INTERACTIONS BETWEEN NATURAL AND SYNTHETIC ORGANICS IN THE COAGULATION PROCESS

by

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INTERACTIONS BETWEEN NATURAL AND SYNTHETIC ORGANICS

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ABSTRACT

The removal of fulvic acid, the most soluble fraction of humic matter, with aluminum and polyacrylamide was investigated. The experimental conditions were similar to those usually encountered in practice. The pH ranged from 6 to 8, the aluminum dosage from 10^{-5} M to 0.5×10^{-3} M, and the polymer concentration from 0 to 1 mg/L. The fulvic acid concentration was constant at 10 mg/L.

The removal of fulvic acid with aluminum was found to depend on the particle size of the aluminum-fulvic acid flocs. This was demonstrated by both the increased removals when filters with a pore size of 0.10 µm were used (as opposed to filters with a pore size of 0.45 µm) and the beneficial effect of the presence of nonionic polyacrylamide. The nonionic polymer promoted both the removal after settling and the removal after filtration. The latter was attributed to the flocculation of micro-colloidal particles which in the absence of the polymer passed through the pores of the filter.

Based on a three-level factorial experimental design an empirical statistical model of the removal of fulvic acid was developed. The model was based on the consideration that for a narrow operating region, the response surface may be approximated with a quadratic mathematical expression. By applying this technique the effect of the pH, aluminum dosage and polymer dosage were quantitatively modelled. A polymer dosage of 0.1 mg/L was found to be optimal because it gave the minimum cost of chemicals for the desired high degree of removal.

Finally, the most significant factors that affected the removal of fulvic acid with aluminum, in addition to the pH, the aluminum dosage and the polymer dosage, were the calcium present in the water and the interaction of calcium with the pH. The effect of calcium was larger at pH 8 than at pH 7. The effect of the polymer properties was not as large as the effect of the calcium, with the effect of the polymer molar mass being more important than the effect of the degree of hydrolysis of the polyacrylamide.

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COD	Chemical Oxygen Demand
FA	Fulvic acid
FA_o	Initial fulvic acid concentration
HA	Humic acid
NTU	Nephelometric Turbidity Units
PEI	Polyethyleneimine
TOC	Total Organic Carbon

CHAPTER ONE

INTRODUCTION

Humic substances are probably the most extensively distributed natural organic materials. In natural waters humic substances cause the yellowish-brown color, which characterizes usually the water from marshy areas.

Historically, the removal of humic substances was mainly connected with the removal of color for aesthetic reasons (AWWA Joint Committee Report, 1970). Other reasons, for which humic matter had been considered undesirable, were their contribution to taste and odour problems, the increase in chlorine demand, and the interference with water processing operations, especially ion exchange and coagulation.

Rook (1974) first presented data showing that chlorination of water led to the formation of haloforms at significant levels. He argued that the formation of halogenated organics was the result of action of chlorine on naturally present organics. The discovery that chloroform could cause cancer and the proposed level of 100 µg/L for total trihalomethanes (AWWA Committee Report, 1979) stimulated an increased interest in effectively removing humic substances, so as to prevent trihalomethane formation.

Other concerns occur because humic substances interact strongly with metal ions and organics, change significantly the solubility of them and affect their immobilization and transport in aquatic environments (Schnitzer and Khan, 1972). While there is no evidence that humic substances themselves are harmful, their association with heavy metals and/or toxic organics (such as pesticides) increases the necessity of having them removed from the water.

Because of the highly hydrophilic nature of the humic matter, the removal of humic substances is accomplished either by advanced, and therefore expensive, processes, such as activated carbon adsorption, ion exchange and membrane processes, or through an improvement of more traditional processes, such as precipitation/coagulation and filtration. This thesis investigates the removal of fulvic acid, the most soluble fraction of the humic substances, with aluminum coagulants in the presence of polyacrylamide, a water-soluble polymer.

CHAPTER TWO

LITERATURE REVIEW AND OBJECTIVES

The universal occurrence of the humic matter and its environmental significance has made it an extensively studied subject by scientists from a variety of disciplines. The reviewed literature as it relates to the nature of the humic substances is, therefore, selective and nonexhaustive. A detailed review on the removal of humic substances by coagulation during the treatment of water is also presented in this chapter. Finally, after the literature is reviewed and the need for more research is identified, the objectives for undertaking the work are presented.

2.1 HUMIC SUBSTANCES

Humic substances constitute the majority of organic matter in most waters and soils. These are amorphous, brown or black, hydrophilic, acidic, polydisperse substances of molar mass ranging from several hundreds to tens of thousands. Despite the extensive investigations during the last twenty years, the structure, and physical and chemical properties of humic substances have not been completely elucidated. A review of these investigations is given in this section.

2.1.1 Classification

The most widely classification scheme of humics is based on the solubility in alkali and acids. They are classified as: (a) Humic Acid (HA), which is soluble in dilute alkaline solution but precipitates under acidic conditions; (b) Fulvic Acid (FA), which is soluble in both acid and base; and (c) Humin, which cannot be extracted by dilute base and acid. Further classifications are possible, mainly of the humic acid fraction. Figure 2.1 summarizes the fractionation of humic substances.

The three main fractions are structurally similar, but they differ in molar mass, ultimate analysis and functional group content. The fulvic acid fraction has a lower molar mass but higher content of oxygen-containing functional groups per unit mass (Schnitzer and Khan, 1972).

Another important characteristic, exhibited by all humic fractions, is resistance to microbial degradation and the ability to form water-soluble and water-insoluble complexes with metal ionic species, clays and organic compounds.

The synthesis of humic substances, known as the humification process, has not been yet elucidated. Felbeck (1971) summarized the existing four theories about the formation of humic substances:

(i) The plant alteration hypothesis implies that lignified plant tissue is altered superficially in the soil to form humic substances.

(ii) The chemical polymerization hypothesis considers that plant tissue is degraded microbially to simple compounds that are further used by microbes for the synthesis of more complex products, such as phenols and aminoacids. These products are excreted into the environment where oxidation and polymerization leads to the formation of humic substances.

(iii) The cell autolysis hypothesis considers humic substances as condensation and free radical polymerization products

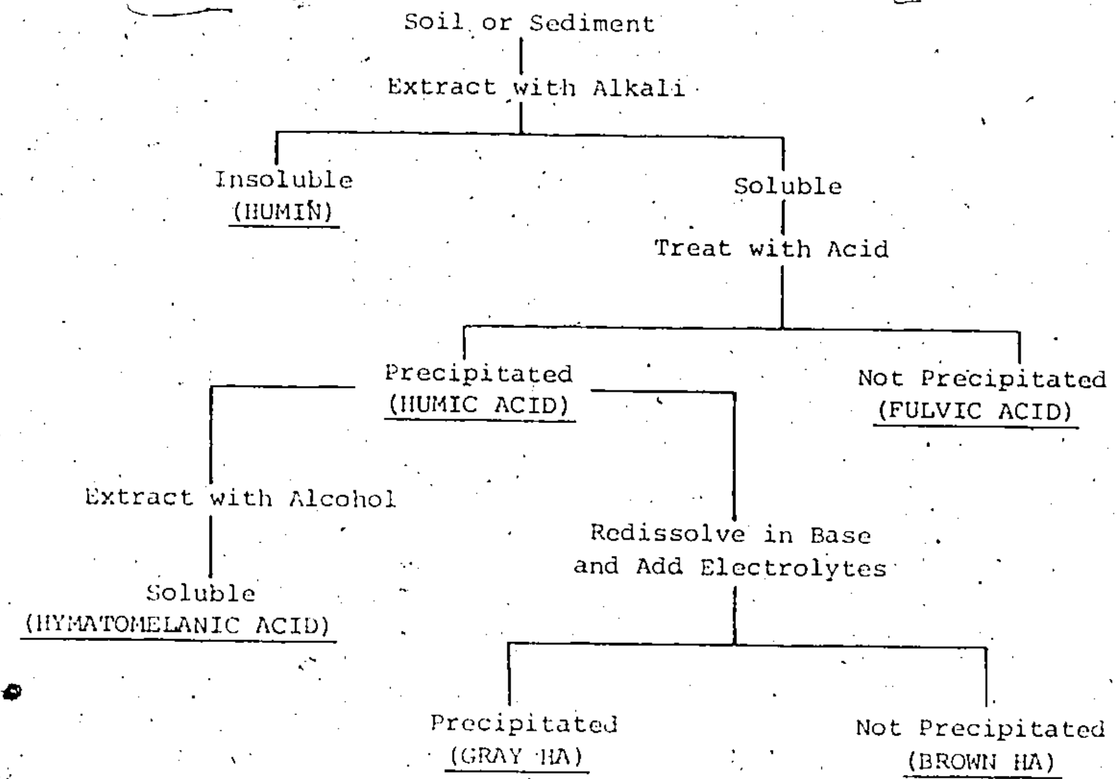


FIGURE 2.1 Fractionation of humic substances

(From : Schnitzer and Khan,1972)

of compounds formed during the autolysis of cells after their death.

(iv) The microbial synthesis hypothesis assumes that microbes synthesize intracellularly high-molar-mass humic-like substances. After the death of microbes these compounds are released into the environment where they are degraded to humic and fulvic acids.

Although it is not understood which mechanism prevails, the most popular hypothesis is that the more complex high molar mass humic materials are formed first, and that these are degraded, most likely oxidatively, into lower molar mass substances.

The effect of the environment on the structure and characteristics of humic substances has not been investigated extensively. Although there is evidence that certain differences exist among fresh water humics and marine humics (Stuermer and Payne, 1976; Nissenbaum and Kaplan, 1972), humus in the soil and in freshwater seems to show similar gross physical and chemical characteristics (Rashid et al., 1972; Gjessing, 1976).

The concentration of humic substances in natural waters varies. Considering that humic substances constitute the majority of organics in water, their concentration, expressed in terms of TOC, was found to be between 0.1 and 2 mg/L for groundwaters and between 1 and 20 mg/L for most surface waters (Kavanaugh, 1978). Most of the aquatic humus exists in the form of fulvic acid, due to the higher solubility of this fraction. Black and Christman (1963) analysed colored surface waters and found that the organic matter consisted mainly of fulvic acid (87 percent). Midwood and Felbeck (1968) demonstrated that 80 percent of the organic matter existing in colored water was fulvic acid. Fotiyev A.V. (1967, cited by Schnitzer, 1977) found that 85 percent of organic matter in swamp water was fulvic acid. In summary, the humic substances in surface waters contain about 80 to 90 percent fulvic acid.

Historically most of the research has been done on humic acids, because they precipitate easily at low pH. Recently, however, the use of synthetic resins enabled the isolation, concentration and use of fulvic acids.

2.1.2 Chemical Characterization

Humic substances consist mainly of Carbon, Oxygen, Hydrogen, Nitrogen and Sulphur. Elemental analysis of humic and fulvic acids in various soils is given in Table 2.1 and in water in Table 2.2.

Gjessing (1976) claims that aquatic humus generally exhibits a lower carbon and nitrogen content, whereas the hydrogen content is usually a little higher. Fulvic acids contain less carbon and nitrogen but more oxygen than humic acids. It should be noted that humic substances analysis always yields an ash content, indicative of inorganic constituents associated with the organic molecules.

Another important characteristic of humic substances is the distribution of oxygen-containing functional groups. The major groups are carboxyls ($-CO_2H$), phenolic and alcoholic hydroxyls (OH), carbonyls (C=O) and methoxyls (OCH_3). Between 68 and 91 percent of the oxygen in HA's can be accounted for in functional groups, whereas more than 90 percent of oxygen in FA is similarly distributed (Schnitzer and Khan, 1972). Table 2.3 presents data on the distribution of oxygen-containing functional groups in humic substances.

TABLE 2.1 Elemental analysis of soil humus

(From : Schnitzer and Khan,1978)

Element	Humic Acid		Fulvic Acid	
%	Range	Mean	Range	Mean
C	53.6-58.7	56.2	40.7-50.6	45.7
H	3.2-6.2	4.7	3.8-7.0	5.4
N	0.8-3.5	3.2	0.9-3.3	2.1
S	0.1-1.5	0.8	0.1-3.6	1.9
O	32.7-38.3	35.5	39.7-49.8	44.8

TABLE 2.2 Elemental analysis of aquatic Humus

Element	Aquatic humus		Fulvic Acid			Humic Acid		
%	Ref. 1	Ref. 2	Ref. 2	Ref. 3	Ref. 3	Ref. 2	Ref. 3	Ref. 3
C	43	41.5	40.6	51.1	45.7	46.63	53.4	59.5
H	5.5	5.72	5.45	3.62	4.26	5.22	3.73	5.11
N	1.1	1.98	1.53	1.13	1.57	1.32	2.10	1.95
O	NA	50.80	49.78	NA	NA	46.83	NA	NA

Ref. 1 : Gjessing (1976)

Ref. 2 : Black and Christman (1963)

Ref. 3 : Weber and Wilson (1975)

TABLE 2.3 Oxygen-containing functional groups in humic substances (meq/g)

	Total Acidity	Carboxyls	Phenolic OH	Alcoholic OH	Carbonyls	Methoxyls	Ref.
Soil HA	6.7*	3.6	3.9	2.6	2.9	0.6	1
Soil FA	10.3*	8.2	3.0	6.1	2.7	0.8	1
Water HA	8.2	4.5	3.7	NA	4.3	NA	2
Water FA	10.6	6.8	4.3	NA	4.3	NA	2

* These values represent means and therefore they do not equal the sum of carboxyls and phenolic OH.

Ref. 1 : Schnitzer and Khan (1978)

Ref. 2 : Weber and Wilson (1975)

The carboxylic content of FA is appreciably higher than that of HA. This relationship was found to occur irrespective of the source of the organic matter. On the other hand, both materials contain approximately the same amounts of phenolic, carbonylic and methoxylic groups per unit weight. The acidity of humic substances is considered to be mainly due to the presence of dissociable hydrogen in the carboxylic and phenolic groups.

Because of the chemical complexity of the humic materials, the structure of humic substances has not been identifed. Many investigators have used degradative methods, trying to identify products whose structure could be related to the starting materials. The degradative methods, that have been applied on humic sustances, included oxidations in alkaline and acidic media, reduction, hydrolysis, thermal, radiochemical and biological degradations.

The major HA and FA degradation products are phenolic and benzenecarboxylic acids (Schnitzer and Khan, 1972). It is not known whether these have originated from more complex aromatic structures or existed in the initial humic in the same form but held together by weak bonding.

Other components that have been identified include n-alkanes and n-fatty acids (Ogner and Schnitzer, 1970). Part of these is loosely held, which is believed to be physically adsorbed, while the remaining is part of the humic structure. The role of the latter aliphatic compounds is not well understood. Christman and Ghassemi (1966) postulated that aliphatic chains link together the aromatic nuclei. The same suggestion was made by Hall and Lee (1974), who also considered ether and ester bonds for the linking of aromatic subunits. However, neither aliphatic structures nor large fragments of the original structure were isolated and identified when degradative methods were employed. This led Schnitzer to conclude that the identified phenolic and benzenecarboxylic acids were the "building blocks" of humic sustances (Schnitzer and Khan, 1972). According to Schnitzer, most of the tightly held aliphatic structures are esterified to phenolic OH groups. The humic sustances, then, are not single macromolecules, but rather associations of molecules, the "building blocks". The aggregation appears to be brought about by hydrogen bonding, Van der Waals forces and interaction between π -electrons of adjacent aromatic rings. High energy bonding, such as C-O and C-C bonds, is not excluded, but it seems not to be significant. It is considered, therefore, that the structure of humic substances is flexible perforated by voids of varying dimensions that can trap or fix organic and inorganic compounds. A proposed chemical structure for soil fulvic acid is shown in Figure 2.2.

The flexibility in the structure permits the "building blocks" to aggregate and disperse reversibly, depending on the pH, ionic strength and the presence of metal ions. At low pH humics tend to aggregate forming elongated fibres and bundles of fibres. As the pH increases, these forces become weaker, and, because of increasing ionization of carboxylic and phenolic OH groups, particles separate, so that the molecular arrangements become smaller but better oriented (Schnitzer, 1980). These postulations were supported by X-ray analysis, scanning electron microcopy and viscocity measurements.

2.1.3 Physical Characterization

Humic substances were considered to be hydrophilic colloids, mainly because of their large molecular size. In water, under ordinary

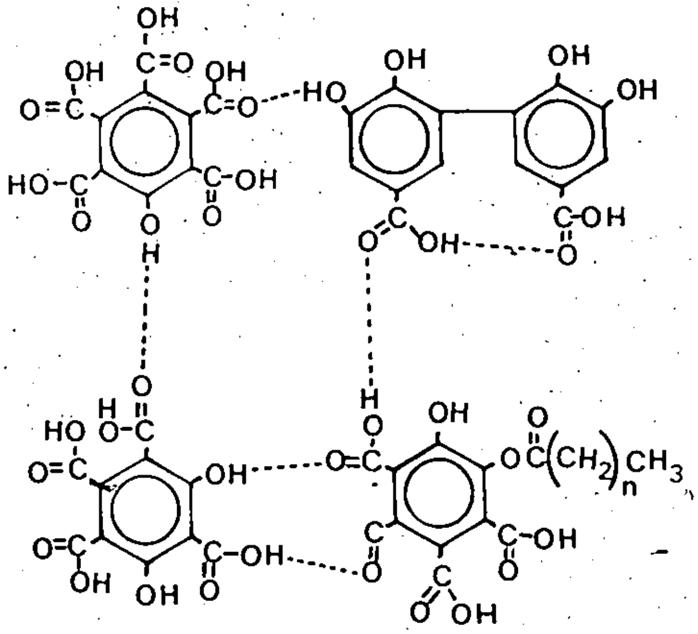


FIGURE 2.2 A partial chemical structure of fulvic acid

(From : Schnitzer and Khan , 1978.)

conditions, they are negatively charged, due to the dissociation of carboxylic and phenolic groups (Black and Christman, 1963).

Because of the ability of the "building blocks" to aggregate, one should distinguish between the molar mass of the humic molecule and the molar mass of the aggregate. Many methods have been employed for the molar mass determination of humic substances. These methods are classified into (i) those measuring number-average (osmotic pressure, cryoscopy, diffusion, isothermal distillation); (ii) those measuring mass-average (viscosity, gel filtration); and (iii) those measuring Z-average (sedimentation-ultracentrifugation).

