially three consecutive stages in the adsorption process. The first, called film diffusion, involves the transport of the adsorbate to the exterior surface of the adsorbent; the second, called pore diffusion, is the diffusion of the adsorbate into the pores of the adsorbent; and the third step is the adsorption of solute on the interior surfaces of the adsorbent. It is felt that for column applications, the rate-limiting step is film diffusion, while pore diffusion is the limiting step for batch reactors (*15*).

From kinetic studies with granular activated carbon, Weber and Morris (*16*) observed that the following factors affected the rate of adsorption in batch reactors: size of individual carbon particle, initial solute concentration, and molecular size and configuration of the adsorbate. They postulate that the overall rate of adsorption is directly proportional to the pore size, carbon dose, and solute concentration and inversely proportional to the particle size and the molecular weight of the solute.

One advantage of PAC over GAC is that it has a faster adsorption rate. Davies and Kaplan (*14*) found that 90% of the equilibrium adsorption capacity of PAC can be obtained in 5 min using turbulent mixing of a wastewater. Rickles (*17*) also observed rapid adsorption rates using PAC to remove residual organic matter from secondary effluents.

Boening et al. (*18*) used GAC in a batch reactor to determine the adsorbability of a commercial humic acid. A bituminous carbon and a lignite carbon were used in their study. The capacities of the two were found to be very similar even though the bituminous carbon had a much larger surface area. However, the pore sizes of the bituminous carbon were much smaller than those of the lignite carbon, which hindered the adsorbability of the high molecular weight humic acid molecules. Snoeyink and McCreary (*19*) also observed that the extent of adsorption decreased with increasing molecular size.

A review of the literature indicates that adsorption is improved with decreasing pH. Snoeyink and McCreary (*19*) found that pH had a marked effect on adsorbability of humic materials with adsorption improving with decreasing pH. Boening et al (*18*) found that adsorption of organic matter from well water was more effective at a pH of 3.1 than 7.0, but noted little difference between pH 7 and 10.8. However, they found little change in the adsorbability of humic substances at pH's of 3.1 and 7.0. Still, the adsorbability was much less effective at a pH of 10.8.

In the National Organics Reconnaissance Survey of 80 cities (*1*), a total of 19 surface water treatment plants were found to be using PAC. The dosages used by these plants ranged from 0.6 to 17.5 mg/L with a median of 2.3 mg/L. In all but one, the average total THM concentration was less than that of the average of all those surveyed. Stevens et al. (*5*) used GAC columns to determine the effectiveness of THM precursor removal from Ohio River water. The GAC was found to be effective in removing THM precursors, but the use of the GAC was limited to only a few weeks. Bowie (*20*), using GAC columns to remove organic color from Mississippi groundwaters, found that the carbon could reduce the color by 95%, but the effectiveness was limited to only about 24 h.

In summary, it was concluded from the literature that while activated carbon has been shown to be an effective adsorbent for some organic substances, its adsorption capacities are variable, and that field studies should always be performed to determine its effectiveness for a particular situation.

EXPERIMENTAL METHODS AND PROCEDURES

This study was divided into two phases. The objective of the first phase was to determine an optimum pH range and dosage for the removal of humic material using aluminum sulfate–polyelectrolyte coagulation. The objective of the second phase was to evaluate the effectiveness of powdered activated carbon (PAC) as an adsorbent to remove humic substances and the possibility of using it to increase the efficiency of the alum–polyelectrolyte coagulation process.

Synthetic Groundwater

A synthetic, tea-colored groundwater was used in this study. It was prepared by placing a commercial peat in a container and flooding it with a 0.01 *N* sodium hydroxide (NaOH) solution. The solution was then allowed to stand for several days to extract organic color. It was then filtered through Whatman #2 paper filters to separate suspended matter from the solution. The filtrate was analyzed for chemical oxygen demand (COD), alkalinity, hydroxylated aromatics, turbidity, color, and hardness. After characterization, the filtrate was refrigerated and used as the stock organic solution throughout this study.

Phase I: Aluminum Sulfate–Polyelectrolyte Coagulation

The aluminum sulfate–polyelectrolyte coagulation phase of this study was based upon jar tests performed with 500 mL samples prepared from the stock synthetic groundwater solution. The polyelectrolyte employed in this research was Calgon Cat-Floc. This cationic polymer was found by Bowie (*20*) to be effective in removing organic color from groundwaters.

Three different dilutions of the stock synthetic groundwater solution were used in this phase of the study. To determine the optimum pH range and alum dosages required for maximum humic material removal, jar tests were conducted over a range of pH values and various alum dosages using a constant polymer dose of 1 mg/L (identified by lab tests to be the optimum dose). To maintain a constant pH during a particular battery of test, pH adjustments were made using either 1 *N* sodium hydroxide or 1 *N* sulfuric acid. The optimum alum dosages and pH range were determined by analyzing the supernatant from the jar tests for residual turbidity, true color, and hydroxylated aromatics (samples for these analyses were obtained from near the surface of the beaker after a 20-min settling period had elapsed).

Phase II: Powdered Activated Carbon Study

The second phase of this study was the evaluation of the effectiveness of PAC as an adsorbent for humic material and to determine the feasibility of applying it in the alum–polyelectrolyte coagulation process. The powdered activated carbon employed in this study was Aqua Nucha, manufactured by the Westvaco Co. This particular carbon is characterized by a high iodine number, which is indicative of a large surface area, and a decolorizing index indicative of large pore volumes. At dosages around 21.6 mg/L this carbon has been found to be an effective adsorbent of THM precursors for a surface water.

The optimum carbon contact time was determined by measuring the COD of the filtrate after various contact periods. A plot of COD versus contact time was used to determine the optimum contact time. During the jar test the pH was maintained at a constant value.

Jar tests were also used to determine the effectiveness of PAC for the removal of humic material. This was accomplished by varying the dosage of carbon over the pH range found to be optimum in the coagulation process described in Phase I. The solution was filtered using glass fiber filters, and the filtrate was analyzed for hydroxylated aromatics, true color, and COD.