There are wide differences between results obtained with the various methods. Chemical methods give a molar mass of 1300 to 13,000 for humic acids. Osmometry, cryoscopy and the diffusion and viscosity methods give values of about 700-26,000 for HA and 200-300 for FA, while ultracentrifugation and light-scattering 30,000 to 80,000 (Orlov et al., 1971). These discrepancies were attributed to the polydispersion of humic substances, aggregate instability and ash content, pH values and ionic strength. Differences also appeared because some methods do not measure molar mass but rather micellar (aggregate) size.

Gel filtration is extensively employed since it allows the determination of molecular size distribution. Humic acids show polymodal molar mass distributions, while fulvic acids are more uniform and are usually divided into two fractions. Gel filtration data indicate that the range of mass average molar mass of humic acids is very broad, from several thousands to 200,000-300,000. Distinction should be made, however, as to what these values represent. Orlov et al. (1971), in light of the structural configuration of the humic substances, considered that gel filtration data indicated the size of the aggregates rather than the size of the individual molecules. They considered that a range of 50,000 to 90,000 should be taken for the mass average molar mass of humic acids at a molecular length of 30-50 Å. The number average molar mass of HA was considered not to exceed 8000 to 10,000, while FAs exhibited a narrower range of values, and their number and weight average molar mass were nearly the same and ranged from 4,000 to 7,000. The humic acid aggregates were considered to have a somewhat elongated ellipsoidal shape with a ratio of axes 1:6 to 1:12.

Humic substances show uncharacteristic spectra in the visible region (400-800 nm). Absorption spectra of neutral, alkaline and acidic solutions are featureless, showing no maxima or minima. The optical density decreases as the wavelength increases. Optical densities are measured at 465 nm, which is in the region of high absorbance. The effect of pH on optical density is shown in Figure 2.3. It can be seen that optical density increases with increase in pH. This effect is greater at low wavelengths. Generally, the color of HA is more intense than that of FA, based on equal concentrations.

The ultraviolet spectra are featureless. The optical density decreases as the wavelength increases. Humic substances are known to fluoresce under visible and UV light. This property has been extensively used for the quantitative determination of humic compounds (McCreary and Snoeyink, 1980).

Infrared spectrophotometry has been repeatedly applied to yield information on the structure and the reactions of humic substances. Generally IR spectra exhibit broad bands because of extensive overlapping of individual absorptions.

Electron spin resonance spectrometry showed that humic substances

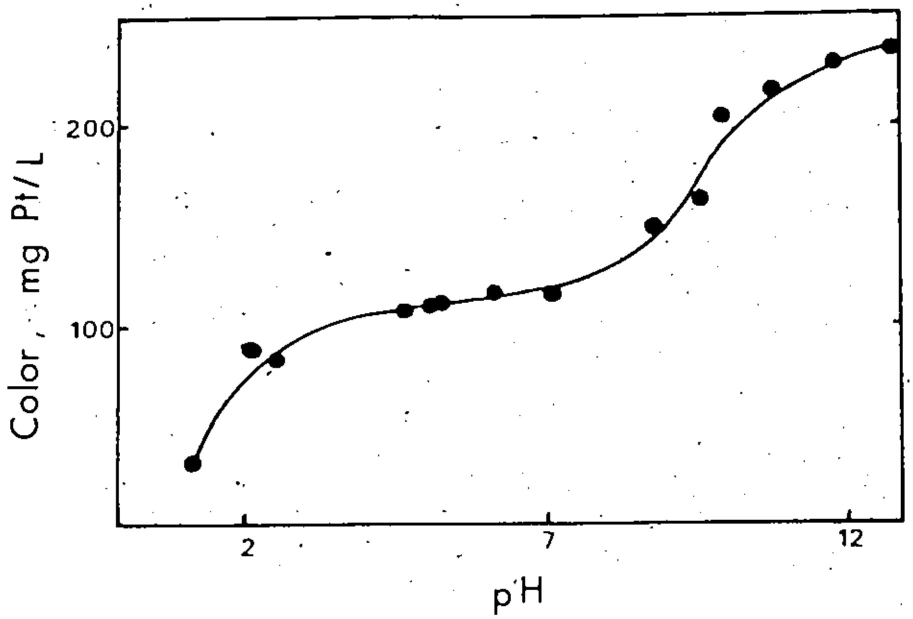


FIGURE 2.3 Change of color of humic acid with change of pH.

(From : Gjessing,1976)

contain relatively high concentrations of stable free radicals. These radicals are considered to be associated with semiquinone groups. Via free radicals, humic substances can participate in oxidation-reduction reactions with transition metals, or they can detoxify adsorbed pesticides.

2.1.4 Interaction with Metal Ions

Metal ion concentrations in natural waters are usually in excess of calculated equilibrium ones, considering only inorganic species. This is attributed to the presence of organic matter. Gjessing (1976) reported that a positive correlation was found between iron and COD in humus water. He also reported that an elemental analysis of colored surface water showed the existence of 18 elements (mostly metals) in association with humic substances. Lind and Hem (1972) reported that the polymerization of aluminum hydroxide is inhibited by the presence of organic matter.

It is not, however, universally agreed how the natural organic macromolecules change the solubility of metals. There are two general trends: The first one considers the formation of soluble chelates or complexes between the humic substances and metal ions (Gamble and Schnitzer, 1973), while the second one considers the formation of highly dispersed colloidal precipitates, which pass through a 0.45 µm membrane filter (Stumm and Morgan, 1981). It is most likely that both mechanisms occur, and the prevailing one depends on the pH, metal and organics concentrations and ionic strength of the medium.

The formation of the micro-colloids is particulary important for trivalent ions, such as Fe(III) and Al(III). Shapiro (1964) demonstrated that, although most of the "organic iron" passed through a 0.45 µm filter, it was retained on a 0.10 µm membrane filter.This led him to conclude that iron was dispersed as precipitated ferric hydroxide. Peptization occurred when humic acids adsorbed on the surface of the hydroxide particles. Stumm and Morgan (1981) considered that Fe(III) formed coordination products with the color-causing compounds and hydroxyl ions. These products were considered to be insoluble and present as highly dispersed colloids, which can not be operationally distinguished from dissolved substances.

The colloidal character of iron-organic matter particles was confirmed by coagulating them with inorganic cations. The coagulation followed the Schulze-Hardy rule, i.e. trivalent ions were many times more efficient than divalent ions, which in turn were more efficient than monovalent ions (Shapiro, 1964; Ong and Bisque, 1968; Boyle et al., 1977). Ong and Bisque (1968) considered that upon the addition of the coagulants the hydrophilic character of the colloids (highly hydrated, stretched configuration) changed to a hydrophobic one (less water, coiling of the chain). Orlov and Yeroshicheva (1967) reported that peptization of humic acids with a 3 percent ash content occured at somewhat higher pH values than coagulation. They attributed that to a HA particle association preceeding the start of coagulation, as a result of hydrogen bonds.

The ability of the humic materials to form complexes with metal ions is an important property. Complexation occurs between the oxygen-containing functional groups and the metal ions, particularly the alkaline earths, such as Ca and Mg, and transition metals, such as Cu, Fe, Cd, Zn and Ni. Monovalent cations, Na or K for instance, form weak electrostatic bonds with anionic groups on the humic molecule.

The ability of the humic substances to form complexes with metal ions is environmentally important for two reasons: first, it affects the biological availability and toxicity of the metal ions, and second, it changes their geochemical mobility. Factors that affect the humic matter-metal ion complexation and the determination of the stability constants are the source of humic matter, the method of isolation, the concentration of the humic matter, the pH, ionic strengh and temperature of the solution, along with the method of analysis for complexes and the method of data manipulation and stability constant calculation (Saar and Weber, 1982).

The formation of soluble and insoluble complexes is also considered to be a possible cause of the unexpected trends of the solubilities of metal ions in the presence of humic compounds. Sholkovitz and Copland (1981) examined the solubilities of several metal ions and concluded that solubilization at high pH (3-9.5) and precipitation at low pH (3-1) indicated that complexation with humic substances was an important process. Schnitzer and Kerndorff (1981) investigated the solubility in water, separately and after mixing, of fulvic acid and 11 metals over the pH range 4 to 9. The solubility of the components was greatly affected by the presence of fulvic acid, particularly high dosages (higher than 200 mg/L). This was attributed to the formation of soluble complexes, inhibiting the formation of metal hydroxides. Fulvic acid over metal weight ratios greater than 2 favoured the formation of soluble complexes, while over the pH range 5 to 7, Fe(III), Al, Cr(III), Pb and Cu showed the greatest tendency to form water-insoluble complexes. The mechanisms of interaction were considered to be chelation, inner and outer complex formation, adsorption and coprecipitation.

Truitt and Weber (1979) studied the removal of metals from water at pH ranging from 5 to 7 by alum coagulation. They found that the presence of fulvic acid leads to higher removals. They attributed this to the formation of complexes between natural organics and metals, which are adsorbed on the alum flocs.

The ways metal ions react with humic substances have been reviewed by Schnitzer (1980). Metal ions are electron acceptors and, therefore, they can react with electron donors (organic groups) to form chelates or complexes (depending on whether structural rings are formed or not). The organic groups that were found to participate were carboxylic and phenolic hydroxyls. By blocking specific groups on the humic molecule, it was found that alcoholic hydroxyls did not contribute at all in the complexation of metals. Mantoura and Riley (1975) by using gel filtration also showed the existence of two different types of binding sites on the fulvic acid molecule. These sites were considered to be carboxylic and phenolic groups.

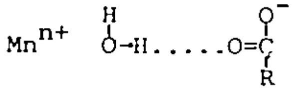
The ways, these groups interact with the metal ions, are (Schnitzer, 1980):

(i) One COOH group reacts with one metal ion to form an organic salt or monodentate complex.

(ii) One COOH and one adjacent OH group react simultaneously with the metal ion to form a chelate.

(iii) Two adjacent COOH groups react simultaneously with the metal ion to form a chelate.

It was also reported that Mn^{2+} (and it is most likely to occur with other metal ions as well) was complexed to fulvic acid by electrostatic binding as $Mn(OH_2)^{2+}$ with FA donor groups in outer sphere complexing sites. It was also found that FA could be linked to the cation via hydrogen bonding through water molecules associated with the metal, according to the scheme:



$$\mathrm{Mn}^{n+}\quad \overset{\mathrm{H}}{\overset{|}{\mathrm{O}}}-\mathrm{H}\ldots\ldots\mathrm{O}=\overset{\mathrm{O}^-}{\overset{|}{\underset{\underset{\mathrm{R}}{|}}{\mathrm{C}}}}$$

A study of stability constants showed that Fe^{3+} and Al^{3+} formed the most stable complexes with fulvic acid. The stability constants decreased as the ionic strength increased, while an increase in pH resulted in an increase of them. The stability constants of metal-humic complexes were found to be lower than those for complexes formed between the same metal ions and synthetic organic complexing agents such as EDTA.

Concluding the review on metal-humic interactions, it should be mentioned that often very high humic concentrations were employed, a fact that cannot always be extrapolated to low concentrations usually encountered in water treatment facilities.

2.1.5 Summary

Humic materials are reasonably well characterized, naturally occurring organic substances. In natural waters their concentration ranges from 0.1 to 20 mg/L for the various types of natural waters. Fulvic acid is the most common fraction of aquatic humic matter. Fulvic acid that occurs in natural water has 6.8 meq/g carboxylic, 4.3 meq/g phenolic OH and 4.3 meq/q carbonyl as oxygen containing functional groups. Although molar mass measurements depend on the measuring technique, fulvic acid has a lower molar mass than humic acid ranging from a few hundred to a few thousand. Fulvic acid complexes with metal ions and may form precipitates.

2.2 ORGANICS REMOVAL BY COAGULATION

Coagulation is a process traditionally associated with the removal of suspended colloidal matter. Inorganic coagulants and organic flocculants, however, have been shown to remove dissolved organic substances in water treatment plants (Robinson, 1979).

Although dissolved organic matter is not generally removed by the same mechanisms as colloidal particles, the term "Coagulation" has been used to denote the removal of organics by means of coagulants. In this context, the term coagulation has also the general meaning of removing the organics and does not imply any specific mechanism. Because fulvic acid is highly hydrophilic, its removal during coagulation is accomplished through its association with a solid phase. Therefore, the measurement of the removal is contingent upon the separation of the solid from the liquid phase. Such separation could be either by settling or by filtration. In actual water treatment plants clarification and sand filtration are used, while in the laboratory settling in jars and membrane filtration are most common.

2.2.1 Aluminum Coagulation of Humic Substances

Aluminum and ferric salts are the most extensively used inorganic coagulants. The two metals exhibit similar behavior and seem to work equally well on an equivalent basis (Hall and Packham, 1965). Therefore, most of the following arguments about aluminum should apply to iron as well. A list of the most pertinent published research in the past two decades is presented in Table 2.4. In the same table the various experimental conditions are also given.

Among the factors that influence the removal of humic substances,

TABLE 2.4 Summary of the experimental conditions of published articles regarding the removal of humic substances during coagulation

Reference	Type of humic	Conc. of humic , mg/L	Variables	Range	Removal measured by
Black et al (1963)	Natural waters	Not measured	pH Fe	2.5-5.5 $0.2\text{x}10^{-4}$-$0.6\text{x}10^{-3}$M	Color remaining after filtration (paper filter)
Hall et al (1965)	Aquatic HA Aquatic FA	5-50 5-50	pH Al Fe Clay	2.5-8.5 $0.9\text{x}10^{-4}$-$6\text{x}10^{-4}$M $0.9\text{x}10^{-4}$-$6\text{x}10^{-4}$M 0 and 50 ppm	Supernatant absorbance after filtration (0.45 μm membrane filter)
Maulding and Harris (1968)	Natural water	Not measured	pH Fe Temperature Ca Mg Na Cl SO_4	3.0-4.0 $0.4\text{x}10^{-3}$M 3^oC-42^oC 4-1500 mg/L 2.4-1500 mg/L 23-230 mg/L 35.5-355 mg/L 48-480 mg/L	Color remaining after filtration
Mangravite et al,(1975)	Peat HA	5 and 10	pH Al	2.5-10.0 10^{-5}-10^{-3}M	Absorbance after settling or microflotation
Narkis et al (1977)	Soil HA Peat FA	5-50 25-100	pH Al	5.8-6.7 $0.7\text{x}10^{-4}$-$0.3\text{x}10^{-3}$	Absorbance after centrifugation

TABLE 2.4 (continues)

Reference	Type of humic	Conc. of humic , mg/L	Variables	Range	Removal measured by
Edzwald (1979)	Peat HA	5-20	pH Al	5.0-8.0 0.4×10^{-4}-0.4×10^{-3}M	Supernatant absorbance after filtration (glass fiber)
Babcock et al (1979)	Peat HA Peat FA	10 and 50 10 and 50	pH Al	4.5-7.0 0.1×10^{-3}-0.7×10^{-3}M	Supernatant TOC/absorbance after filtration(0.45 μm)
VanBreemen et al (1979)	Natural water	35-40 mg/L TOC	pH Al	2.5-7.5 0.2×10^{-3}-0.9×10^{-3}M	Color/TOC/COD after filtration (1.2 μm membrane filter)
Semmens et al (1980)	Natural waters	10-16 mg/L TOC	pH Al	3.0-9.0 0.1×10^{-4}-0.4×10^{-3}M	Absorbance/TOC after filtration
Randtke et al (1981)	Groundwater Soil HA Peat FA Soil FA Groundwater FA	4 mg/L TOC 4 mg/L TOC 5 mg/L TOC 6 mg/L TOC 6 mg/L TOC	pH Al Fe	3.0 , 6.0 , 8.3 0.6×10^{-4}-0.2×10^{-3}M 0.1×10^{-4}-0.3×10^{-3}M	Supernatant TOC/UV absorbance after filtration (glass fiber filter)
O'Melia et al (1982)	Aquatic FA	3.5 mg/L TOC	pH Al	3.0-8.0 10^{-4}M	TOC after settling and filtration

TABLE 2.4 (continues)

Reference	Type of humic	Conc. of humic , mg/L	Variables	Range	Removal measured by
Bersillon (1983)	Natural water	11 mg/L TOC	pH Al	5.0-8.5 0.1×10^{-3}-1.0×10^{-3}M	TOC after filtration (0.45 μm membrane filter)
Dempsey et al (1984)	Aquatic FA	3.5-14 mg/L	pH Al	3.0-8.0 10^{-5}-0.2×10^{-3}M	Absorbance/TOC after filtration and settling
Reckhow et al (1984)	Aquatic FA	4.1 mg/L TOC	pH Al	4.0-8.0 0.3×10^{-4}-0.2×10^{-3}M	TOC/Absorbance after filtration (glass fiber filter)

the pH and the aluminum dosage are the most important. For each water there is a specific range of pH values and coagulant doses within which most of the organics are removed (Black et al., 1963).

The pH affects both the ionization of the functional groups on the humic molecules and the hydrolysis of the aluminum ions. A summary of the optimum pH ranges as reported in the literature is shown in Table 2.5. Maximum removals occur at acidic pH values and it may be concluded that in general the optimum pH for aluminum coagulation of humic materials lies between 5 and 6. At pH values higher than 6, higher dosages are required for effective coagulation due to increased ionization of the humic functional groups, mainly phenolic groups. This is demonstrated in Figure 2.4. It should be mentioned that Hall and Packham (1965) also found that the optimum pH values for ferric coagulation lay between 3.5 and 4.5. The lower pH was due to the more acidic character of the ferric ion, because of its larger affinity for hydroxyl ions.

Not all humic fractions show the same removal characteristics. Humic acids can be removed more readily by alum than fulvic acids. The latter require higher aluminum dosages, due to the higher density of acid functional groups (Hall and Packham, 1965).

There is usually a fraction of the organic matter that cannot be removed by coagulation. Babcock and Singer (1979) found that color appeared to be preferentially removed, while a significant amount of TOC (Total Organic Carbon) remained in solution. Van Breemen et at. (1979)

TABLE 2.5 Optimum pH range as reported in the literature

Type of humic	Conc. of humic , mg/L	Aluminum dosage	Optimum pH	Reference
Humic acid	25	0.9×10^{-4}-0.6×10^{-3} M	5.0-6.0	Hall and Packham (1965)
Fulvic acid	25	1.5×10^{-4} M	4.5-6.0	
Humic acid	50	0.19×10^{-3} M	less than 6	Babcock et al (1979)
Fulvic acid	50	0.19×10^{-3} M	less than 5.5	
Humic acid	10	0.19×10^{-3} M	less than 7	Edzwald (1979)
Humic acid	10	0.90×10^{-4} M	less than 5.5	
Natural water	33 mg/L TOC	0.44×10^{-3} M	4.5-6.5	VanBreemen et al (1979)
Fulvic acid	4.1 mg/L TOC	0.3×10^{-4}-0.2×10^{-3} M	4.5-6.0	Reckhow et al (1984)
Fulvic acid	3.5 mg/L TOC	10^{-4} M	4.5-7.0	Dempsey et al (1984)

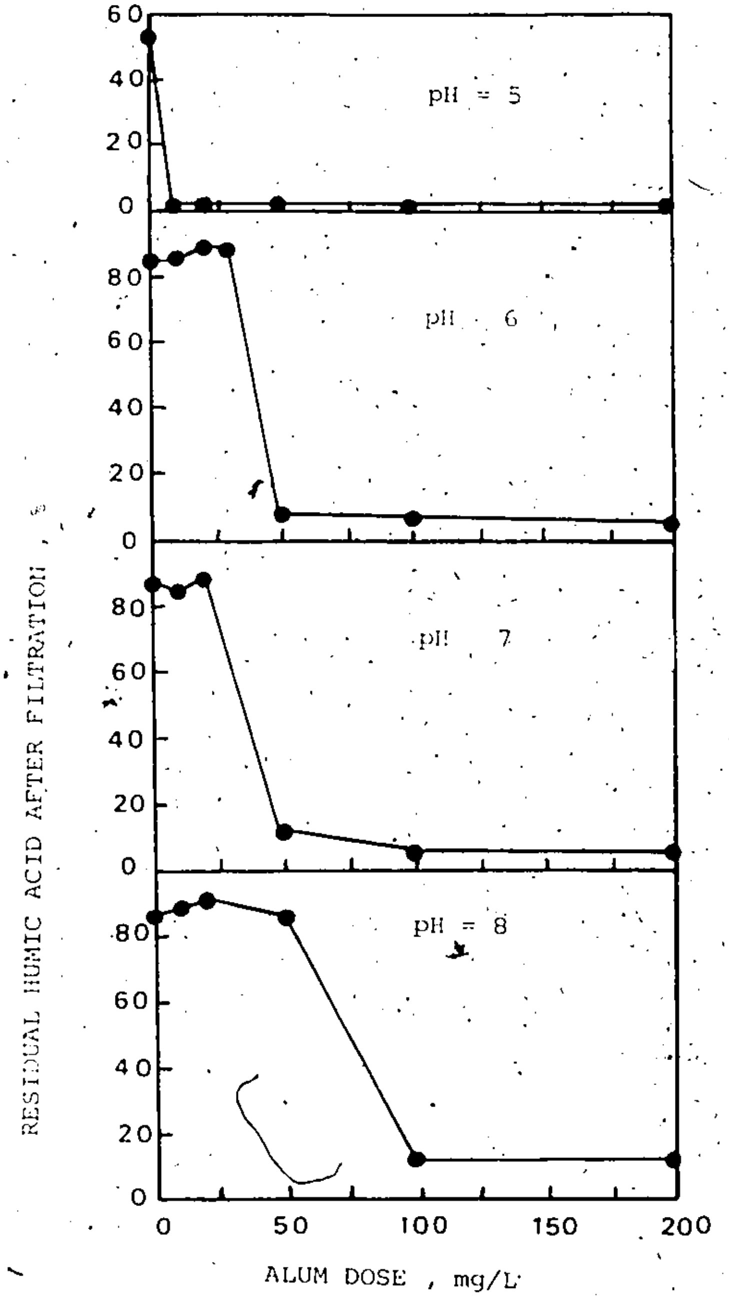


FIGURE 2.4 Effect of pH on the coagulation of 10 mg/L humic acid with alum (From : Edzwald, 1979)

observed that coagulation preferentially removed the fulvic acid fraction with a relatively high carboxylic group content. The 60 percent of the fulvic acid that was removed contained 95 percent of the carboxylic groups originally present, and it also held 96 percent of the original color. It appeared, therefore, that the preferential removal of the colored fraction occurred because this fraction was highly substituted with carboxylic groups. It was not clear, however, whether the non-removed fraction was structurally part of the fulvic acid or consisted of other organics associated with it.

At constant pH, two distinct patterns of removal after filtration have been generally observed (Randtke and Jepsen, 1981):

(i) The first one is characterized by a sharp drop in concentration of humics at a certain coagulant dosage below which removal is minimal and above which removal is completed. This removal pattern has been observed mostly with pure humic fractions.

(ii) The second pattern shows a gradual decrease in the concentration of the organics with an increasing coagulant dose, approaching maximum but incomplete removal at high dosages. This second removal pattern typifies behavior of typical water supplies and domestic wastewaters. This pattern characterizes heterogeneous mixtures of organic molecules.

The presence of various ionic species significanly affects the removal of humic substances. Maulding et al. (1968) investigated the effect of the presence of certain cations on ferric coagulation of colored natural waters at optimum pH. They found that the presence of Na^+, Ca^{2+}

and Mg^{2+} increased the effectiveness of color removal and extended the pH range of good coagulation upward. The order of effectiveness was Mg $>$ Ca $>$ Na. It is worth mentioning that calcium and magnesium did not remove any color when they were used as the sole coagulants. The beneficial effect of calcium was also observed when aluminum was employed (Randtke and Jespen, 1981). Addition of $CaCl_2$ reduced the alum dosage required to remove peat fulvic acid from water. Maulding et al. (1968) also studied the effect of Cl^- and SO_4^{2-} anions. While the presence of Cl^- did not seem to have any effect, SO_4^{2-} ions exhibited a deleterious effect on color removal at acidic pH. Bersillon (1983) also observed that the presence of the sulfate ion had a slightly negative impact on the removal of the fulvic acid with aluminum at pH 6 but this effect diminished as the pH increased.

The effect of temperature was also investigated by Maulding et al. (1968). As temperature increased by 40°C, the optimum pH for effective color removal moved to lower values, but less than one pH unit. Temperature was considered to affect the dissociation of the ionic species and the water, the rate of the hydrolysis reactions and the reactions between the color compound and the iron hydrolysis products. However, because of the unknown structure of the species present and the reactions involved, theoretical calculation of the effect of temperature was not possible.

The effect of the presence of clay on the removal of color was examined by Hall and Packham (1965). The results obtained in the presence of 50 mg/L Kaolin particles resembled closely those obtained in the absence of clay. The coagulant dose and the optimum pH were independent of the presence of clay. On the contrary, turbidity removal was largely influenced by the presence of humic material. The optimum conditions for turbidity removal are not always the same as the optimum conditions for organics removal (Semmens and Field, 1980). Usually slightly lower pH (AWWA Committee Report, 1979) and larger alum dosages are required for effective organics removal (Semmens and Field, 1980). The same authors noticed that under optimum conditions for good organics removal good turbidity removal was always obtained. It should be mentioned, however, that in most of the studies the clay suspension was added to the humic water prior to coagulation. Such a system does not represent the behavior of the real water system, where clay and organics appear in an organo-clay complex form (Narkis and Rebhun, 1975).

The mechanism of the removal of humic substances by aluminum or iron is still a matter of speculation. Most of the problems arise from the unknown structure of both the humic materials and the hydrolysis products of aluminum. If humic matter is considered to exist in colloidal form, coagulation mechanisms (as applied to the removal of colloids) may be employed to explain the observed results. The fact that humic materials cannot be coagulated by calcium or magnesium alone, as pointed out by Shapiro (1963) and Maulding et al. (1968), indicates that such a coagulation mechanism is not a major one. It may become significant, however, when iron or aluminum, associated with the organic matter, exist in a peptized (highly dispersed) form. This may be a reason for the observed improvement in the removals of the humic substances by iron in the presence of Mg^{2+} and Ca^{2+} as reported by Maulding et al. (1968).

Hall and Packham (1965) found that the removal of humic material differed significantly from that of clay suspension. They postulated that humics were removed by the formation of insoluble basic aluminum humates or fulvates. These precipitates were formed by the interaction of partially hydrolyzed aluminum ion and the ionic groups (mainly carboxylic and phenolic) on the organic molecule. The fixation of multivalent cations onto the ionized groups on hydrophilic colloids may be electrostatic or chemical in nature (Stumm and Morgan, 1962). Such interactions lead to the formation of soluble or insoluble complexes, as it was mentioned in the previous section of this chapter.

Because of the direct interaction between the aluminum species and the ionic groups on the humic molecule, one would expect that optimum aluminum dosages are proportional to the initial humic concentrations. This was observed to occur at low dosages (Narkis and Rebhun, 1977; Edzwald, 1979). At high dosages, aluminum hydrolysis probably led to more charged products resulting in deviations from the proportionality. This linear relationship is referred to as stoichiometry. Figure 2.5 demonstrates the stoichiometry between the initial fulvic acid concentration and the optimum aluminum concentration for pH 5.0 and 6.0. Despite the differences in the source of the humic matter and the experimental design, there exists a reasonable linearity betwen the initial TOC and the optimum aluminum dosage. In constructing Figure 2.5 it was assumed that the carbon content of the humic acid was 50 percent of the total humic mass, while the carbon content of the fulvic acid was 45 percent of the mass. However, for aluminum dosages smaller than the optimum one, this stoichiometric relationship did not hold (Edzwald, 1979). The sharp increase in removal over a narrow aluminum dose is characteristic of a complex chemical reaction, where all the ionic functional groups must be complexed by the aluminum species for precipitation to occur.

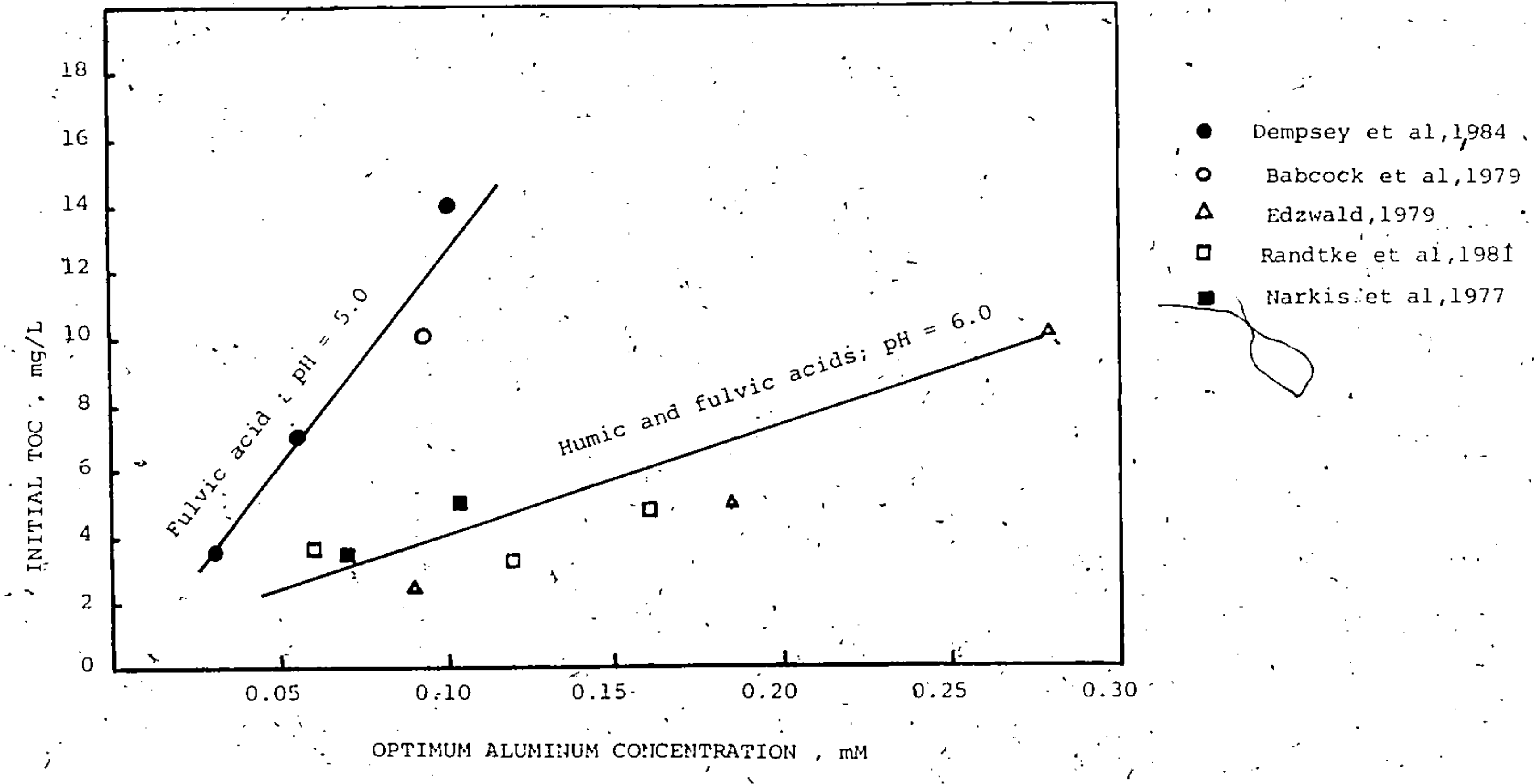


FIGURE 2.5 Stoichiometry of the coagulation of humic substances with aluminum

A precipitation-complexation mechanism is also compatible with the existence of an optimum pH. At lower pH values aluminum species are highly charged, while the acidic functional groups on the humic molecule are partially protonated. Therefore the complexes are soluble and carry a positive charge. As the pH increases more acid groups dissociate and more hydroxyl ions participate in the reaction products to neutralize the positive charge, until precipitation occurs. At higher pH values, precipitation is hindered by the complete ionization of the acidic groups and the formation of insoluble aluminum hydroxide. The importance of aluminum humate precipitation at acidic pH and low aluminum doses was also pointed out by Oldham and Gloyna (1969) and Mangravite et al. (1975).

The complexation mechanism can also explain the deleterious effect of SO_4^{2-} mentioned above. Sulfate ions can compete with the acidic (carboxylic) groups for the coordination sites of aluminum or iron and deteriorate the removal of organics or increase the required dose for effective removal. The presence of cations (such as Ca^{2+} and Mg^{2+}) would be beneficial either by reacting with SO_4^{2-} or by participating in the complex.

Precipitation-complexation is not the only mechanism. High aluminum dosages result in the precipitation of aluminum hydroxide, which can further adsorb humic substances from the solution. Evidence of the adsorption mechanism has been given by Davis and Gloor (1981), who showed that dissolved lake organics can be adsorbed on colloidal alumina γAl_2O_3. Semmens and Field (1980) found that recycle of the sludge, formed during coagulation of humic matter by alum, led to increased uptake of the organic material, and that was attributed to an adsorption mechanism. Adsorption effects were also employed to explain the coagulative behavior of polymeric aluminum species. It is known that partial neutralization of aluminum chloride with alkali results in an aluminum polymeric species that is highly substituted with OH. Such species was slightly more effective for organics removal than simple aluminum ions (Van Breemen, 1979; Diamadopoulos, 1981). This higher effectiveness was attributed to the existence of a non-settleable gel which may have been able to adsorb the organics. O'Melia and Dempsey (1982) compared the fulvic acid removals with alum and polymerized aluminum chloride. They found that polymerized aluminum chloride extended the pH range for effective removal after filtration towards lower pH. They explained this difference as the result of the existence of aluminum polymers in the polymerized aluminum chloride solution which reacted directly with the fulvic acid. They postulated that the mechanism of fulvic acid removal depends on the pH and the aluminum dosage. At pH less than 5, removal may occur by the direct precipitation of fulvic acid by monomeric aluminum species. Between 5 and 6, the aluminum polymers are the cause of the fulvic acid precipitation, while for pH values greater than 7, adsorption of fulvic acid or soluble complexes of fulvic acid and aluminum on aluminum hydroxide is the predominant mechanism (Dempsey et al, 1984). Bersillon (1983) estimated the ligand number in the solid phase during the precipitation of aluminum in the absence and presence of fulvic acid and for pH ranging from 5 to 8.5. He found that the ligand number was 3 irrespective of the presence of fulvic acid, the nature of the aluminum coagulant and the operating pH. He concluded that the removal of fulvic acid was accomplished by the adsorption of the organic molecules on the precipitated $Al(OH)_3$.

The maximum adsorptive capacity of the floc decreased with increasing pH and increasing hydrolysis of the coagulant. The adsorption was reversible and was characterized by fast kinetics.

Summary

Most researchers used as the criterion for the removal of fulvic substances by aluminum the absorbance or the TOC of the supernatant after filtration by membrane filters, and/or settling. The removal of humics by aluminum depends strongly on the pH and the aluminum dosage. For concentrations of organics of practical importance (less than 25 mg/L TOC) and typical aluminum dosages (0.5×10^{-4} - 0.5×10^{-3} M), the optimum pH seems to be between 5 and 6. Not all humics behave the same. Humic acids are more readily removed than fulvic acids, because of the lower density of the acidic groups on the humic acid molecules. Also, color is easier to remove than TOC. Mg^{2+}, Ca^{2+} and Na^{+}, although ineffective themselves, could increase the removal and extend the optimum pH range to higher pH values. At around neutral pH, the effect of the sulfate ion is not very large. The presence of 50 mg/L clay had no effect on either the optimum pH range or the optimum aluminum dosage for good organics removal but the presence of humics increased the aluminum requirement for good turbidity removal. Numerous mechanisms have been proposed to describe the removal of humics but the mechanism seems to depend strongly on the pH range and the issues have not been adequately resolved.

2.2.2 Polymer Coagulation of Humic Substances

Organic polymers have been extensively used for the removal of colloidal particles from water. Their major use in liquid-solid separation is to enhance flocculation and increase the settling rates.

Polymers have been shown to remove color-causing compounds in various industries dealing with natural organics, such as the pulp and paper industry (Kisla et al., 1978) and the production of leather (Tomlinson et al., 1975). Removal of organics from drinking water has been also reported to occur (Robinson, 1979). A summary of the published research regarding the removal of humic substances with polymers alone or in combination with aluminum along with the various experimental conditions is shown in Table 2.6.

Cationic Polyelectrolytes

Humic substances, being negatively charged under ordinary conditions, can be removed by cationic polymers. Coagulation of humic material by cationic polymers is characterized by an optimum polymer dosage (at constant pH) and a restabilization area due to overdosing (Narkis and Rebhun, 1975) (Figure 2.6). This overdosing characteristic at constant pH did not appear when alum was used, even when high aluminum dosages were employed (Edzwald, 1979).