The possibility of enhancing the adsorption process by permanganate oxidation was also investigated. Jar tests were conducted by dosing with $KMnO_4$ and rapid mixing for 1 h prior to the PAC addition, followed by slow mixing for 4 h. The samples were filtered using glass fiber filters, and the filtrate was analyzed for COD.

Laboratory Test Methods

True color determinations were made by determining the absorbance of the samples relative to platinum-cobalt standards. Samples were centrifuged for 30 min at 3000 rpm during Phase I and were filtered through a glass filter during Phase II in order to remove all fine carbon particles.

The hydroxylated aromatics test was used to measure the humic matter in the solution. This is a colorimetric method of analysis for what are described as "tannin, lignin, tannin-like, lignin-like compounds, or hydroxylated aromatic compounds" (*21*). The calibration curves were prepared with solutions of tannic acid at a wavelength of 700 nm. The calibration curve obeyed Beer's law to approximately 8.5 mg/L.

RESULTS AND DISCUSSION

Results from this study indicate that the use of aluminum sulfate–polyelectrolyte coagulation is an effective means of removing humic material from colored water. However, the use of powdered activated carbon in conjunction with alum–polymer coagulation was not effective in improving the removal of humic matter from the synthetic groundwater solutions used in this study.

Alum dose, pH, and the hydroxylated aromatics concentration were all found to have an effect on the removal of humic material from the synthetic groundwater solutions used in this investigation. Carbon dosage, pH, and contact time were all varied during Phase II of the study in an effort to determine the optimum conditions for the adsorption of the humic material. In Phase II, an oxidizing agent (potassium permanganate) was added in an effort to enhance the adsorption process.

In this section data are presented and discussed with regard to solution characterization, aluminum sulfate–polyelectrolyte coagulation, and carbon adsorption.

Synthetic Groundwater Stock Solution Characterization

During the course of this study two different stock solutions extracted from two different commercially available peats were used. The stock solutions, which will be referred to as Solution A and Solution B, were analyzed for pH, hydroxylated aromatics, turbidity, chemical oxygen demand, alkalinity, true color, and total hardness. A summary of the characteristics of each solution is presented in Table 1. These data indicate that Solution B had more than 2.5 times the color of Solution A. In order to explain the cause of this color difference, both solutions were acidified with hydrochloric acid to a pH near 1.0. After a 15-min period, precipitates had formed in both solutions. When the precipitates were allowed to settle, it was observed that the color in Solution B was very close to that in Solution A. The precipitates which formed were thought to be humic acids which are insoluble under acid conditions. Since humic acids are approximately 10 times more colored than fulvic acids, it is felt that Solution B contained more humic acids, while the composition of Solution A consisted more of fulvic acids.

The COD of the two solutions differed almost by a factor of 2, while the hydroxylated aromatic concentrations of the solutions were very near equal. This would seem to suggest that the humic acids fraction of Solution B contained small numbers of the more difficult to oxidize aromatic functional groups, but contained significant numbers of other more easily oxidizable functional groups.

Total alkalinity as well as total hardness for the two solutions differed

TABLE 1

Characteristics of Synthetic Groundwater Stock Solutions

Parameter	Solution A	Solution B
Hydroxylated aromatics, mg/L	15	16.2
Turbidity, JTU's	0.4	5.6
COD, mg/L	209	406
pH	7.6	7.8
Alkalinity, mg/L as $CaCO_3$	44	156
True color, units	460	1200
Total hardness, mg/L as $CaCO_3$	3	45

substantially. Solution A contained much less alkalinity and hardness than Solution B. This was not surprising since the peats were from two different areas.

The suspended solids concentrations of both solutions were low because they were filtered using Whatman paper filters. Filtration was necessary to reduce the turbidity, since one of the main differences between groundwater and surface water is the low suspended solids content of groundwater. By filtering the solution, an experimental system was provided in which all mechanisms in the coagulation and carbon adsorption processes relate to the removal of the naturally occurring humic substances rather than to a colloidal–macromolecular complex.

Phase I: Aluminum Sulfate–Polyelectrolyte Coagulation

The primary purpose of this phase of the study was to identify an optimum pH range as well as an optimum coagulant dose for the removal of humic material. This was accomplished through a series of jar tests where the coagulant dose was varied over a specified pH range. Results of these experiments were analyzed by constructing plots of hydroxylated aromatics, true color, and turbidity versus pH for various alum dosages.

The relationship of residual hydroxylated aromatics concentration versus pH for alum dosages of 50, 80, 100, and 150 mg/L with a constant polymer dose of 1 mg/L are given in Fig. 2. The synthetic groundwater used to generate the data presented in this figure had an initial hydroxylated aromatics concentration of 7.5 mg/L and was prepared from Solution A. The responses presented in Fig. 2 show that:

(1) Hydroxylated aromatics (humic material) removal is strongly pH and dose dependent.

(2) The maximum hydroxylated aromatics removal occurs within the pH range 5.0 to 5.5 for the larger alum dosages of 100 and 150 mg/L. Outside this pH range restabilization occurs.

(3) As the alum dose is increased, the optimum pH range becomes broader.

(4) At the low alum dose of 50 mg/L very little hydroxylated aromatics removal occurs, but for the small amount that is removed, the greatest removal is observed at pH 6.0.

(5) At the intermediate alum dose of 80 mg/L the greatest hydroxylated aromatics removal occurs at pH 5.0, and restabilization occurs at pH 5.5.

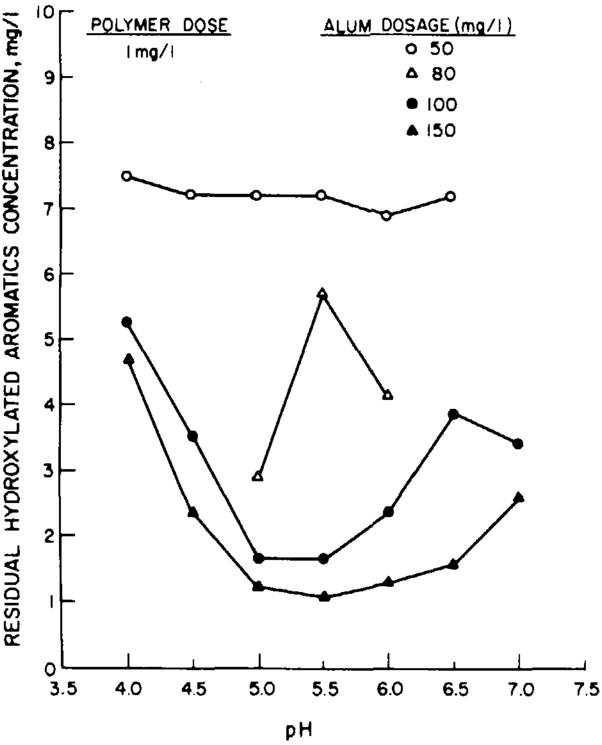


FIG. 2. Relationship between residual hydroxylated aromatics concentration, pH, and alum dosage for a synthetic groundwater with an initial hydroxylated aromatics concentration of 7.5 mg/L.

To explain these observations, consider that humic material can be viewed as an acid so that there is a pH below which it is in its fully protonated form (uncharged, i.e., zero charge density) and a pH above which it is in its fully deprotonated form (fully charged, i.e., maximum charge density). The charge density (number of ionized groups per unit mass) increases with increasing pH between these two extreme pH values. Thus, for a specified solution, the total hydroxylated aromatics concentration will be constant, but the charge density of the material will vary with pH between the extremes of zero charge density and the maximum charge density associated with the total hydroxylated aromatics concentration.

The log [species concentration] versus pH diagram for aluminum in water is given in Fig. 3. This diagram shows that the minimum aluminum hydroxide solubility occurs around pH 6.5 (i.e., for a specified alum dose the

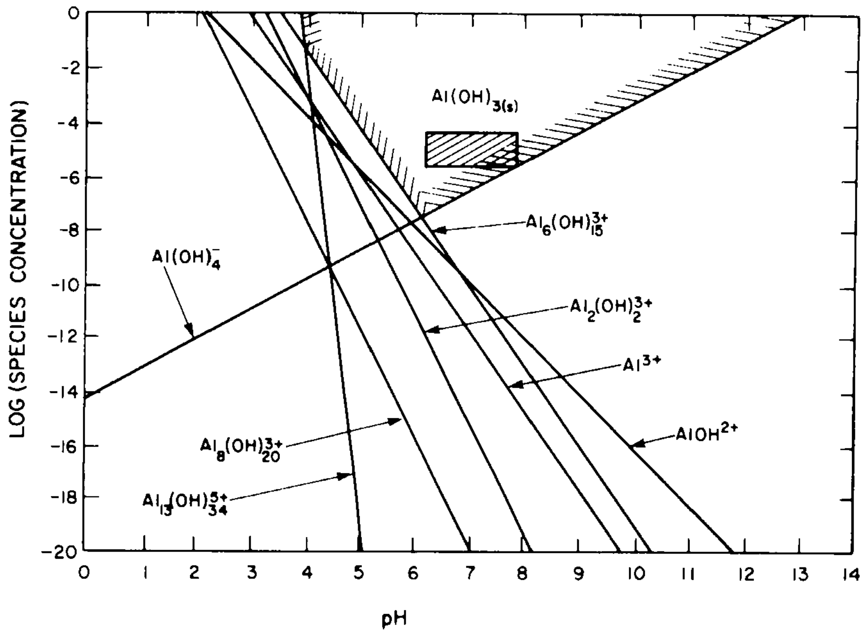


Fig. 3. Solubility diagram for aluminum hydroxide.

maximum amount of aluminum hydroxide will form near pH 6.5). Figure 4 shows that the solubility of aluminum hydroxide is increased if the pH falls below 6.5 because of the formation of highly charged soluble cationic aluminum species such as $Al_{13}(OH)_{34}^{5+}$. The solubility of aluminum hydroxide is also increased if the pH increases above 6.5; however, in this case the increased solubility is due to the formation of the negatively charged soluble $Al(OH)_4^-$ specie.

At a pH of 4, Fig. 3 shows that for the range of aluminum dosages used in this study ($10^{-3.82}$ to $10^{-3.35}$), all the aluminum will be present as soluble cationic aluminum hydrolysis species. Furthermore, at this low pH the charge density associated with the humic material will be quite small. By way of explanation, consider that for the adsorption-neutralization mechanism, destabilization is brought on by the fact that certain soluble cationic aluminum hydrolysis species adsorb rather strongly to the humic material. When this occurs, the negative charge of the humic material is reduced. When the negative charge is reduced to near zero, the colloids are able to stick together (agglomerate) when collisions occur. Hence the amount of alum required for destabilization should be directly related to the amount of humic material present and the charge density of these colloids. Thus, if it is

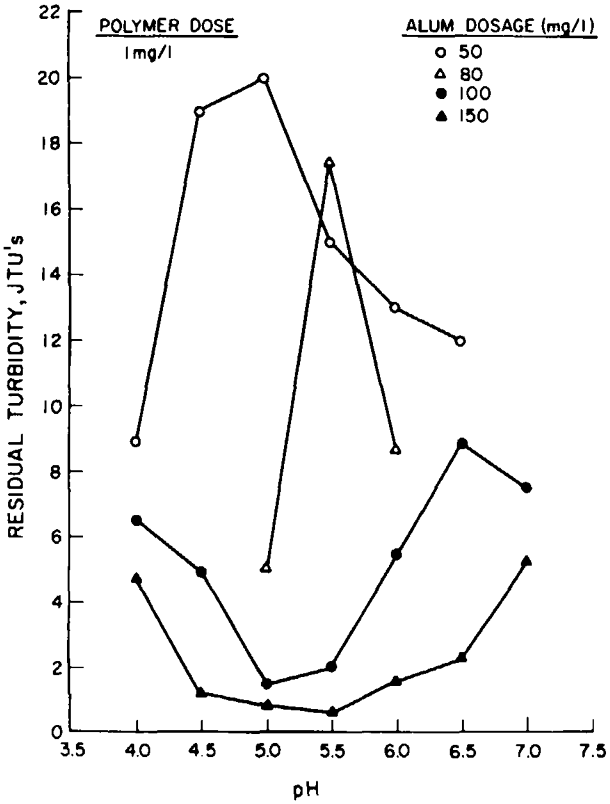


FIG. 4. Relationship between residual turbidity, pH, and alum dosage for a synthetic groundwater with an initial hydroxylated aromatics concentration of 7.5 mg/L.