The effect of pH on the efficiency of cationic polymers is similar to the metal coagulants case. The pH affects the ionization of the functional groups on both the humic molecule and the polymer. Increased ionization of the humic functional groups at higher pH results in an increase of the polymer dose required for effective coagulation. Since variations in the solution pH also affect the polymer cationic groups, the optimum pH range is a function of the polymer dosage. At low pH the flocculant demand is reduced, but the dose range for maximum removal is narrowed (Narkis and Rebhun, 1977). For a 10 mg/L sodium humate solution and with Polyethelenimine as the cationic polymer, the

TABLE 2.6 Summary of the experimental conditions of published research regarding the removal of humic substances with polymers alone or in combination with aluminum

Reference	Type of humic	Concentration of humic, mg/L	Variables	Range	Removal measured by
Narkis et al (1975)	Soil HA Peat FA	10 50	pH Cationic Polymer clay	8.0 0.1-55 mg/L 150 mg/L	Absorbance after centrifugation
Narkis et al (1977)	Soil HA Peat FA	5-50 25-100	pH Cationic Polymer	2.8-8.0 0-16 mg/L	Absorbance after centrifugation
Edzwald et al (1977)	Peat HA	5 and 10	pH Cationic Polymer Anionic Polymer Nonionic Polymer Al	6.0 0.01-100 mg/L 0.01-100 mg/L 0.01-100 mg/L 0 ; 0.2×10^{-4}M ; 0.4×10^{-4}M ; 0.2×10^{-3}M	Absorbance after filtration (paper or glass fiber filter)
Bowie et al (1977)	Natural Groundwaters	3-10 mg/L COD	pH Al Rapid Mix Time Flocculation Time Velocity Gradient Polymer conc.	2.0-9.0 $0-10^{-2}$ M 0-5 min 0-60 min 9.7-77.3 s^{-1} 2-20 mg/L	Color remaining after settling

TABLE 2.6 (Continues)

Reference	Type of humic	Concentration of humic, mg/L	Variables	Range	Removal measured by
Fung (1978)	Natural waters	0-19 mg/L TOC	pH Al All types of polymer	7.0-7.5 0.4×10^{-4}-0.2×10^{-3}M 0.05-10 mg/L	Reduction in trihalomethane formation potential (THMFP) after settling
Glaser et al (1979)	Soil HA	5	pH Cationic Polymer	5.5-6.0 0.2-25 mg/L	Absorbance after filtration (glass fiber filter)
Edzwald (1979)	Soil HA Soil FA	2.5,5,10 7.3	pH Al All types of polymer	4.0-9.0 0-0.2×10^{-3}M 0.01-100 mg/L	Absorbance after filtration
Amy et al (1983)	Natural and synthetic waters	5.8-16.7 mg/L TOC	pH Cationic Polymer clay	6.5-8.5 0-30 mg/L 0 and 50 mg/L	Supernatant TOC/Absorbance THMFP after filtration (0.45 μm membrane filter)
THIS WORK (1984)	Soil FA	10	pH Al Non/An/ionic polymer Ca Polymer Molar Mass Degree of Hydrolysis	6.0-8.0 10^{-5}-0.5×10^{-3}M 0.01-1.0 mg/L 0,4 and 40mg/L 5M and 14M 0% and 25%	Absorbance after settling and filtration (0.10 and 0.45 μm membrane filter)

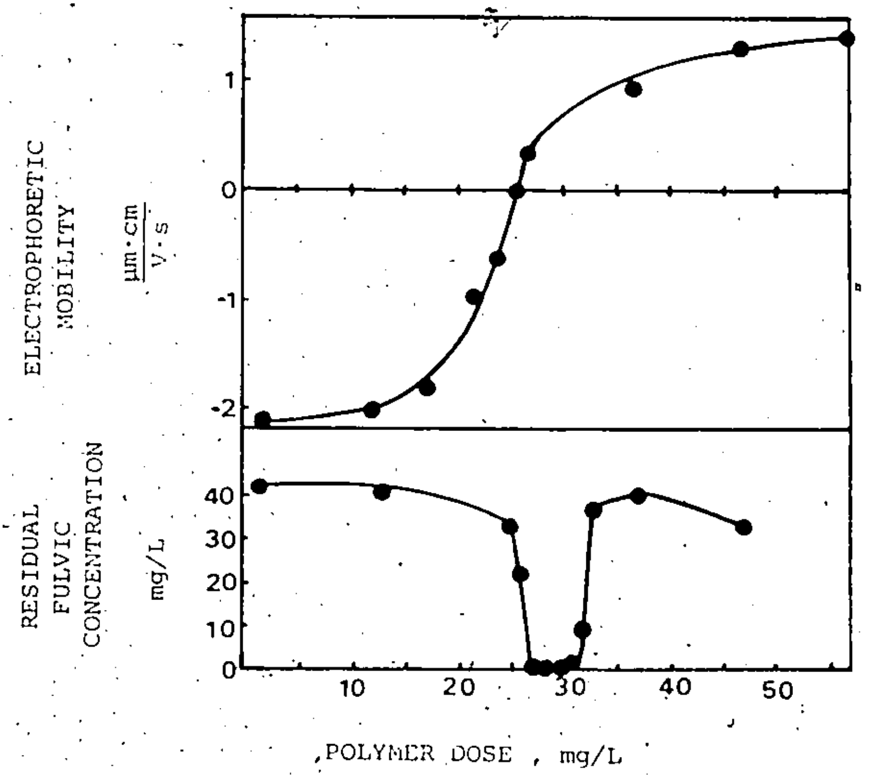


FIGURE 2.6 Effect of cationic polyelectrolyte on the residual fulvate concentration and the electrophoretic mobility (From : Narkis and Rebhun,1975)

Sodium fulvate concentration = 50 mg/L

pH = 8.0

optimum polymer range at pH 4 was 1.8 to 2.5 mg/L, while at pH 8 the optimum polymer dosage ranged from 5.0 to 7.7 mg/L.

The effects of cationic polymer on humate and fulvate solutions were similar. However, humic acid was coagulated more efficiently than fulvic acid (Amy and Chadik, 1983) and complete removal of fulvate was not obtained (Narkis and Rebhun, 1977).

When ~~the~~ cationic polymer is added into the humic solution, turbidity is formed and the electrophoretic mobility of the product particles moves from negative values towards zero. For polymer doses up to the optimum one, low removals are observed and almost all the polymer, along with the humic material, remains in solution. At the optimum dosage a sharp increase in removal occurs (removals may reach about 100 percent) and the polymer concentration in solution drops to a minimum (Narkis and Rebhun, 1975) (Figure 2.6). The presence of the cationic polymer in solution under optimum conditions is attributed to the formation of a product of low molar mass that remains in stable colloidal dispersed form and can not be removed by centrifugation. The optimum dose is the one that occurs when the isoelectric point is reached. At higher doses the electrophoretic mobility of the particles becomes positive and the removal deteriorates.

The effect of the polymer molar mass on the removal was investigated by Glaser and Edzwald (1979). They tested the cationic polymer Polyethylenimine with various molar masses. The investigators concluded that the optimal polymer dosages were independent of the molar mass of the polymer. Replotting their data, however, indicates that the polymer molar mass does affect the removal of humic acid. This can be seen in Figures 2.7 and 2.8 for the two different molar masses

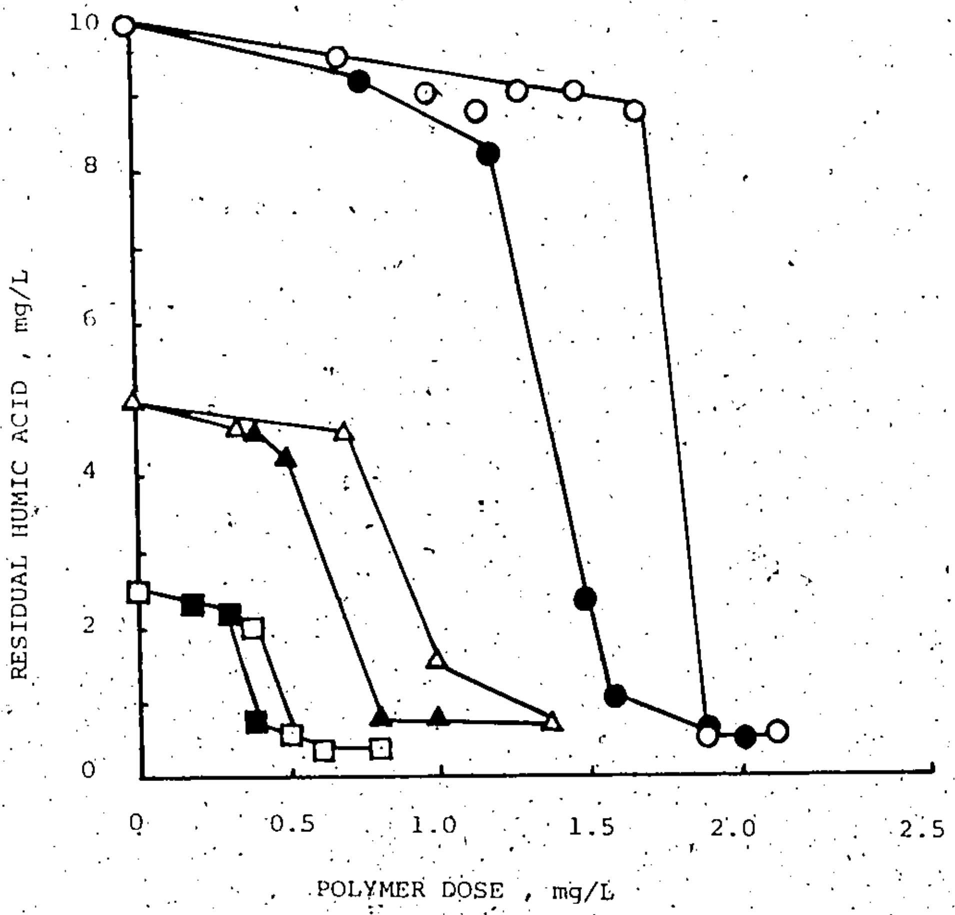


FIGURE 2.7 : Effect of polymer Molar Mass on the removal of various concentrations of humic acid (From:Glaser and Edzwald,1979)

● PEI-6
○ PEI-1000
Humic acid = 10 mg/L

▲ PEI-6
△ PEI-1000
Humic acid = 5 mg/L

■ PEI-6
□ PEI-1000
Humic acid = 2.5 mg/L

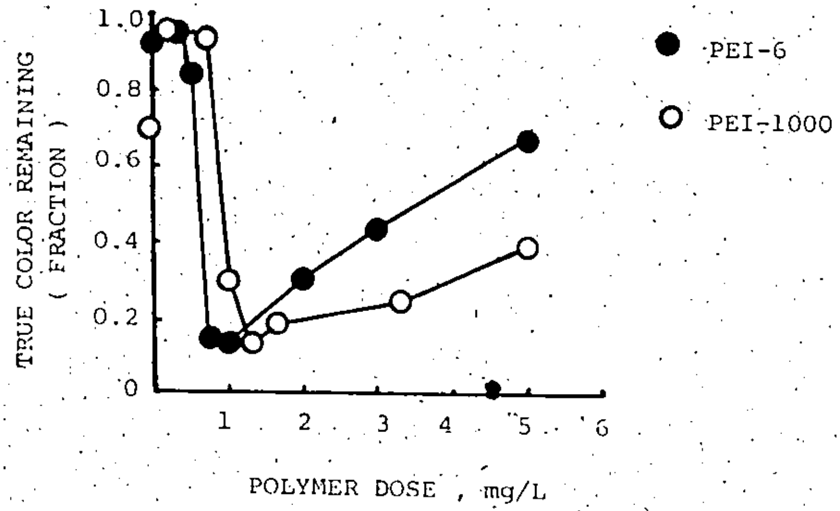


FIGURE 2.8 Effect of the polymer Molar Mass on the restabilization of humic flocs (From:Glaser and Edzwald,1979).

presented in their paper, specificly PEI-6 (MM 600) and PEI-1000 (MM 50,000-100,000). Lower dosages were required for the low molar mass polymer. The maximum removals were not affected markedly, while restabilization was faster with the low molar mass polymer (Figure 2.8).

The effect of the presence of various ionic species in the solution (with the exception of aluminum) was never investigated.

The effect of the presence of clay was studied by Narkis and Rebhun (1975). They observed that much higher dosages were required for the removal of clay from water in the presence of humic materials than in their absence. They concluded that only after complete interaction with the humate or fulvate (independently if they are adsorbed on the clay or in the solution) the polyelectrolyte is able to flocculate the clay particles. They attributed this to the higher mobility and-charge density, which characterizes the humic compounds, as compared to clay. On the other hand, the presence of kaolinite clay enhanced the removal of humic matter from natural waters by as much as 20 removal percentages (Amy and Chadik, 1983). It was considered that the clay promoted nucleation sites for floc formation.

Concerning the mechanism the removal of the humic materials from water by the use of cationic flocculants is considered to be essentially the result of charge neutralization (Narkis and Rebhun, 1977; Glaser, 1978). The electrostatic attraction between the negatively charged carboxylic and phenolic groups on the humic molecules, and the positively charged groups (in most cases amine groups) on the cationic polymer leads to strong association and precipitation. After the neutralization of the charges a bridging step is postulated to follow (Narkis and Rebhun, 1975). The charge neutralization mechanism is supported by the stoichiometry found between the humic material concentration and the optimum polymer dosage. Narkis and Rebhun (1977), after assuming that all effective functional groups were dissociated at pH 8, observed that under optimum conditions, the equivalents of anionic groups (phenolic and carboxylic) are approximately equal to those of the cationic groups. This stoichiometric relationship was found to deviate at high concentrations.

When cationic polyelectrolytes were used, the flocs formed showed poor settleability (Fung, 1978). Glaser (1978) attributed that to the size of the product particles. He considered that the particle size (around 1 μm) is such that it limits the effectiveness of both perikinetic and orthokinetic flocculation, therefore leading to low rates of particle contacts. To overcome this problem Glaser (1978) and Scheuch and Edzwald (1981) proposed a treatment scheme which involves the direct filtration of low turbidity humic water in the presence of cationic polyelectrolytes. Filtration was proved to be more efficient than coagulation due to increased particle contact opportunities.

Anionic and Nonionic

Edzwald et al. (1977) employed an anionic polyelectrolyte (Betz 1120). For an initial humic acid concentration of 5mg/L they observed maximum removals of approximately 35 percent at dosages of 10mg/L. At higher dosages restabilization once again was observed.

Nonionic polymers were ineffective exhibiting no removals (Edzwald et al., 1977; Narkis et al., 1968). No explanation was given for the behavior of the anionic or nonionic polymers.

Aluminum and polymers

The combined addition of alum and polymers was investigated by Edzwald et al. (1977) and Edzwald (1979). Such a system proved to be the most efficient one in removing humic substances from water. The reported advantages of this treatment scheme over using alum or polymer alone were a reduction in the coagulant dose, operation at higher pH, and production of large flocs that settle readily. For a humic acid concentration ranging from 2.5 to 10 mg/L and an alum dose of 10 mg/L at pH 6.0, the presence of 0.1 mg/L nonionic polymer resulted in increases in the removal after filtration by up to 35 percent. Similar increases in the removal were reported by Chadik and Amy (1983). They reported that the addition of 2 mg/L cationic polymer as coagulant acid resulted in increase of the trihalomethane formation potential (THMFP) removal by 3 to 22 percent for most waters, while for one type of natural water ranged from 29 to 51 percent.

Good results were obtained with all three types of polymers, namely cationic, anionic and nonionic. No explanation was given as to how the polymers, particularly the anionic and the nonionic, interacted with the aluminum and enhanced its efficiency. Figure 2.9 shows how the presence of the anionic polymer promoted the removals.

A study of some operational parameter on the removal of organic color was performed by Bowie and Bond (1977). They found that the best results were produced when the sequence of treatment was alum addition followed by pH adjustment and polymer addition. More specifically they observed that the optimum interval of mixing of the alum was thirty seconds. Following the alum rapid mix, acid addition and a one-minute rapid mix proved most effective. Finally, the polymer should be added followed by a rapid mix period of up to 30 seconds. They also found that color removal was a function of both the mean velocity gradient, G, and the flocculation time (slow mix period).

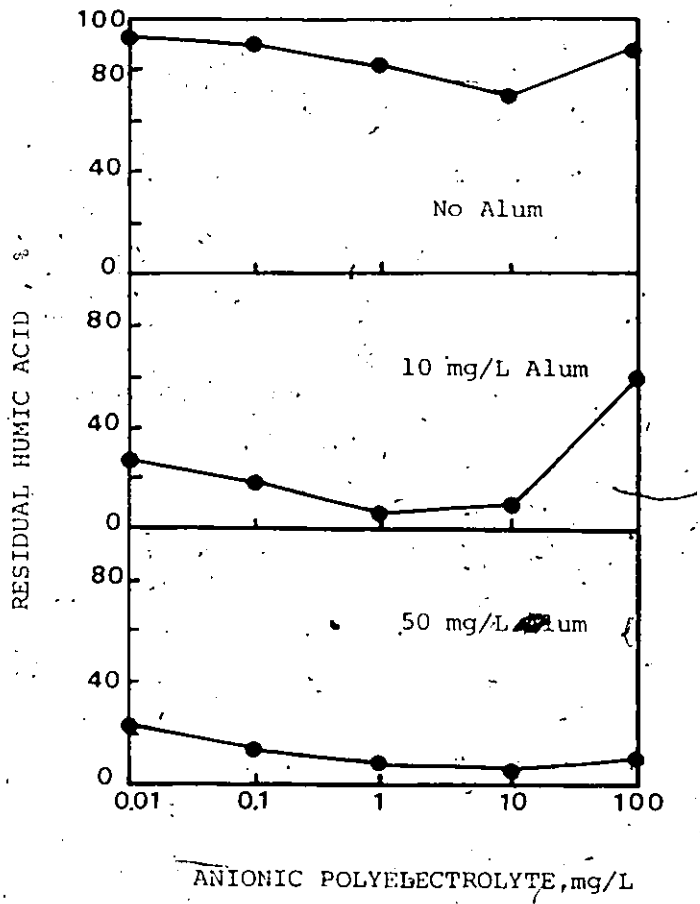


FIGURE 2.9 Coagulation of 5 mg/L humic acid at pH 6 with alum and a high molar mass anionic polymer

(From : Edzwald, 1979)

Summary

Cationic: Humic substances can be removed from water by cationic polymers. The optimum pH range and the optimum polymer dosages are inter-dependent. At lower pH the polymer demand is reduced, but the optimum polymer range is narrowed. The optimum dosage corresponds to the isoelectric point, which suggests that the removal is accomplished by the electrostatic attraction of the oppositely charged molecules. At polymer dosages higher than the optimum one restabilization of the particles occurred. There is some indication that a cationic polymer with lower molar mass requires lower dosages but narrower operating range. The flocs formed showed poor settleability.