assumed that destabilization occurs by adsorption-neutralization at this pH, it would be expected that there is an aluminum concentration below which no hydroxylated aromatics removal would occur (this value would increase as the initial hydroxylated aromatics concentration increased), and as the aluminum concentration increased above this value, increased hydroxylated aromatics removal would be observed. This is what is shown in Fig. 2.

Increasing the pH from 4 to 4.5 increases the charge density of the humic material. According to Fig. 3, for the alum dosages employed in this study, all the aluminum will continue to be present as soluble cationic aluminum hydrolysis species. For an adsorption-neutralization destabilization mechanism it might be expected that a smaller hydroxylated aromatics removal would be realized at pH 4.5 than at pH 4.0 when the same alum dose is applied. However, according to Fig. 2, the reverse was found to be true. One plausible explanation for this observation is particle bridging. With the increase in charge density also comes an increase in the number of adsorption sites on the humic material. This will increase the rate at which the soluble cationic aluminum hydrolysis species adsorb to the humic material. When these coated colloids collide, the adsorbed aluminum hydrolysis species may act like polyelectrolytes so that secondary adsorption occurs as free ends of these species attach to an open adsorption site on the second colloid. Thus a bridge between the colliding colloids is formed and the collision is a favorable one, i.e., agglomeration occurs. It must be remembered, however, that the hydrolysis reactions which occur when alum is added to water are very complex. There is still much to be learned about exactly what aluminum species form and how long they exist. Still, it is known that positively charged aluminum species are formed and that the time of existence, type of specie, and specie charge are dependent on the pH of the solution. Thus the increased hydroxylated aromatics removal observed at pH 4.5 could be the result of a number of different factors. Enhanced particle bridging is just one possibility.

The increase in turbidity between pH 4.0 and pH 4.5 for the 50 mg/L alum dose shown in Fig. 4 probably occurs because some agglomeration of humic material is realized. However, the alum dose is not sufficient to promote agglomeration to the point where a readily settleable floc is formed.

When the pH is increased from 4.5 to 5.0, the charge density (and adsorption sites) of the humic material is increased. Furthermore, according to Fig. 3, a small amount of aluminum hydroxide would precipitate for all the alum dosages employed if an ideal solution was used and equilibrium was achieved. However, in the transition from the trivalent aluminum ion to aluminum hydroxide, the aluminum ion proceeds through a series of transition species by hydrolysis reactions and by polymerization. According to O'Melia (*22*), the time necessary for formation of monohydroxo complexes such as $AlOH^{2+}$ is very short (10^{-10} s), while the formation of hydrometal complex (polymers) is somewhat slower (10^{-2} to 1 s). These reactions are extremely rapid compared to the rate at which aluminum hydroxide forms. Hence, for the 50 mg/L alum dose shown in Fig. 2, irreversible adsorption of the transition species probably occurs to such an extent that very little aluminum hydroxide precipitation takes place. Agglomeration of humic material is realized, but the dose is not sufficient to promote agglomeration to the point where a readily settleable floc is formed (see Fig. 4 where an increase in turbidity between pH 4.5 and 5 is indicated). At alum dosages of 100 and 150 mg/L a slighly larger amount of aluminum hydroxide probably forms. An increase in hydroxylated aromatics removal is observed at these alum dosages. This occurs because of a specific interaction between the humic material (via the increased number of adsorption sites), the soluble cationic aluminum hydrolysis species, the long-chained cationic polyelectrolyte, and the aluminum hydroxide precipitate, which results in the formation of a readily settleable complex. This explanation is supported by the parallel decrease in turbidity observed between pH 4.5 and 5.0 and is illustrated in Fig. 4.

The explanation presented in the preceding paragraph holds when the pH is increased from 5.0 to 5.5, except that now the solubility of aluminum hydroxide is further reduced so that a larger amount of $Al(OH)_3$ will form at all alum dosages. Hence, at pH 5.5 the available soluble cationic aluminum hydrolysis species concentration is reduced to the point that no increase in hydroxylated aromatics removal is realized, even for the larger alum dosages. Furthermore, at the intermediate alum dose of 80 mg/L a dramatic increase in both residual hydroxylated aromatics concentration and turbidity is noted at pH 5.5. This is probably the result of an alum dose which is too low to provide enough insoluble aluminum hydroxide for effective agglomeration and the production of a readily settleable floc, but large enough so that the amount of aluminum hydroxide formed will substantially increase the solution turbidity. Since the samples for hydroxylated aromatics measurements were taken from the surface of the beaker, any destablized but unsettled insoluble complex would be measured. Thus a parallel increase in both residual hydroxylated aromatics concentration and turbidity is noted for the 80 mg/L alum dose.

Increasing the pH from 5.5 to 6.0 results in an increase in the residual hydroxylated aromatics concentration for both the 100 and 150 mg/L alum dosage. However, the increase is not nearly as dramatic as that shown in Fig. 2 when the pH is decreased from 5.0 to 4.5 for the same alum dosages. On the other hand, the respective turbidity levels at pH 4.5 and 6.0 for the alum dosages of 100 and 150 mg/L are very nearly the same. Furthermore, hydroxylated aromatics removal is significantly increased for the 50 and 80 mg/L alum dosages when the pH is increased from 5.5 to 6.0. When considered together, these different system responses suggest that an additional hydroxylated aromatics removal mechanism is present at pH 6.0. It is possible that this mechanism is the precipitation of aluminum humates. In support of this premise, consider that if an insoluble aluminum humate precipitate is formed for certains conditions, it should be possible to write an equilibrium solubility expression of the form (*23*):

$$K = [Al_H]^M [HA]^N \qquad (1)$$

where $[Al_H]$ represents the equilibrium concentration of the controlling aluminum hydrolysis specie and [HA] represents the equilibrium hydroxylated aromatic concentration. Then, if $[Al_H]$ and [HA] depend on the alum dose, Eq. (1) can be modified to the form

$$K = [\text{alum dose}]^X [\text{HA}]^Y \tag{2}$$

or

$$\log K' = X \log\ [\text{alum dose}] + Y \log [\text{HA}] \tag{3}$$

Equation (3) can be rearranged to give

$$\log [\text{HA}] = -\frac{X}{Y} \log [\text{alum dose}] + \frac{1}{Y} \log K \tag{4}$$

A plot of log [HA] versus log [alum dose] should give a straight line plot of slope $-X/Y$. Such a plot is shown in Fig. 5 to approach a linear trace for a

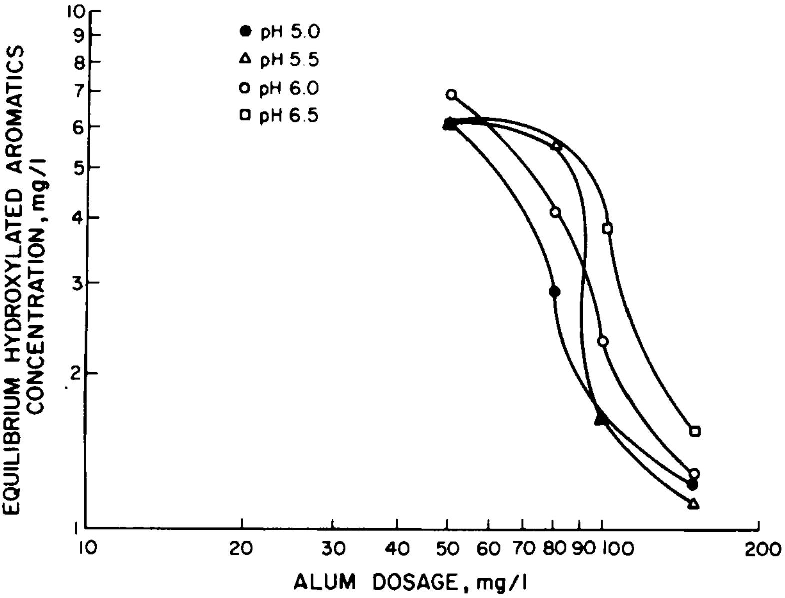


FIG. 5. Log-log plot of equilibrium hydroxilated aromatics concentration versus alum dosage for a synthetic groundwater with an initial hydroxylated aromatics concentration of 7.5 mg/L and solution pH's of 5.0, 5.5, 6.0, and 6.5.

solution with an initial hydroxylated aromatics concentration of 7.5 mg/L when the solution pH is 6.0. Similar plots at other pH's for the same solution show a much greater deviation from linearity. This it would appear that the precipitation mechanism (if indeed it does exist) is dependent upon the solution characteristics, and it is only activated at the proper combination of aluminum hydrolysis specie concentration, hydroxylated aromatics concentration, and pH.

When the pH is increased from 6.0 to 6.5, the possibility of aluminum humate precipitation can no longer be supported. Furthermore, the residual soluble cationic aluminum species concentration is decreased. This occurs because the solubility of aluminum hydroxide is very near its minimum, so that the amount of aluminum hydroxide solid formed per unit dose of alum is near the maximum. The overall effect is a decrease in hydroxylated aromatics removal for all alum dosages. At pH 6.5 the predominant destabilization–agglomeration mechanism is probably enmeshment by the aluminum hydroxide floc and bridging by the cationic polymer.

Increasing the pH from 6.5 to 7.0 results in a decrease in both the residual hydroxylated aromatics concentration and turbidity for the 100 mg/L alum dose while an increase in both these parameters is noted for the 150 mg/L alum dose. The difference in these responses can be explained by considering that bridging by the cationic polymer is probably a very important agglomeration mechanism at pH 7.0. The effectiveness of this mechanism will depend on the alum dose (which controls the quantity of insoluble aluminum hydroxide formed), the polymer dose, and the charge density, as well as the structure of the humic material. For a specific polymer dose it would be expected that the residual hydroxylated aromatics concentration and turbidity would decrease with increased alum dose until some optimum alum dose had been reached. Any increase in dose above the optimum value would result in an increase in residual hydroxylated aromatic concentration and turbidity because the amount of insoluble aluminum hydroxide formed above this point would exceed the capacity of the polymer dose to provide effective agglomeration. However, it would also be expected that if the alum dose were continually increased, the effects of the polymer would be totally masked. At this point, sweep floc coagulation by insoluble aluminum hydroxide would be the predominant removal mechanism, and a further increase in alum dose would result in a decreasing hydroxylated aromatics residual concentration.

The relationship between true color removal and hydroxylated aromatics removal is illustrated in Fig. 6, where the percentage hydroxylated aromatics and true color remaining are given as a function of alum dosage at pH 5.0 for