Anionic and Nonionic: Anionic and nonionic polymers acting alone do not demonstrate any significant efficiency to remove humic substances.

Polymers and Aluminum: In the presence of aluminum all types of polymers promoted the removal of humic substances. Cationic, anionic and nonionic polymers decreased the optimum aluminum dosage and increased the pH range for effective operation. There is inadequate information, however, regarding the role of the polymers in the presence of aluminum.

2.3. QUESTIONS POSED BY THE LITERATURE SEARCH

The removal of trihalomethane precursors, such as humic substances, from water can be accomplished by either employing advanced treatment (carbon adsorption, ion exchange or membrane processes) or improving existing processes. Coagulation is a very common water treatment process used primarily for the removal of colloidal particles that cause turbidity. Increased organics removal during coagulation can be very beneficial in terms of reducing the concentration of trihalomethanes in water, reducing the chlorine demand or extending the operating cycle of subsequent processes, such as carbon adsorption.

Evaluation of the removal of humic substances during coagulation is usually done by measuring the removal after filtration. Membrane and glass fiber filters with various pore sizes were commonly used. The minimum pore size that was employed has been around 0.45 μm. General comments have also been made about the settleability of the flocs for different conditions. In water treatment practice both settling (in the clarifier) and filtration (in the bed filter) are important. Hence, the effect of the same chemical conditions on the removal of humics by both settling and filtration should be resolved.

The removal of humic substances during coagulation shows a complex interaction between pH, aluminum and polymer dosages. The interaction is clouded by the unknown structure of the humic matter. The mechanisms by which all the variables interact are still unresolved. Most of the key research has been done by varying one variable at a time while keeping the rest constant. Should not a statistical analysis be done to account for most of the variables and the interaction among the variables? Improvement of the coagulation process may be achieved with the use of polymeric flocculants. The potential of all types of polymer - cationic, nonionic and anionic - to promote the removal of humic matter by aluminum as demonstrated by Edzwald (1977, 1979) should be further explored. Nonionic and anionic polymers are, in general, more attractive than cationic polymers in terms of cost, manufacturing and property characterization. There is inadequate information, however, regarding the way they interact with the aluminum and the organic matter. The role of these polymers is unclear because little is known about the size of the coagulated fulvic and humic acids, particularly submicron particles. The mechanism of the interaction between the polymers and the aluminum-treated organics should be resolved.

Although various ions, such as Ca^{2+}, Mg^{2+}, SO_4^{2-}, under certain conditions affected the aluminum dosage rates used for coagulation, no work has been reported on the effect of those ions for the polymer-aluminum system. Does alum (aluminum sulfate), the most commonly used coagulant, differ from the behavior of aluminum chloride? While there is some indication that the effect of the sulfate ion is somewhat detrimental at acidic pH (Bersillion, 1984; Maulding and Harris, 1968), the question of similar or different behavior under neutral or slightly alkaline pH values has yet to be resolved.

In addition, the effect of the polymer properties, such as molar mass or functional group density, has not been extensively studied. Although Glaser and Edzwald (1979) have reported that the molar mass of the cationic polymer polyethlene imine did not markedly affect the removal of humic acid by the polymer alone, the effect of the polymer properties in the presence of the aluminum has never been studied.

Furthermore, improved removal of organic matter during coagulation requires not only a better understanding of the interaction between aluminum, fulvic acid and polymers, but also adequate modelling and optimization of the process. The modelling of the removal of organic matter with aluminum and polymer is complicated due to the unknown structure of the humic substances and the mechanism of the humic-aluminum-polymer interaction. Traditional modelling techniques, such as stoichiometric chemical reactions or adsorption isotherms, have limited use in the removal of humic matter with aluminum, since they apply under or require conditions that are not practical. Such conditions may be the measurement of equilibrium reaction constants at very low pH or the exact measurement of the formed precipitate. In addition to these, modelling of the effect of the polymer or the removal after settling by means of traditional techniques is not feasible. For all these reasons, empirical modelling techniques should be advantageous.

This thesis investigates the potential use of anionic and nonionic polymers as flocculants for organics removal. It examines the removal of fulvic acid, the most soluble fraction of the humic materials, with aluminum in the absence and presence of polyacrylamide in its nonionic and anionic forms. The specific objectives of this research are:

1. to investigate the effect of the membrane pore size on the measured efficiency of the aluminum coagulants to remove fulvic acid from water and to clarify the analytical procedures,
2. to investigate whether there are any differences in the efficiency of two aluminum coagulants, namely aluminum sulfate and aluminum chloride, to remove fulvic acid from water at around neutral pH,
3. to contrast the removal of fulvic acid by filtration versus settling under the same chemical conditions (such as pH, aluminum and polymer dosages)
4. to try to discover an understanding of the way that the polymeric flocculant intereacts with the aluminum and the fulvic acid during the coagulation process,
5. to develop a modelling technique that will quantitatively describe the removal of fulvic acid by aluminum in the absence and presence of polymer. Such a modelling technique should account for the simultaneous effect of all variables a[illegible]e easily evaluated by statistical methods,

6. to optimize the removal of fulvic acid with aluminum and polymer in terms of finding the optimum combination of chemicals that result in efficient removal with the minimum cost,
7. to identify the optimal polymer properties, such as the molar mass and the degree of hydrolysis, that in relation to other variables, such as the pH or the calcium concentration of the water, accomplish maximum removals of fulvic acid from water by means of aluminum and polyacrylamide, and
8. to quantify the effect of calcium on the removal of fulvic acid in an aluminum-polymer system.

The research that addresses these issues is described in five parts of this thesis.

* In Chapter 4 the effect of filter pore size on the evaluation of aluminum coagulants to remove fulvic acid from water is discussed.
* In Chapter 5, the focus is on fulvic acid removal with aluminum salts in the presence and absence of nonionic polyacrylamide.
* Chapter 6 considers modelling the removal of fulvic acid with aluminum.
* The modelling and optimization of the fulvic acid removal with aluminum and nonionic polyacrylamide is presented in Chapter 7.
* Finally, the factors affecting the removal of fulvic acid with aluminum and polymers are explored in Chapter 8.

CHAPTER THREE

EXPERIMENTAL

3.1 MATERIALS

3.1.1 Fulvic acid

Fulvic acid was obtained from Contech E.T.C. Ltd., Ottawa. It is a low ash fulvic acid obtained from soil. Standard test solutions were prepared at concentrations of 10.0 mg/L fulvic acid and 200 mg/L $NaHCO_3$. The bicarbonate salt was added as a buffer. The water used was distilled and deionized. At the last part of the experimental work, the study of the effect of the polymer properties on the removal, calcium was also added to the standard test solution at two levels: 4mg/L and 40 mg/L. The solution was prepared in batches of 18 L. Each batch was aerated for two hours to enable equilibration with the atmospheric carbon dioxide.

3.1.2 Aluminum Coagulants

Two analytical grade aluminum salts were used: $AlCl_3 \cdot 6H_2O$ and $Al_2(SO_4)_3 \cdot 16H_2O$ (Alum). They were obtained from BDH Chemicals, Toronto. Stock solutions of 10^{-2} M Al were prepared and stored. To avoid the effect of the aluminum hydrolysis, the aluminum solutions were stored for at least three days before they were used and never used for more than a month.

3.1.3 Polymers

Nonionic polyacrylamide was obtained from two sources. The first one was obtained from Polysciences, Inc., Warrington, PA., and the other from Allied Colloids (Canada) Inc., Mississauga, Ontario (Percol 720). The former had a molar mass of 5 to 6 million, according to data provided by the manufacterer. The molar mass of the latter had been previously measured by means of Gel Permeation Chromatography and found to be 13 to 14 million (Huck, 1977). Since the error associated with the measurement of ultra high molar mass polymers by means of Gel Permeation Chromatography is large, these two polymers are denoted as High Molar Mass polymer and Ultra High Molar Mass polymer, respectively. Anionic polyacrylamide with 25 percent hydrolysis was prepared from the nonionic polymers according to the procedure described in the Appendix.

3.2. COAGULATION STUDIES

3.2.1 Jar Test

A jar-test apparatus was employed in this study. This consists of a Phipps and Bird six-paddle stirrer with 6, one litre jars. It allows the simultaneous investigation of six values per variable per experimental run. The following time periods were used for the jar test after the addition of the aluminum solution:

Rapid mixing:	6 min at 100 rpm (when polymer was used, it was added 3 min after the aluminum addition and the rapid stirring continued for another 3 min)
Slow mixing:	14 min at 30 rpm
Settling:	20 min

Finding the optimum amount of time for the first two functions was not an objective for this work. The values chosen represent traditional conservative values of the same magnitude as those found in similar coagulation studies in the literature. For the system under study it is believed that the rates of ionic species equilibrium and precipitate formation were faster than the pertinent time allowed.

Prior to the aluminum addition a predetermined amount of hydrochloric acid or sodium hydroxide solution was added into the jars so that the final pH of the water would have the desired vaule. Close to the end of the slow stirring a sample was taken from each jar and its turbidity was measured. After the 20 min settling period another sample was taken from each jar from a depth of 5 cm below the water surface. The sample was acidified with 3 drops of concentrated hydrochloric acid to dissolve all suspended matter and the fulvic acid concentration was measured. In specifying the depth of the sampling point and the time of the sample withdrawal two factors were considered: first, that the obtained results should be of practical value, i.e. definite removal of flocs due to settling should occur, and second, the settling velocity should be close to values used in actual clarifiers. Based on preliminary observations and literature data (EPA, 1975) the depth of 5 cm and the time of 20 min were selected. After the end of the settling period the solutions were stirred again to resuspend the particles and samples were withdrawn for filtration.

3.2.2 pH Control

Great care was taken to ensure that the pH when coagulation occurred was known and at the target conditions. Because of the acidic character of the aluminum ion, the addition of the aluminum coagulant to the standard test solution lowered the pH. The decrease of pH depended on the aluminum dosage. The more aluminum added to the fulvic water, the larger the pH drop. To operate at a desired pH level, a predetermined amount of hydrochloric acid or sodium hydroxide solution (0.1 N) had to be added to the jars before the coagulant addition. Thus, several calibration runs were performed ahead of time for each aluminum dosage to determine the effect of aluminum on the pH of the fulvic solution. A typical calibration run is shown in Figure 3.1.

Another problem which is usually encountered during the coagulation process is the attainment of carbonate equilibrium. It is important that the pH does not change during the mixing periods as a result of the CO_2 dissolution. Preliminary studies indicated that for the stirring conditions used in this work the change of pH during the coagulation study was within the experimental error of pH measurement permitted by the standard buffer solutions (0.02 pH units).

3.2.3 Filtration

The solid-liquid separation through filtration was done by means of membrane filters. The membrane filters used were Sartorius Cellulose Nitrate filters 47 mm in diameter obtained from Canlab, Toronto. Two pore sizes were employed: 0.45 μm and 0.10 μm. These values represent mean values, since the membrane structure is a three-dimensional net. All filters were kept immersed in distilled and deionized water for a minimum of 24 h before they were used. The filtering apparatus consisted of a Sargent-Welch Vacuum Pump connected to a Millipore glass filter holder. All vacuum filtrations were performed at an absolute pressure at 13 kPa.

Membrane filters with two pore sizes were employed in order to investigate whether there is a pore-size effect on the evaluation of the aluminum coagulants to remove fulvic acid. Therefore, prior to the coagulation study, a filtration study was performed to check this hypothesis (the results are presented in Chapter 4).

The filtration study involved three steps. In the first, pure water

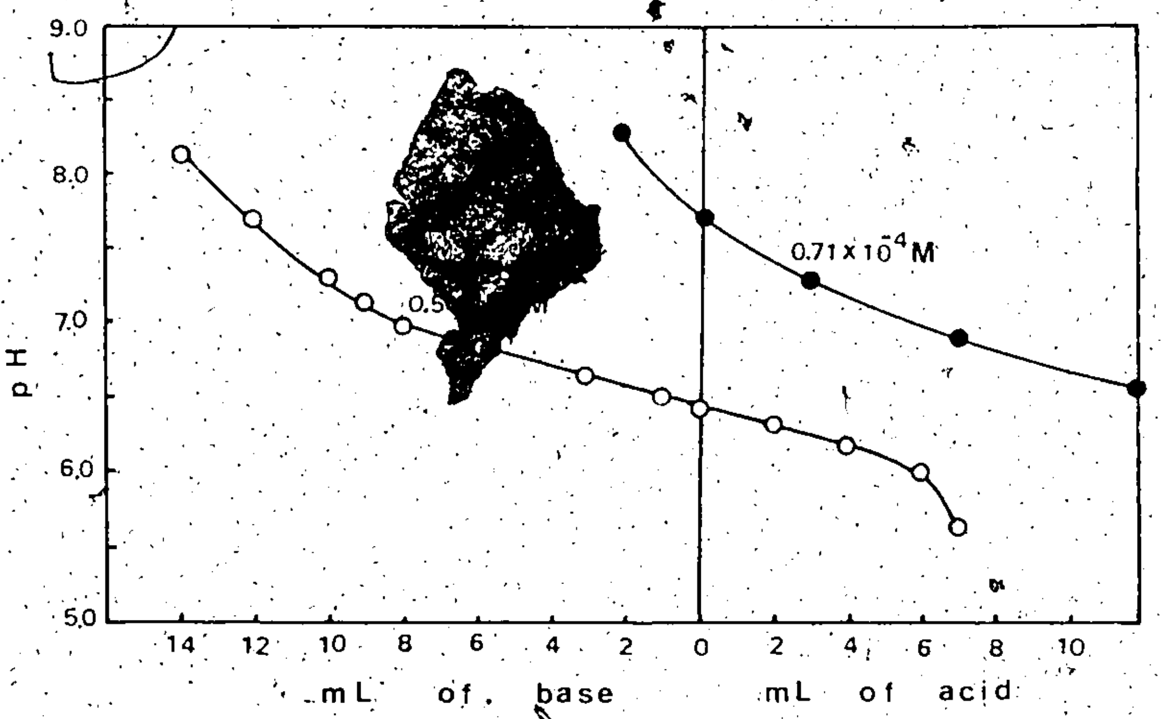


FIGURE 3.1 Final pH of 1L of the coagulated fulvic solution as a function of the acid or base added for two aluminum dosages

was used to examine whether there was any contribution in the UV absorbance by organics leached from the filter. In the second step, fulvic acid solutions were used, while the third step involved the filtration of aluminum-treated fulvic acid solutions. For the last two steps the filters were rinsed with 150 mL of distilled and deionized water prior to the filtration of the samples. Each sample, of 150 mL, was filtered in aliquots of 10 mL, and the filtrate aliquots were analyzed separately for their UV absorbance.

As a result of the filtration study, prior to obtaining the filtrate for the fulvic acid analysis during the coagulation experiments, 150 mL of distilled and deionized water and 100 mL of aluminum -treated solutions were filtered through each membrane filter.

3.3 ANALYTICAL METHODS

3.3.1 Fulvic acid

Fulvic acid concentrations in the filtered liquid samples were measured by means of a UVD-21 Bausch and Lomb Spectrophotometer (Bausch and Lomb Co., Baton, N.Y.) at a wavelength of 254 nm using a 1 cm square cell. The absorbance of a fulvic acid solution increased with pH as illustrated in Figure 3.2. The difference between pH 8 and 6 (the pH range investigated in this study) was around 5 percent. To avoid this error, all samples prior to analysis were acidified with three drops of concentrated hydrochloric acid and all absorbance measurements were made on the acidified samples of pH 2. Calibration of the spectrophotometer was done with standard fulvic acid solutions of various concentrations. The relationship between the measured absorbance and the fulvic acid concentration was linear, with the slope depending on the pH (Appendix A3).

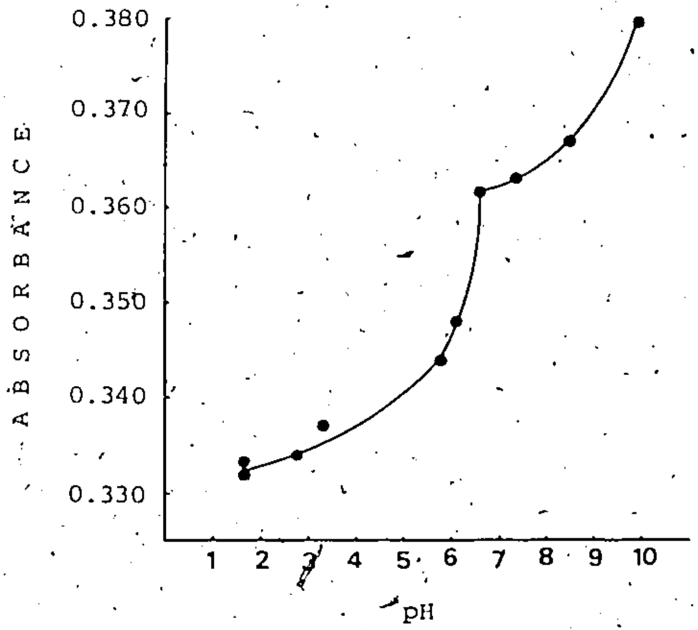


FIGURE 3:2 Dependence of the absorbance on the pH for 10 mg/L fulvic acid in distilled water

The discontinuity in the curve is due to structural changes as a result of changes in pH, such as protonation of functional groups. Thus, this curve is analogous to a titration curve.

3.3.2 pH measurements

The pH of the solutions was measured with a model 801 ORION Ionalyzer (ORION, Cambridge, Mass) using Fisher glass and reference (calomel) electrodes (Fisher Scientific Co., Toronto). The electrodes were calibrated with standard buffer solutions obtained from Fisher. Great care was taken in ensuring that the electrodes gave fast and accurate response. The reference cell was cleaned weekly to ensure free flow of the electrolyte through the junction and to minimize the junction potential.

3.3.3 Turbidity measurements

Turbidity measurements were made with a model DRT 1000 HF Instruments Turbidimeter.