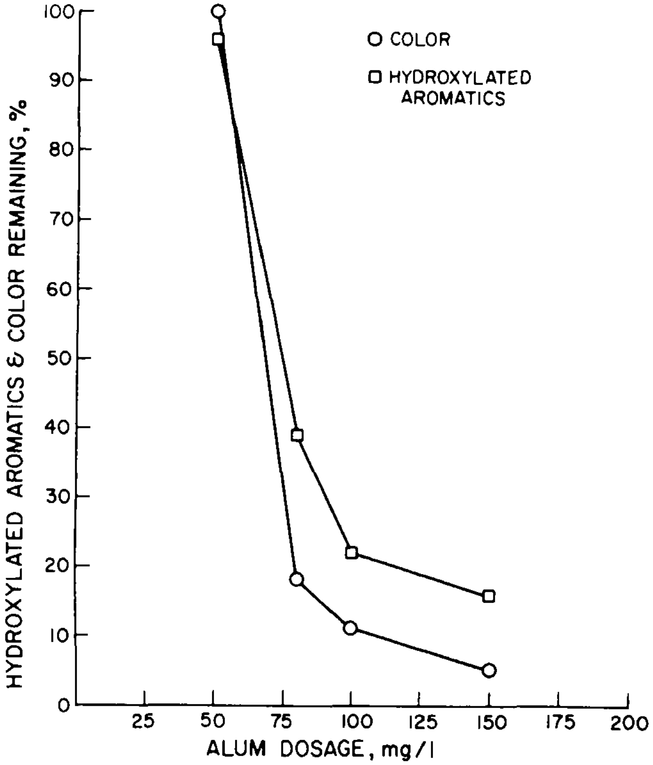
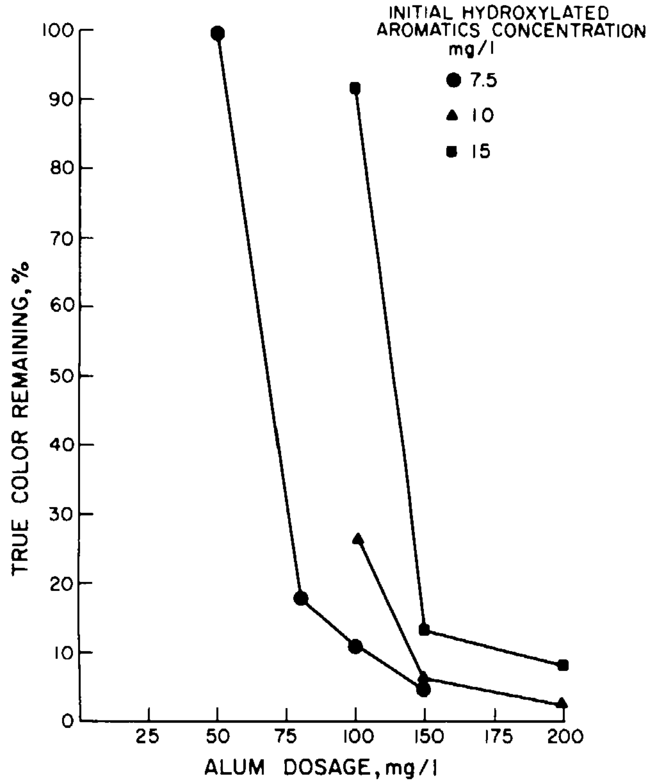


FIG. 6. Percentage hydroxylated aromatics and true color remaining as a function of alum dosage at pH 5.0 for a synthetic groundwater with an initial hydroxylated aromatics concentration of 7.5 mg/L.

synthetic groundwater with an initial hydroxylated aromatics concentration of 7.5 mg/L. Very little hydroxylated aromatics or true color removal is observed at the 50 mg/L alum dose because, as stated earlier, this alum dose is inadequate for destabilization. A weak stoichiometric relationship between true color removal and alum dosage is shown in Fig. 7. Data used in the construction of this figure were obtained at pH 5.0. This pH is within the range where the maximum hydroxylated aromatics removal and true color removal were observed to occur.

An analysis of the experimental data obtained from synthetic groundwaters with initial hydroxylated aromatics concentrations of 10 and 15 mg/L showed response patterns to alum addition which were basically the same as



IG. 7. Percentage true color remaining as a function of alum dosage at pH 5.0 for the three synthetic groundwaters employed in this investigation.

hose presented and discussed for the synthetic groundwater with an initial ıydroxylated aromatics concentration of 7.5 mg/L.

Semmens and Field (*23*) have presented data which show a linear elationship at a specific pH between total organic carbon (TOC) removed er unit amount of alum added and total organic carbon remaining in solution see Fig. 8). These workers note that the linear response indicates that if a ow alum dose is employed, the TOC removal per mg of alum added is reater than if a larger alum dose is applied. An attempt was made to onstruct a similar plot using the hydroxylated aromatics removal data btained in this study at pH 5.0. The results of such a plot are presented in ig. 9 where hydroxylated aromatics removal per mg/L alum added is elated to the residual hydroxylated aromatics concentration. The U-shaped

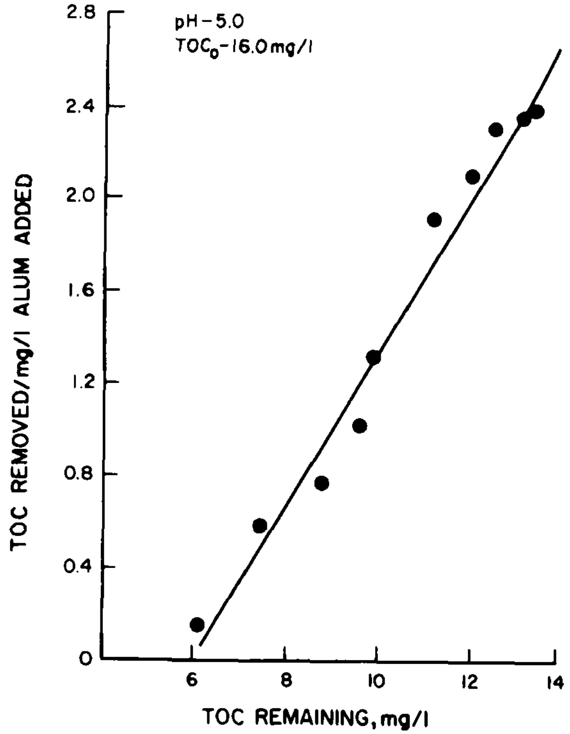


FIG. 8. TOC removed/mg/L alum added as a function of equilibrium TOC. [Reprinted from *Journal of the American Water Works Association, 72*(8), (1980), by permission. Copyright 1980, the American Water Works Association.]

responses shown in this figure occur because, for a specified initial hydroxylated aromatics concentration, fairly large alum dosages are required to achieve low hydroxylated aromatics residual concentrations. As the residual hydroxylated aromatics concentration becomes small, increasing the alum dose results in only a very small increase in hydroxylated aromatics removal. Hence hydroxylated aromatics removal per mg/L alum added will decrease as the residual hydroxylated aromatics concentration becomes small. The other extreme occurs at low alum dosages (approaching the minimum dose required to achieve hydroxylated aromatics removal) where the mg/L hydroxylated aromatics removal is much less than the mg/L of alum added. This also results in a small hydroxylated aromatics removed per mg/L alum added ratio. However, the residual hydroxylated aromatics

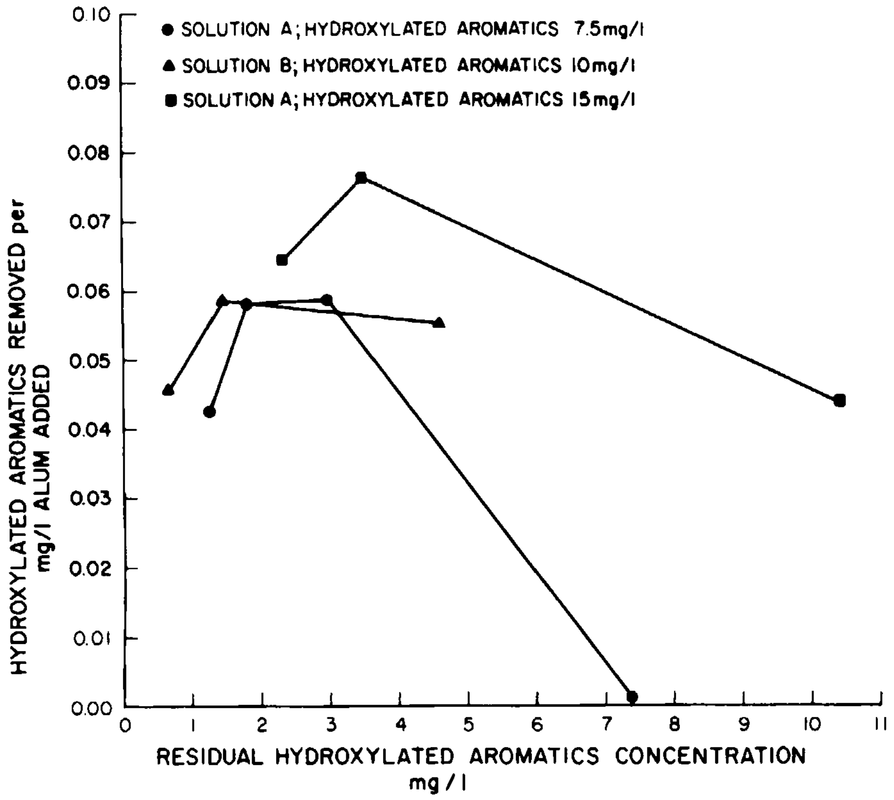


FIG. 9. Hydroxylated aromatics removed per mg/L alum added versus residual hydroxylated aromatics concentration at pH 5.0 for the three synthetic groundwaters employed in this investigation.

concentration associated with this small ratio approaches the initial hydroxylated aromatics concentration. For hydroxylated aromatics removals between these two extremes, the hydroxylated aromatics removed per mg/L alum added ratio will be relatively large.

In Fig. 10 a log-log plot of initial hydroxylated aromatics concentration per mg/L of alum added versus residual hydroxylated aromatics concentration for coagulation tests conducted at pH 5.0 gave a linear relationship. The data presented in this plot cover a range of alum dosages between 50 and 200 mg/L and include synthetic groundwaters derived from two solutions with significantly different characteristics. This suggests that hydroxylated aromatics removal by alum–polyelectrolyte coagulation will be similar, even for groundwaters with different characteristics, as long as the groundwaters

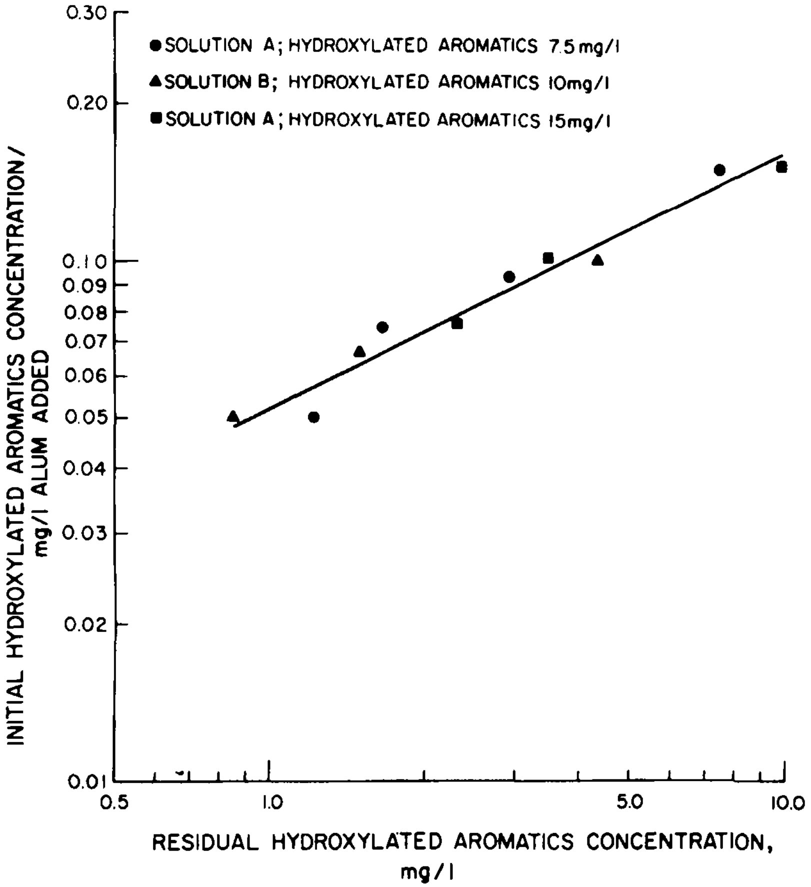


FIG. 10. Initial hydroxylated aromatics concentration per mg/L alum added versus residual hydroxylated aromatics concentration at pH 5.0 for the three synthetic groundwaters employed in this investigation.

share a common pH where maximum hydroxylated aromatics removal occurs and data obtained at this pH are used for comparison.