3.3.4 Electron microscopy

A Phillips EM 300 Transmission Electron Microscope was used to examine the morphology of the flocs. Copper grids were covered with a carbon film and then were immersed 30 times into the aluminum-treated fulvic acid solution. This procedure was sufficient for the deposition of particles on the grids. The grids were allowed to dry in a dust-free place and then examined under the microscope.

3.4 STATISTICAL TREATMENT

3.4 Variables

There are two sets of variables that were used in this work. The first set was used in the general coagulation study (Chapter 5), the modelling in the absence of polymer (Chapter 6) and the modelling in the presence of polymer (Chapter 7). The variables used were the pH (ranging from 6 to 8), the aluminum dosage (ranging from 10^{-5} M to 0.5×10^{-3} M) and the polymer dosage (ranging from 0 to 1 mg/L). The pH and aluminum ranges define the borderline of the aluminum application conditions usually used in practice. The temperature was kept fixed at room temperature.

The second set of variables was used in the study of the factors that affect the removal of the fulvic acid with aluminum and polymers (Chapter 8). These variables were the calcium concentration in the fulvic water, the polymer molar mass and degree of hydrolysis, the pH and the polymer dosage. The aluminum dosage was kept constant at 10^{-4} M (or 2.7 mg/L Al). The study of the five variables was made according to 2 resolution V fractional factorial experimental design (Box and Hunter, 1961 a; 1961 b). The five variables used in the experimental design with their high and low levels are presented in Table 3.1. The study of the five variables according to the experimental design requires 16 runs, while repeat runs were also performed in order to obtain an estimate of the standard error.

3.4.2 Model development

The modelling of the removal of fulvic acid with aluminum is clouded by the unknown nature of fulvic-aluminum interaction. Historically, the first mechanism postulated the formation of insoluble aluminum fulvate through an electrostatic or chemical interaction between the carboxylic and phenolic groups on the fulvic molecule and the aluminum hydrolysis species. As was seen in the literature review part of this thesis, a complexation mechanism was used to explain the existence of an optimum pH, the effect of the presence of other ions and the linear relationship between the inital fulvic acid concentration and the optimum coagulation dosage. Modelling of the complexation reactions involves the estimation of the reaction equilibrium constants. Although values of the

TABLE 3.1 Independent variables of the fractional factorial experimental design

Variable	Calcium Concentration mg/L	Degree of Hydrolysis %	Molar Mass	pH	Polymer Concentration mg/L
X	1	2	3	4	5
+	40	25	Ultra High	8	0.1
-	4	0	High	7	0.01

reaction constants have been estimated (Schnitzer, 1971; Schnitzer and Hansen, 1970) they were obtained at highly acidic pH (pH = 2), where no precipitation had occurred. These equilibrium constants represent conditional equilibrium constants and they are of doubtful practical use around neutral pH. Hence, a model based on a complexation mechanism is limited because of the inadequacies of the reaction equilibrium constants.

On the other hand, an adsorption mechanism has also been postulated to occur, either as the sole mechanism or in parallel with the complexation reactions. Modelling based on adsorption involves an estimation of the coefficients in a Langmuir or Freundlich adsorption model. Since the fulvic acid represents a mixture of poorly-defined organic substances the empirical Freundlich isotherms were used. The estimated values of the coefficients in the Freundlich isotherms depended on the pH (Bersillon, 1983). The use of isotherms requires that adsorption is the only mechanism responsible for the removal and that the amount of the solid phase (aluminum hydroxide) formed is known. The amount of aluminum hydroxide that precipitates is affected by the presence of other inorganic or organic species, such as calcium or sulfate, while the mathematical expression that describes the Freundlich isotherms is quite complex. For these reasons, and until most ambiguities about the aluminum-fulvic interactions are resolved, the use of empirical modelling was selected. Because the modelling is done empirically, it may be very flexible in terms of using variables as diverse as the pH, the aluminum dosage and the polymer dosage. In addition to this, various criteria may be used to describe the removal. In this study the criteria were the removal after filtration and the removal after settling.

The modelling of the removal of fulvic acid with aluminum is based on the idea that for a narrow operating region the response surface may be approximated by a second-order mathematical expression. The mathematical expression is quadratic with respect to the independent variables, while third and higher order interactions were assumed to have no significant effect. The model is of the general form:

$$R = b_o + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} \sum_{j=i}^{n} b_{ij} X_i X_j$$

Where

R is the mass percentage removal of fulvic acid measured after filtration or setting

X are the settlings of the independent variables (usually in coded form)

n is the number of the independent variables, and

b are the parameters to be estimated

A response governed by two variables, such as pH and aluminum dosage as in Chapter 6, will be presented as:

$$R = b_o + b_1X_1 + b_2X_2 + b_{12}X_1X_2 + b_{11}X_1^2 + b_{22}X_2^2$$

For these variables, such as pH, aluminum dosage and polymer dosage as in Chapter 7, the model consists of ten terms, the constant b_o, three first order terms b_iX_i, three second order terms $b_{ii}X_i^2$, and the three interaction terms $b_{12}X_1X_2$, $b_{13}X_1X_3$ and $b_{23}X_2X_3$. In these models the logarithm of the aluminum or polymer concentrations were used rather than the concentrations themselves so as to be consistent with the fact that the pH is also a logarithmic function of the hydrogen ion concentration. The quadratic form of the model requires a three-level full factorial design for the estimation of the coefficients (Box et al, 1978). Repeat runs at the centre point can provide an estimate of the pure error. The model is linear with respect to its parameters and, therefore, estimation of the parameters can be easily done by means of linear regression. One of the main advantages of this factorial design is that its orthogonality guarantees uncorrelated estimates of the parameters. Orthogonality, however, requires that the variables have their exact values. While values of the aluminum and the polymer concentrations can be easily adjusted to the desired levels, it is not always possible to obtain the exact value of the desired pH, despite the careful control. The following strategy was, therefore, followed: For the two-variable system (aluminum dosage -pH; Chapter 6) a tolerance of 0.05 pH units was permitted. If the pH of coagulation was within 0.05 pH units of the desired level, the removal obtained under these conditions was considered to be practically identical with that at the exact pH. If the pH of coagulation was outside the tolerance limit, the experimental run was repeated until the pH fell within the tolerance limits. In this way orthogonality is guaranteed in the parameter estimation. For the three-variable model, however, (pH-aluminum dosage-polymer dosage; Chapter 7) this strategy would result in a large number of repeated experimental runs. In this case, the values of the pH variable on the model was given the corresponding real values. This resulted in a mathematical system which is not exactly orthogonal and therefore the parameter estimates were slightly correlated.

Quadratic models based on factorial designs have been employed to determine the optimum conditions for the use of polymers in the flocculation of metal hydroxides present in neutralized mine drainage

(Huck, 1977) and to study the influence of various factors on the clarification in the activated sludge process (Cashion and Keinath, 1983).

In the above analysis, the quadratic form of the model is considered to account for nonlinearities. It is also assumed that the observations R are independently normally distributed with constant variance. If these assumptions are not satisfied in terms of the original observations, improvement on the statistical analysis of the model may be done after a suitable transformation of the observations. Although there is an infinite number of possible transformations, one that has been extensively investigated (Box and Cox, 1964) is of the form:

$$Z^{(\lambda)} = \begin{cases} \dfrac{y^{\lambda} - 1}{\lambda \cdot \dot{y}^{\lambda - 1}} & \lambda \neq 0 \\ y \cdot \ln y & \lambda = 0 \end{cases}$$

where

$Z^{(\lambda)}$	are the transformed observations,
y	are the untransformed observations (i.e. Removals),
λ	is the transformation coefficient, and
$\dot{y}$	is the geometric mean of the observations.

A particular advantage of this type of transformation is that it is continuous at $\lambda = 0$.

Inference about the transformation and about the model parameters can be made by calculating the maximized likelihood function and the posterior distribution. One can then calculate a value for the transformation parameter that maximizes the maximized likelihood function or equivalently minimizes the residual sum of squares for the transformed observations (Box and Cox, 1964). The residual sum of squares represents all deviations not accounted for by the model. There are two possible sources of these deviations: the pure error sum of squares and the lack of fit sum of squares. The former represents all deviations due to experimental error, and it can be estimated from the repeat runs. The latter is calculated after subtracting the pure error sum of squares from the residual sum of squares and accounts for all deviations caused by a possible lack of fit. A F-test can be performed to examine whether there is sufficient evidence for lack of fit (Draper and Smith, 1966). From a practical point of view, however, an evaluation of the adequacy of the model can be assessed by examining the average difference between predicted and observed values. Depending on the specific system and the accepted tolerance average deviations of up to 10 percent may be acceptable for engineering applications.

Further evaluation of the model can be done by examining the significance of the estimated parameters. Parameters that are significantly different from zero should not include the zero value within their estimated confidence limits. In addition, a plot of the residuals may also reveal inadequacies of the model (Daniel, 1976).

The three variable model allows for the optimization of the removal of fulvic acid with aluminum and polymer, in terms of minimizing the combined cost of these two chemicals. In the optimization process the minimum cost is identified along the removal surface defined by the experimentally determined model. The optimization technique is somewhat different from a response surface method (Box et al, 1978) in that the main objective is not to maximize the removal function, as given by the model, but rather to minimize the cost of the chemicals function subject to a certain desired removal. In other words in this case the removal equation is a constraint in the optimization problem.

CHAPTER FOUR

THE EFFECT OF FILTER PORE SIZE ON THE EVALUATION OF ALUMINUM COAGULANTS TO REMOVE FULVIC ACID FROM WATER

The evaluation of metal coagulants, such as aluminum and iron salts, for the removal of soluble or colloidal matter from water requires the separation of the solid from the liquid phase. Membrane filters have been used extensively for this purpose. One would expect that those working in coagulation studies involving naturally occurring organics would carefully assess which filter pore size is most appropriate for the process being studied. Unfortunately, it seems that many working in the removal of humic substances with aluminum and iron salts have used filters with a pore size of 0.45 μm or larger. The purpose of this part of the work was to investigate whether data collected with such filters may accurately reflect the removals.

In general there are two sources of error associated with the use of membrane filters. The first is related to the filter itself as well as to the filtering apparatus, and the other to the water sample. The former source of error is due to the adsorption/desorption of solutes on the filter or the filtering equipment or the desorption of filter trace constituents (Robertson, 1965; Spencer and Mannheim, 1969; Marvin et al., 1970;

Florence, 1977). The latter source of error occurs because it is difficult to distinguish operationally between dissolved and colloidal matter (Stumm and Morgan, 1981; Trussell and Tate, 1979). When membrane filters are used, it is usually implicitly assumed, but rarely stated, that whatever passes through the pores of the filter is soluble. Therefore, any colloidal matter that is small enough to pass through the filter will appear as soluble. This is of particular importance in the study of equilibrium in natural waters, since it has been found that "soluble" metal concentrations ("soluble" defined by filtration) are often much higher than those predicted from thermodynamic solubility data (Kennedy et al., 1974; Boyle et al., 1977; Mill, 1980). The high metal concentrations have been associated with high organic carbon in the water samples. Whether the organics keep the metals in a true soluble state by complexing them or they stabilize the metal hydroxide sols is not completely distinguishable. On the other hand, the filterable fraction of the metals and the organics was found to depend on the membrane pore size or the amount of water filtered (Kennedy et al., 1974; Danielsson, 1982).

When metal coagulants are used to remove organic matter from water, any errors associated with the distinction between the soluble and the particulate matter will also be included in the apparent efficiency of the coagulants. This work addresses some of the problems introduced by the use of membrane filters when they are used in the removal of natural organics, such as fulvic acid, by aluminum. Specifically, the objectives of this section were:

1 To investigate the interactions between fulvic acid and the membrane filter during the routine work of filtration, in the presence and absence of aluminum, and

2 To determine the effect of the membrane pore size on the apparent efficiency of aluminum to remove fulvic acid from water.

4.1 RESULTS AND DISCUSSION

The absorbance of membrane organics leaching into the solution is shown in Figure 4.1. In these experiments only pure water was used. Some leaching did occur in the beginning of the filtration but the overall increase in the absorbance was not very large. In terms of fulvic acid concentration the maximum error introduced by leaching was less than 0.5 mg/L (or approximately 0.015 absorbance units). This can be significant when low level solutions are used if prior rinsing of the filter is not done. After rinsing the filter with 100 mL of water no more leaching was observed. Based on these results, for all subsequent tests the filters were rinsed with approximately 150 mL of distilled and deionized water prior to fulvic acid sample filtration, even though fulvic acid concentrations of up to 10 mg/l were employed. The data in Figure 4.1 show no noticeable difference between the two types of filters.

Figure 4.2 shows the filtrate concentration of a fulvic acid solution. The fulvic acid concentration was 10.0 mg/L. The behavior of the two kinds of filter appeared identical. The fulvic acid concentration of the first aliquot (10mL) was, for both types of filter, lower than the solution concentration, but this difference was on the average less than 0.040 in absorbance (1 mg/L in terms of fulvic acid concentration). However, the filtrate absorbance leveled off at the original absorbance after the first aliquot. The initial decrease in absorbance can be viewed as adsorption of fulvic acid on the clean filter and the filtering apparatus. Similar results were obtained when a 25 mg/L fulvic acid solution was used, with the absorbance of the first aliquot being lower than that in the original

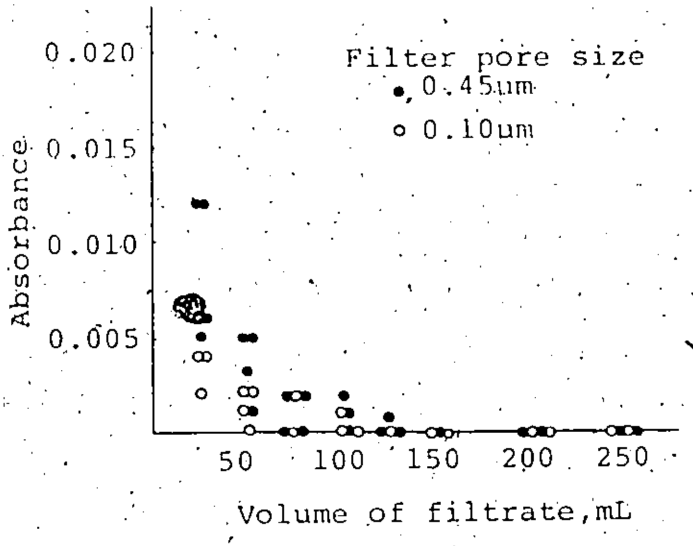


FIGURE 4.1 Filtrate absorbance as a function of water filtered for pure water

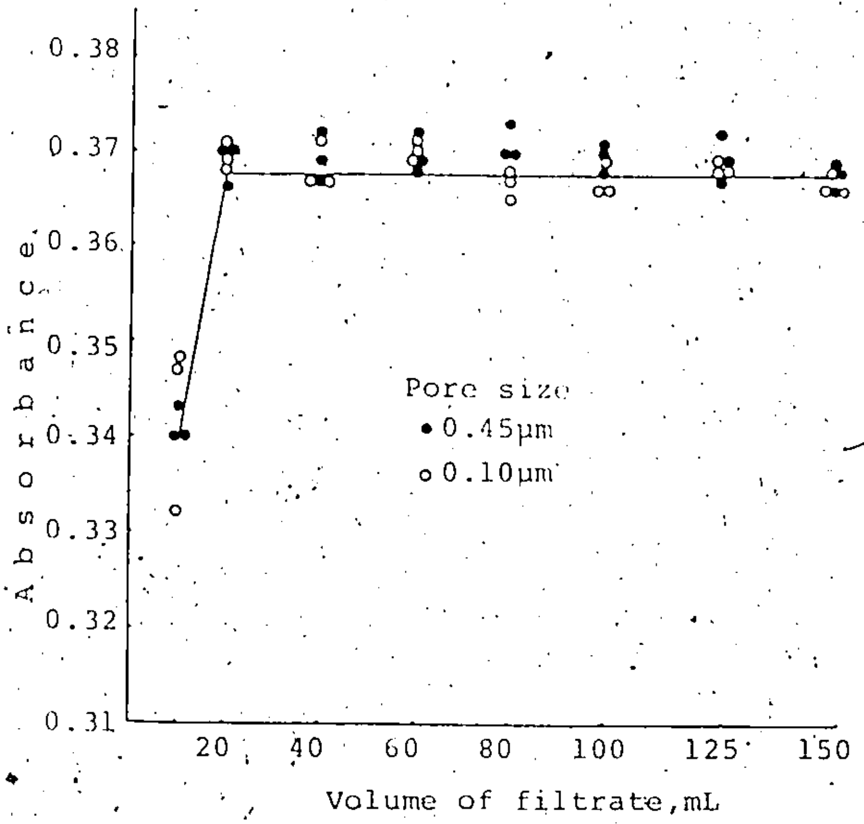


FIGURE 4.2 Filtrate absorbance of a fulvic acid solution

Absorbance of the solution = 0.368

sample, while the rest of the filtrate aliquots exhibited the same absorbance as in the original sample. The above results indicate that the specific fulvic acid used in this work acted like a "soluble" substance, "soluble" in the sense that no retention on the filter was observed, at least for the small quantities filtered.

The rest of this section refers to aluminum-treated fulvic acid solutions. Figure 4.3 depicts the filtrate absorbance of a 10.0 mg/L fulvic acid solution treated with $AlCl_3$ at a concentration of 0.5×10^{-3} M and a pH = 5.96. It can be seen that the absorbance is practically zero, which indicates that 100 percent removal was achieved. This high removal was expected because of the high aluminum dosage and the favourable pH. The filtrate absorbance was also independent of the amount of solution filtered and there was no noticeable difference in the performance of the two types of filter.

Differences, however, in the behavior of the two kinds of filters were observed when the pH of the precipitation was around 8 (Figure 4.4). While the filtrate absorbance in the case of the 0.10 μm filter practically leveled off after the first 10 mL at an absorbance of 0.035 (or 0.9 mg/L in terms of fulvic acid concentration), the behavior of the 0.45 membrane filters was somewhat anomalous. The filtrate absorbance was high in the beginning (to levels up to 80 percent of the original absorbance) and then dropped to the same level as with the 0.10 μm filter. The 0.45 μm filter exhibited characteristics of a deep filter: in the beginning of the filtration, when all filter pores were clean, particles smaller than the pore size passed through the filter. When, however, clogging of the pores occurred, even the small particles were removed due to the reduction of the pore size.

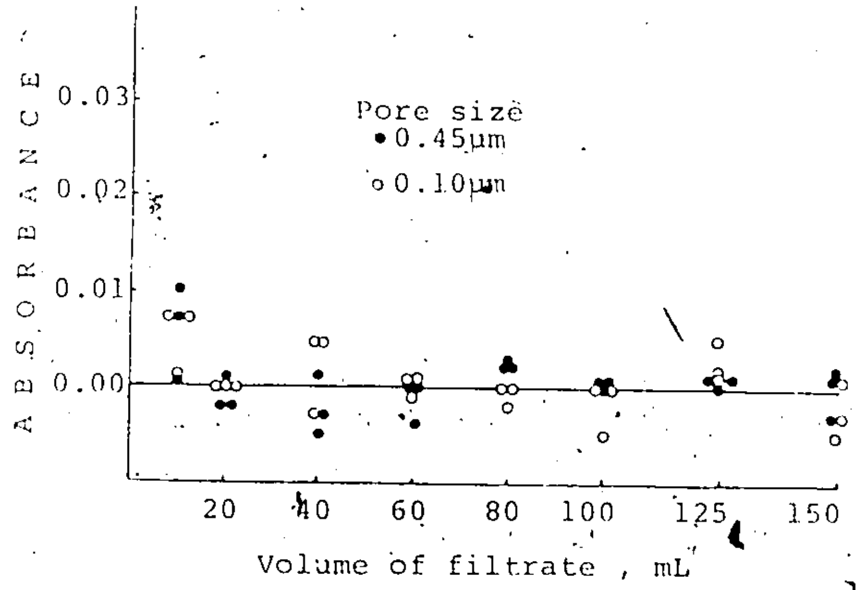


FIGURE 4.3 Filtrate absorbance of the aluminum-treated fulvic acid solution

Al concentration = 0.5×10^{-3} M

Initial fulvic acid concentration = 10.0 mg/L

pH=5.96

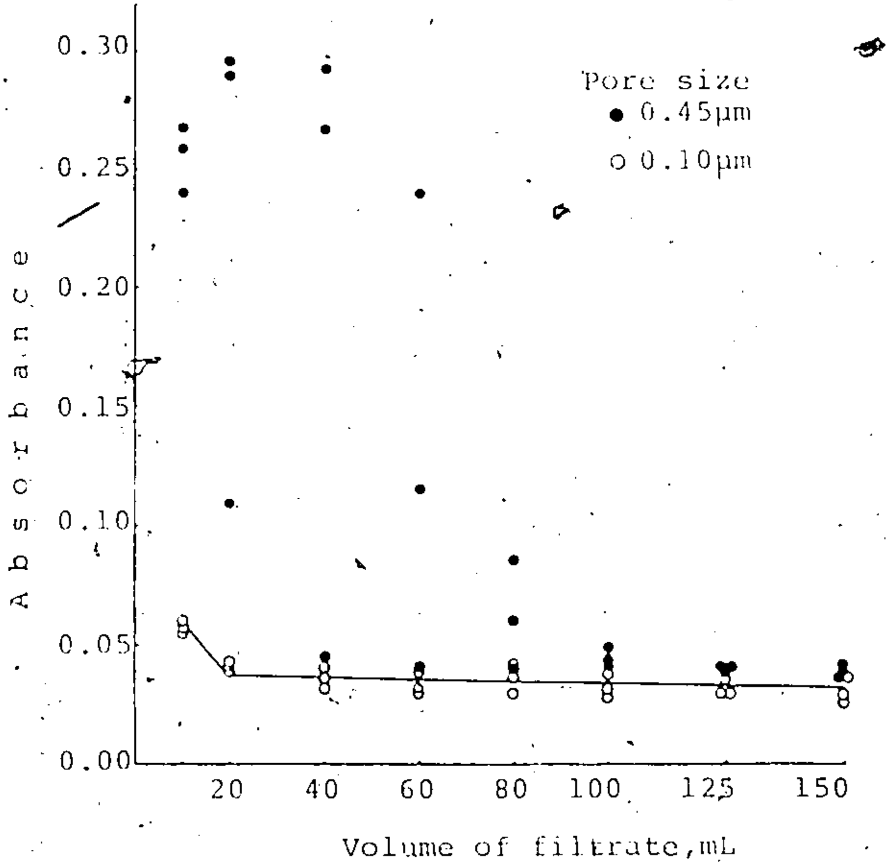


FIGURE 4.4 Filtrate absorbance of the aluminum-treated fulvic acid solution

Al concentration = 0.5×10^{-3} M

Initial fulvic acid concentration = 10.0 mg/L

pH = 8.13

This deep-filter behavior was also observed at pH 6, but at a lower aluminum dosage (Al concentration 0.71×10^{-4} M). As it can be seen in Figure 4.5, while the filtrate absorbance was consistently 0.020 for the 0.10 μm filters, in the case of the 0.45 μm filters the same absorbance was obtained for all the filters only after 100 mL of sample had been filtered. For smaller filtrate volumes, the filtrate absorbance was not consistent but ranged from 0.020 to almost 0.200 (or from 0.5 mg/L to 5.4 mg/L in terms of fulvic acid concentration). These results also indicated that certain differences exist among individual membranes of the same pore size. The low filtate concentration in the first stages of filtration may be due to the adsorption of some of the organics on the filter.

For the same aluminum concentration, 0.71×10^{-4} M, but higher pH, around 8, the results are shown in Figure 4.6. Initially, the filtrate absorbance was low but rapidly increased to its final levels, which were 0.360 (or 9.8 mg/L) for the 0.45 μm filters and 0.345 (or 9.4 mg/L) for the 0.10 μm filters. In terms of removals, they were two percent and six percent for the two filters. It is interesting that the absorbance of the 0.45 μm filtrate did not drop to the same level as the 0.10 μm filtrate. This suggests that clogging of the filter pores was not effective since only a small portion of the precipitate was retained by the filters.

When an even lower aluminum concentration was employed, the results obtained (Figure 4.7) were similar to the pure fulvic acid solution study (Figure 4.2). Initially the filtrate absorbance was somewhat low, probably due to adsorption on the filter, but rapidly rose to its final value, which was the same as in the original fulvic acid samples (10.0 mg/L or 0.370 in terms of absorbance). It seems that any particles formed were so small, that they passed through the pores of both types of filters.

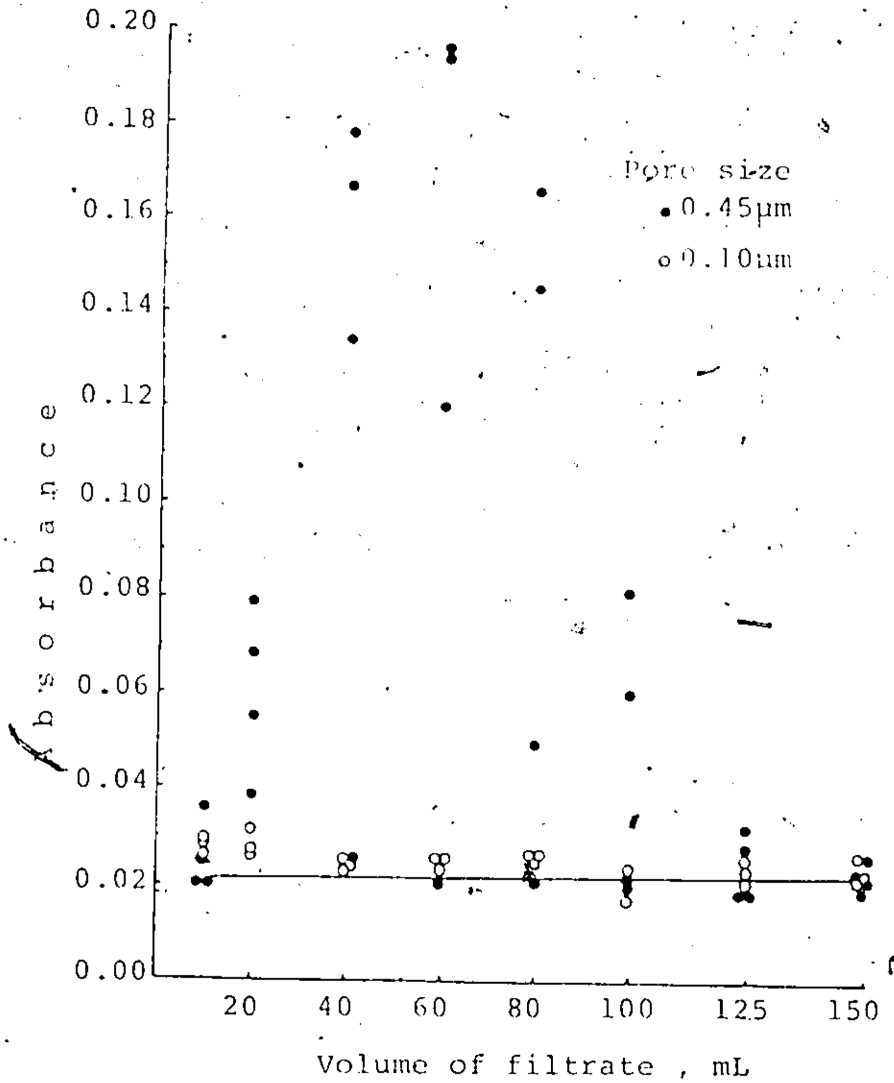


FIGURE 4.5 Filtrate absorbance of the aluminum-treated fulvic acid solution

Al concentration = 0.71×10^{-4} M

Initial fulvic acid concentration = 10.0 mg/L

pH = 6.02

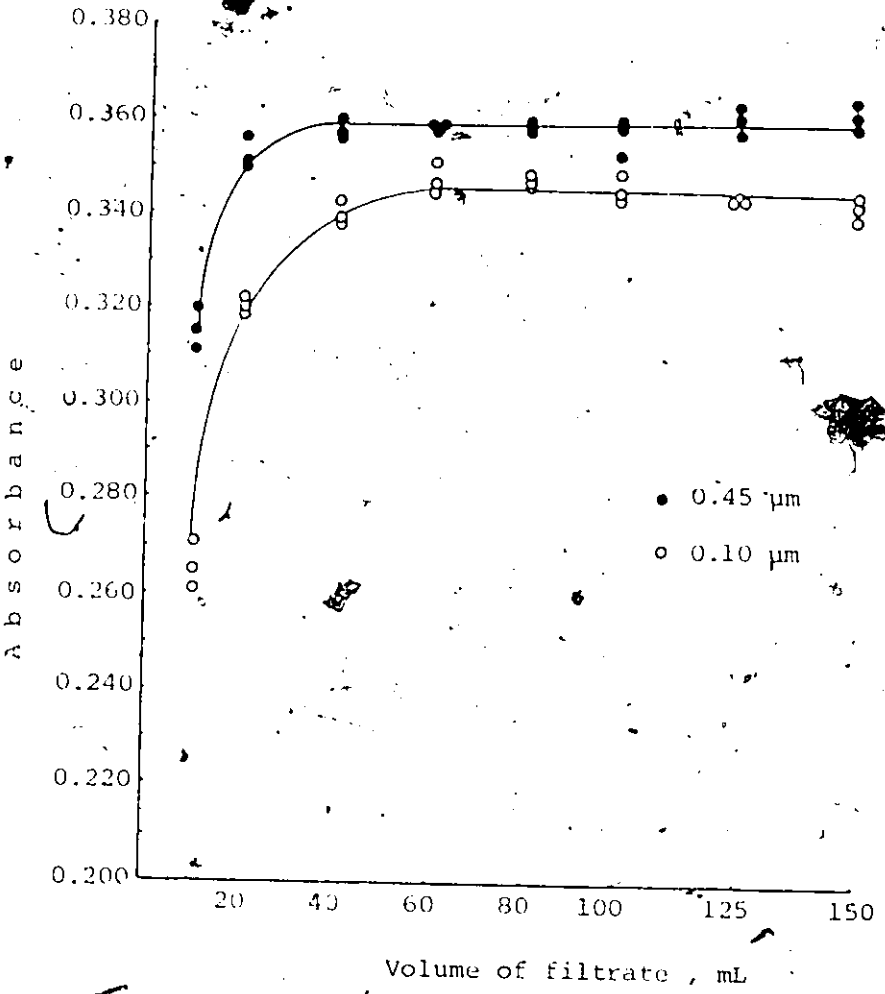


FIGURE 4.6 Filtrate absorbance of the aluminum-treated fulvic acid solution

Al concentration = 0.71×10^{-4} M

Initial fulvic acid concentration = 10.0 mg/L

pH = 7.97

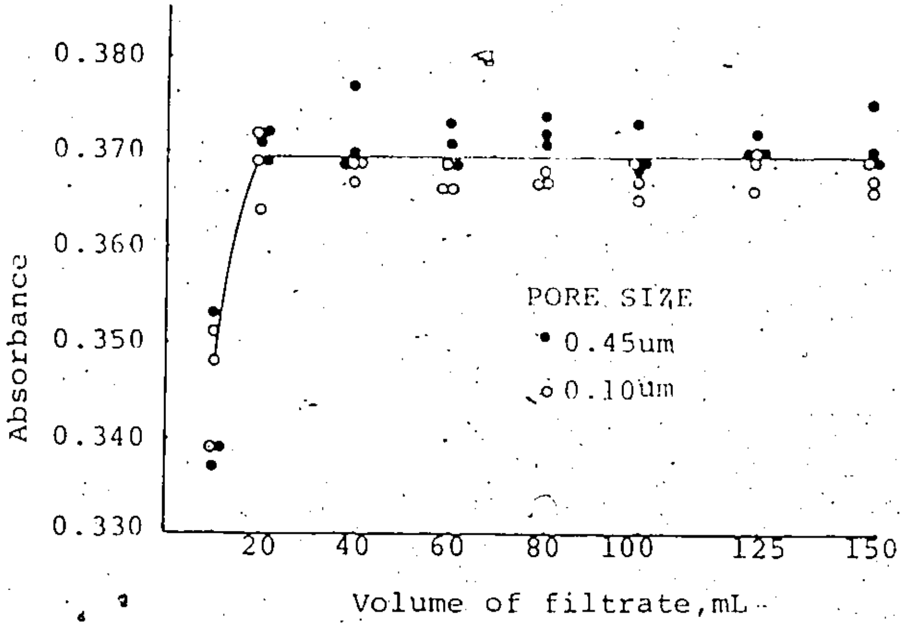


FIGURE 4.7 Filtrate absorbance of the aluminum-treated fulvic acid solution

Al concentration = 10^{-5} M

Initial fulvic acid concentration = 10.0 mg/L

pH = 6.04

These results demonstrate that the apparent effectiveness of the aluminum coagulants to remove fulvic acid from water depends on the capacity of the membrane filter to remove the solid precipitate from the water phase. Therefore the apparent effectiveness of the coagulants will depend on the particle size and the filter pore size. These points are demonstrated in Figure 4.8. There, the fulvic acid fraction which remained in solution is depicted as a function of pH for an aluminum dosage of 0.71 x 10^{-4} M. The fulvic acid fraction is shown in terms of both 0.45 µm and 0.10 µm pore size filters and for two aluminum coagulants, $AlCl_3$ and Alum ($Al_2(SO_4)_3$-16 H_2O). It should be mentioned that in these experiments, prior to obtaining 50 mL of the filtrate for analysis, 150 mL of distilled and deionized water and 100 mL of the aluminum-treated solution were filtered through each membrane. It can be seen that both coagulants demonstrated roughly similar efficiencies in removing fulvic acid. At pH 6 the amount of fulvic acid in the solution was minimal, accounting for less that five percent of the original concentration, while at pH 8 low removals were demonstrated, leaving in solution more than 90 percent of the initial fulvic acid. It is interesting, however, that when different types of filters were used, the removal patterns were also different. When the 0.45 µm filters were employed more fulvic acid remained in solution than when the 0.10 µm membranes were used. These differences account for up to 80 percent of the initial fulvic acid concentration at pH 7.

One can, therefore, conclude that the evaluation of the coagulants for practical purposes may be misleading due to artifacts induced by the filter pore size. Also, because of the particle size and pore size effects it does not seem always possible to interpret or model precipitation

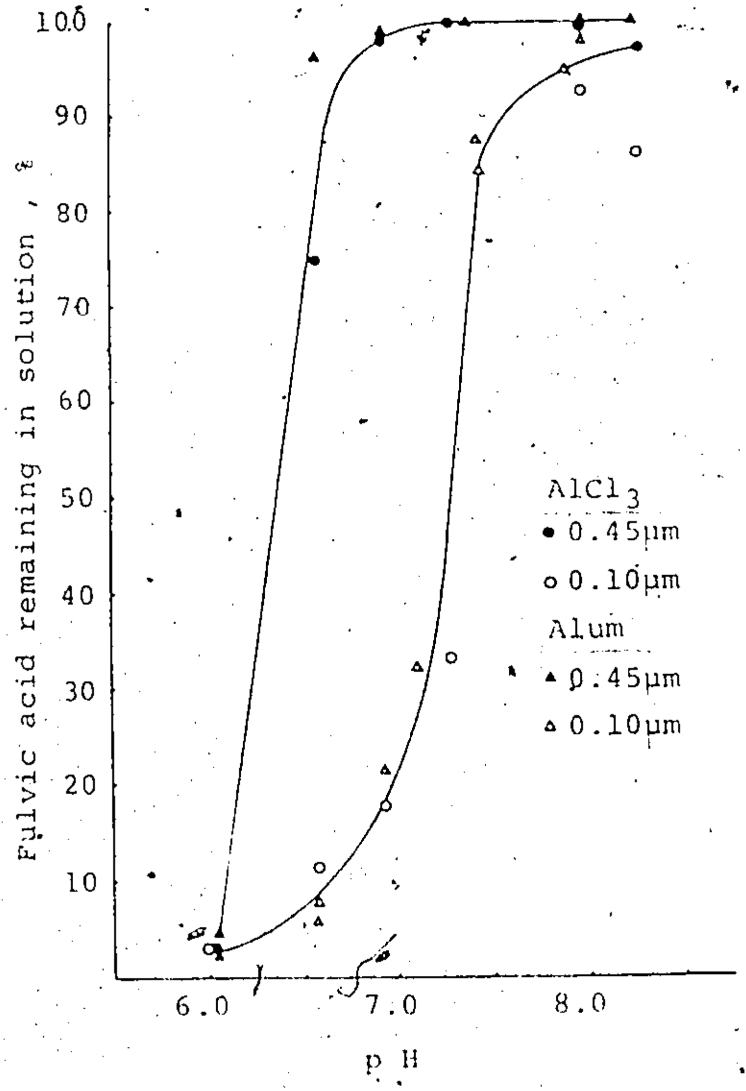


FIGURE 4.8 Efficiency of aluminum coagulants to remove fulvic acid from water

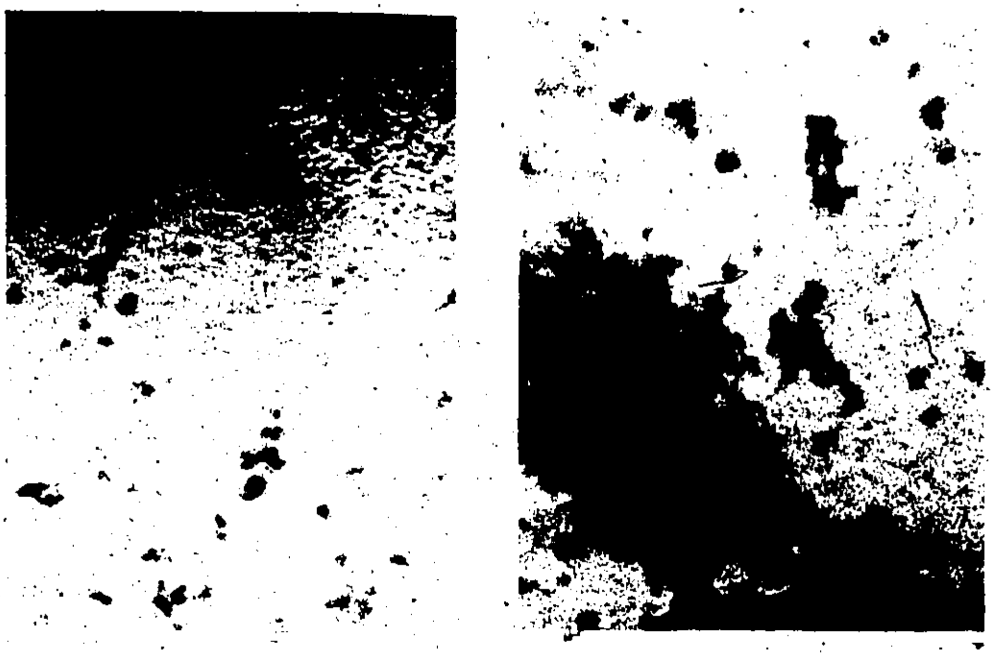
phenomena in terms of chemical equilibrium. In addition to these points, the deep-filter behavior demonstrated by the membrane filters make them impractical under the usual operating conditions to be used for particle sizing.