Phase II: Powdered Activated Carbon Study

The second phase of this study concerned the evaluation of the effectiveness of powdered activated carbon (PAC) as an adsorbent for hydroxylated aromatics and the feasibility of applying it in the alum–polyelectrolyte coagulation process to increase hydroxylated aromatics removal. Before the investigation began it was believed that if PAC addition proved to be a successful modification to the alum–polyelectrolyte coagulation process, the modified process would probably required that PAC be added and a short contact period be provided prior to alum and polyelectrolyte addition. Thus it was felt that a part of the research effort should be directed toward determining an optimum carbon contact time. This was accomplished by measuring the COD of the filtrate obtained after varying periods of contact between a 50 mg/L PAC dose and a synthetic groundwater prepared from Solution B which initially contained 8.8 mg/L hydroxylated aromatics. During the test period the pH of the solution was maintained at a constant value of 5.5. The test results are presented in Fig. 11, where it is seen that a 10-min contact time was found to be optimum for the 0 to 15-min contact period investigated. The initial COD of the solution was approximately 182 mg/L, and the COD after 10 min of contact with 50 mg/L of PAC was only reduced to near 169 mg/L. It was at this point that some doubt began to develop concerning the feasibility of the PAC modification, since to be regarded as successful it was felt that at least a 1% reduction in COD should be realized for each mg/L PAC added when small carbon dosages are applied. For the synthetic wastewater used in this research, the COD reduction at the optimum contact time was approximately 0.14% for each mg/L of PAC added.

Because of the low COD removal observed when the optimum contact time was established, a much more extensive evaluation of the effectiveness of PAC for the removal of organics from the synthetic groundwater used in this study was considered necessary. Synthetic groundwater samples were prepared from Solution B so that the initial hydroxylated aromatics concentration, true color, and COD values were approximately 8.5 mg/L, 715 units, and 200 mg/L, respectively. A battery of tests was then conducted in which the pH of a series of samples was adjusted to 4.0 and held constant. Specific samples were then dosed with PAC in amounts of 100, 200, and 300 mg/L. The individual samples were then mixed for 4 h, after which they were filtered, and hydroxylated aromatics, true color, and COD measurements were made on the filtrate. Similar tests were conducted at pH values of 5.0 and 6.0. No hydroxylated aromatics removal was observed at the 100 mg/L PAC dose, and less than 5% removal was noted at the 300 mg/L PAC dose. COD removals were greater than hydroxylated aromatics removals (near 10% at the 100 mg/L PAC dose and 20% for the 300 mg/L PAC dose) but are still extremely low considering the size of the carbon dose.

In an effort to enhance the adsorption process, pretreatment by premanganate oxidation was investigated. The pH of a series of synthetic groundwater samples was adjusted to 6.0 and held constant. A potassium permanganate

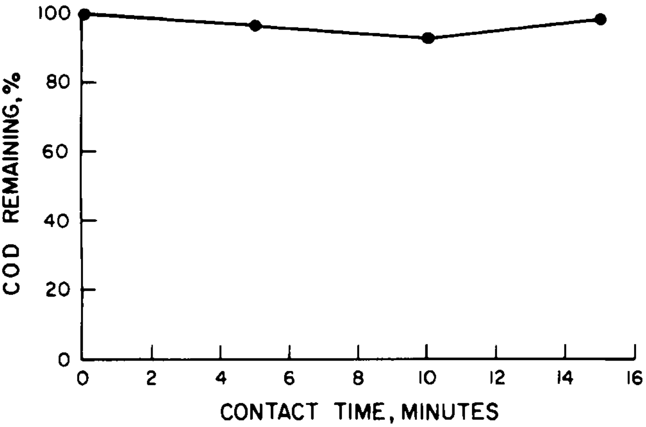


FIG. 11. Percentage COD remaining as a function of contact time at pH 5.5 for a carbon dose of 50 mg/L and a synthetic groundwater with an initial hydroxylated aromatics concentration of 8.8 mg/L.

dose of 50 mg/L was added to each sample. After 1 h or mixing, specific samples were dosed with PAC in amounts of 100, 200, and 300 mg/L. After an additional 4 h of mixing, the samples were filtered and the COD of the filtrate measured. No difference was found in COD removal between the samples with and without permanganate pretreatment.

SUMMARY AND CONCLUSIONS

The results of this study indicate that alum–polyelectrolyte coagulation is an effective means of removing hydroxylated aromatics from water. Hydroxylated aromatics removal was found to be strongly pH and dose dependent. The maximum hydroxylated aromatics removal for a specified chemical dose occurred near a pH of 5.0. For a 1 mg/L polymer dose at a pH of 5.0, a relationship between the initial hydroxylated aromatics concentration per mg/L alum added ratio and residual hydroxylated aromatics concentration was found which indicated that for the synthetic groundwaters used in this investigation, a ratio value less than 0.05 would be required to reduce the residual hydroxylated aromatics concentration below 1 mg/L.

The results of the powdered activated carbon phase of the study indicated that for the synthetic groundwaters employed in this research, the addition of PAC would not provide an economical modification to the alum–polyelectrolyte coagulation process because of the large dose required for any degree of hydroxylated aromatics removal. For a solution pH of 5.0, no reduction in hydroxylated aromatics was observed at a PAC dose of 100 mg/L when a 4-h contact period was used. Furthermore, less than a 5% reduction was measured when the PAC dose was increased to 300 mg/L. Under similar test conditions, COD reductions of only 10 and 20% were observed at PAC dosgages of 100 and 300 mg/L, respectively. Furthermore, no difference was found in COD removal when permanganate pretreatment was employed.

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