Finally, the aluminum-fulvic acid particles were examined under the Transmission Electron Microscope. Many small particles were found deposited on the grids with a size less than 0.1 μm (Figure 4.9a) along with agglomerates of small particles (Figure 4.9b). It is possible that some of these agglomerates were broken down during the course of filtration and this resulted in the increased levels of fulvic acid in the solution, especially in the first stages of filtration.

4.2 CONCLUSIONS

Based on the previous results the following conclusions can be drawn:

1. Membrane filters used for the separation of the precipitate from water initially leached some UV-absorbance-contributing substances into the solution. This may be significant for low level organics and therefore rinsing the filter with pure water prior to filtration is recommended.
2. When pure fulvic acid solutions were filtered through membrane filters, some organics were initially adsorbed on the filter, but the filtrate concentration rapidly rose to the original fulvic acid levels for both types of the filters tested.
3. When aluminum-treated fulvic acid solutions were filtered through membrane filters, the filtrate concentration depended on the filter pore size. In general, filters with a 0.10 μm pore size were able to remove more particles from water than were the 0.45 μm filters.



(a) (b)

FIGURE 4.9 Electron micrograph of aluminum-fulvic acid particles

Al concentration = 0.5×10^{-3} M

pH = 8.13

Differences of up to 80 percent of the original fulvic acid concentration were observed.

4. The 0.45 μm filters showed a deep-filter-like behavior for small particles. When little material was deposited on the filter and the filter pores were relatively clean, small particles, at times accounting for up to 80 percent of the original fulvic acid concentration, passed into the filtrate. After clogging of the pores occurred, the 0.45 μm filters were able to remove smaller particles. This did not happen, however, before at least 100 mL of the sample had been filtered.
5. Because of the deep-filter behavior of the 0.45 μm membrane filters, precipitate particle sizing and the evaluation of the efficiency of the coagulants to remove fulvic acid from water by means of membrane filters may at times be misleading.
6. There was negligible difference in the aluminum chloride and the aluminum sulfate removal for the pH range 6 to 8. The detrimental effect of sulfate as reported by Maulding and Harris (1968) and Bersillon (1983) was not observed in this study because the pH was higher than in these two studies.
7. Since all of the previously reported work used membrane filters (pore size ranged from 0.40 μm to 1.2 μm), glass fiber filters, paper filters, centrifugation or settling, great care is needed in interpreting and comparing the results.

CHAPTER FIVE

FULVIC ACID REMOVAL WITH ALUMINUM SALTS IN THE ABSENCE AND PRESENCE OF NONIONIC POLYACRYLAMIDE

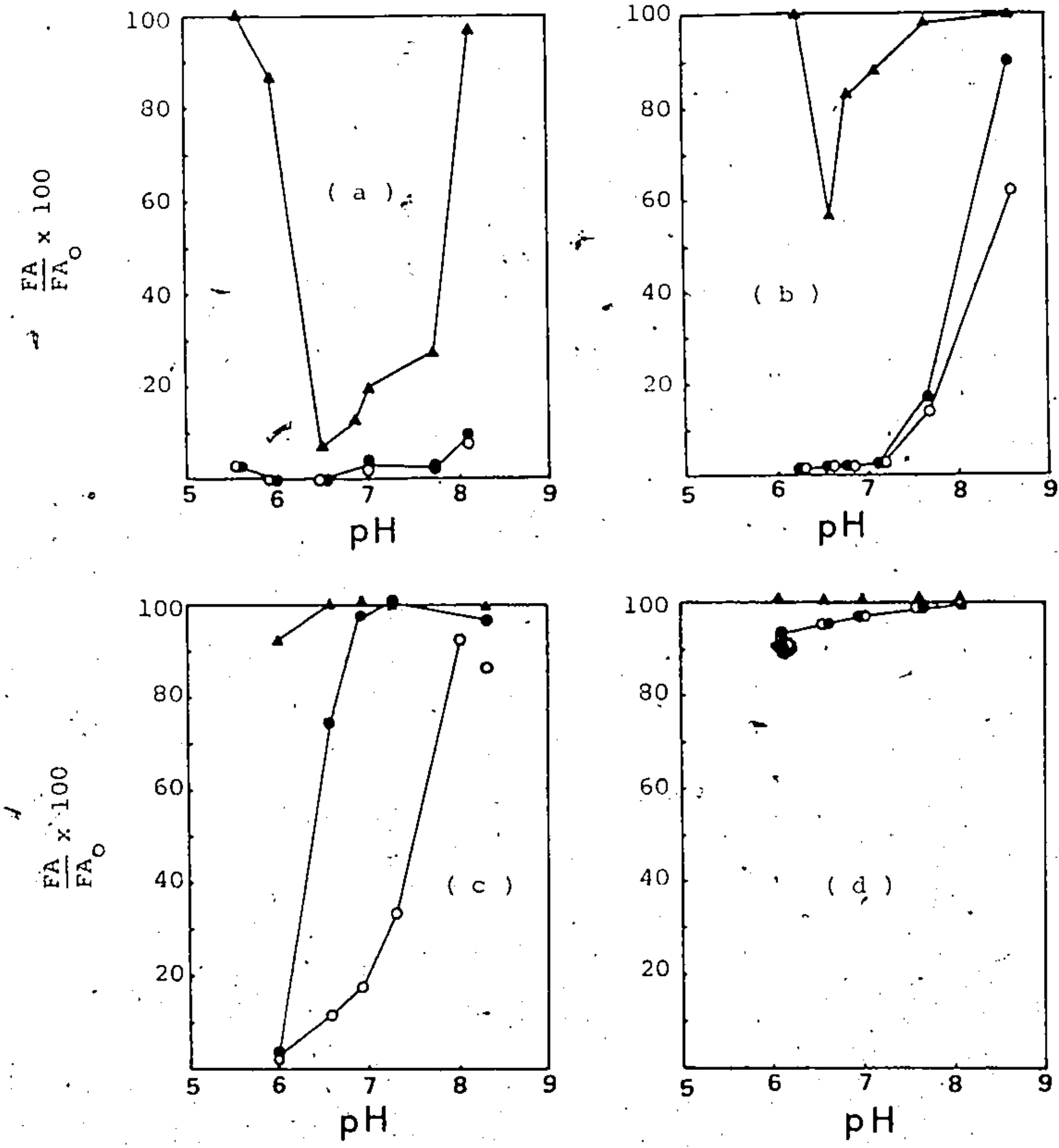
While the understanding of the removal of fulvic acid with aluminum is clouded by the unknown nature of the humic matter and the complexity of the water chemistry of aluminum, improvement of the coagulation process requires an understanding of the role of the polymeric flocculant. This section reports the removal of fulvic acid from water by aluminum in the absence and presence of nonionic polyacrylamide. The objectives of this work were:

1. to examine whether there are differences in the removal efficiencies of two aluminum salts, namely aluminum chloride and aluminum sulfate, in terms of removals as measured by filtration and by settling.
2. to investigate whether removal data (due to filtration or settling) correlate with turbidity data, and
3. to investigate how the presence of nonionic polyacrylamide of various concentrations affects the removal efficiency of alum.

5.1 RESULTS AND DISCUSSION

5.1.1 Effect of aluminum addition

Figure 5.1 shows the percentage fulvic acid which remains in solution (as measured by the percentage reduction in the absorbance)



▲ Settleable fulvic acid

Filterable fulvic acid
○ 0.10 µm pore size
● 0.45 µm pore size

(a) 0.5×10^{-3} M (b) 0.188×10^{-3} M (c) 0.71×10^{-4} M (d) 10^{-5} M

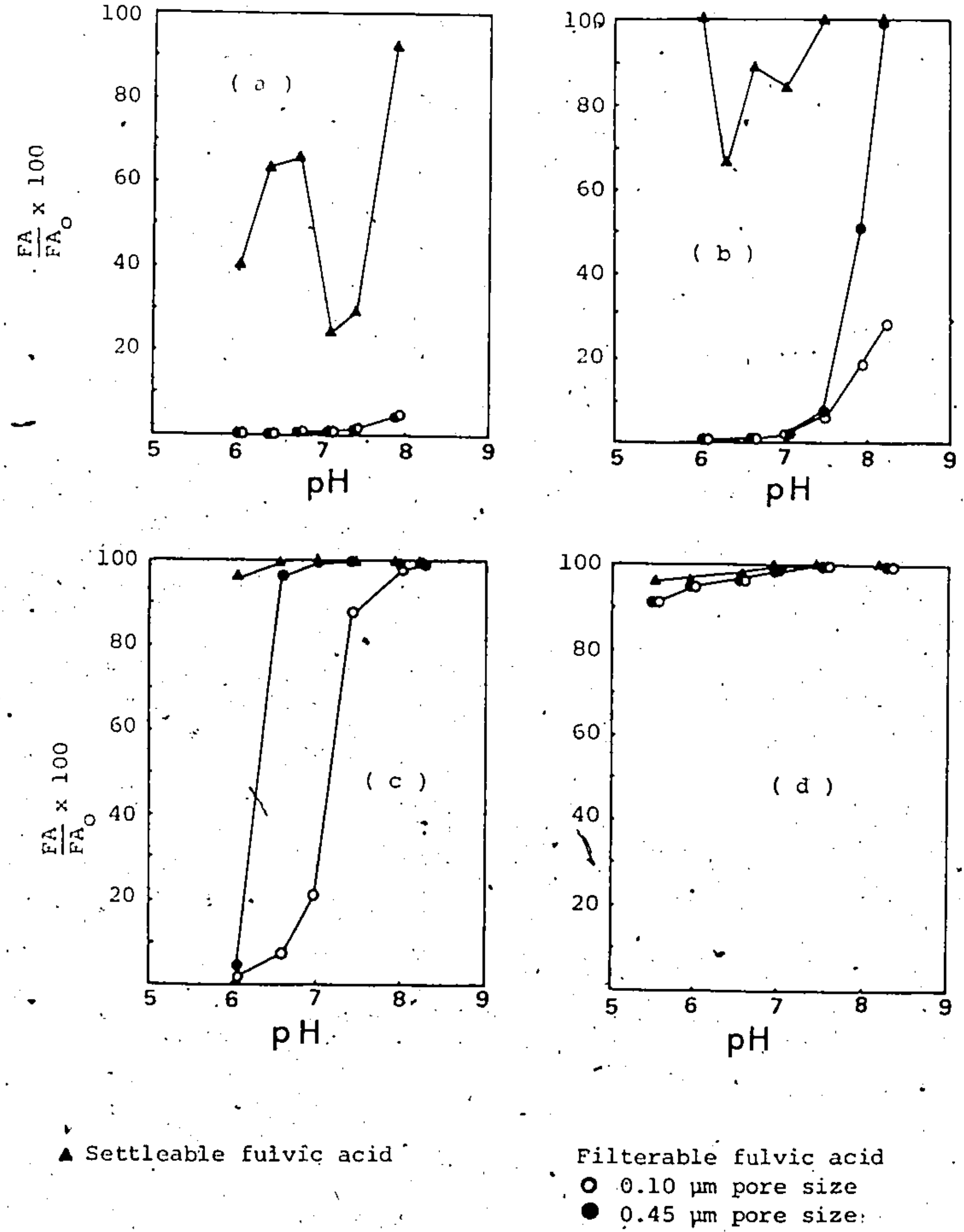
FIGURE 5.1 Fulvic acid remaining in solution after the addition of aluminum chloride after the addition of aluminum chloride. Four aluminum dosages were employed: 0.5×10^{-3} M, 0.188×10^{-3} M, 0.71×10^{-4} M and 10^{-5} M. Each graph shows the fulvic acid level after filtration through 0.45 μm and 0.10 μm pore-size membrane filters, as well as the fulvic acid remaining in solution after 20 min of settling.

The fulvic acid which remained in solution depended on both the aluminum concentration and the pH. As can be seen in Figure 5.1 removals (after filtration) of 100 percent were observed for the highest aluminum dosage (0.5×10^{-3} M) and slightly acidic pH (6.0-6.5). This pH was also very favourable for the removal of fulvic acid when lower aluminum doses were also used (0.188×10^{-3} M and 0.71×10^{-4} M). In these two cases (Figures 5.1b and 5.1c) the percentage fulvic acid remaining in solution was less than five percent of the original fulvic acid level. With increasing pH, the residual fulvic acid concentration increased as well. High aluminum dosages, however, resulted in higher removals even at elevated pH values. For the three higher aluminum doses and a pH of 7.5, the fulvic acid which remained in solution was 3, 10 and 50 percent respectively (for 0.10 μm pore-size filters). When the lowest aluminum dose was employed (Figures 5.1d), the same trends were observed. Removal of fulvic acid at pH 6 was higher than at pH 8. In this case, however, the fulvic acid which remained in solution even at pH 6 was more than 90 percent of the initial concentration.

Another point discernible from Figure 5.1 is that certain differences exist at the filterable fulvic acid levels when the filtration was performed with filters of different pore-size (namely 0.45 μm and 0.10 μm). These differences are not large at the highest or lowest aluminum concentrations or at pH 6 (favourable pH for fulvic acid removal), but they become very important at the intermediate aluminum doses and the higher pH values. For an alumium dosage of 0.71 x 10^{-4} M and a pH of 7, the difference in fulvic acid concentration remaining in solution was as high as 80 percent of the original fulvic acid level (Figure 5.1c). These differences may be attributed to the fact that a large portion of the particles had a size range within the pore size of the membrane filters. These particles can pass through the pores of the 0.45 μm filters, while they can be retained on the 0.10 μm filters. As was mentioned in Chapter 4 the particle size effects were also observed at pH values around 6, at the highest aluminum dose, but the formation of a filter cake after the filtration of 100 mL of aluminum-treated solution seemed to eliminate any differences in the performance of the two types of filters. While high removals due to filtration were observed, particularly around pH 6, the settling of the flocs was very slow. Only for the highest aluminum dose and for the pH range from 6.5 to 7.5 the fulvic acid remaining in solution was less than 25 percent (Figures 5.1a). For all other aluminum concentrations removals due to settling were very low or zero, with the highest one being 50 percent at pH 6.5 for an aluminum dose of 0.188 x 10^{-3} M. It can also be seen that the pH region for the highest removal due to settling (6.5 - 7.5) did not coincide with the pH region most favourable for the removal due to filtration (pH less than 6.5). This is in contrast to what happens in the removal of phosphates with aluminum, where the same pH was favourable for highest removals due to both filtration and settling (Diamadopoulos, 1981). In a system that solely involves a complexation mechanism, such as the phosphate-aluminum system, the most efficient pH for the removal after both filtration and settling will be the one where the combined charges of the ionic species on the particle yield a zero overall charge. In the presence of fulvic acid stabilization of the particles at pH 6 may occur as a result of the adsorption of the negatively charged fulvic acid molecules on either the aluminum fulvate or the aluminum hydroxide or both. Stabilization of the particles due to adsorption of charged aluminum species was postulated to have taken place at pH less than 6 in a study by Mangravite et al. (1975).

The effect of aluminum sulfate on the removal of fulvic acid from water is shown in Figure 5.2. With respect to the filterable fulvic acid concentration, aluminum sulfate and aluminum chloride demonstrated similar efficiencies. The most favourable pH was 6 and lowering of the aluminum dosage resulted in increased fulvic acid concentrations in solutions. Similar differences for the two types of membrane filters were observed in the aluminum sulfate case (Figure 5.2c). Here again membrane filters with a 0.10 μm pore size were more efficient in separating the solid from the liquid phase than were the 0.45 μm filters. The differences in fulvic acid concentration at pH 7.0 is also around 80 percent of the initial fulvic acid level. In general it can be concluded that under these conditions the presence of sulfate had no significant influence on the "filtration" efficiency of aluminum to remove fulvic acid from water. This is in agreement with similar findings by Bersillon (1983) on a natural water. It can be expected, therefore, that alum being the most inexpensive aluminum coagulant in North America will remain in wide use.

Some differences, however, existed in the settling of the flocs primarily at high aluminum concentrations (0.5×10^{-3} M). While 80 percent of the particles remained in suspension at pH 6 for the aluminum



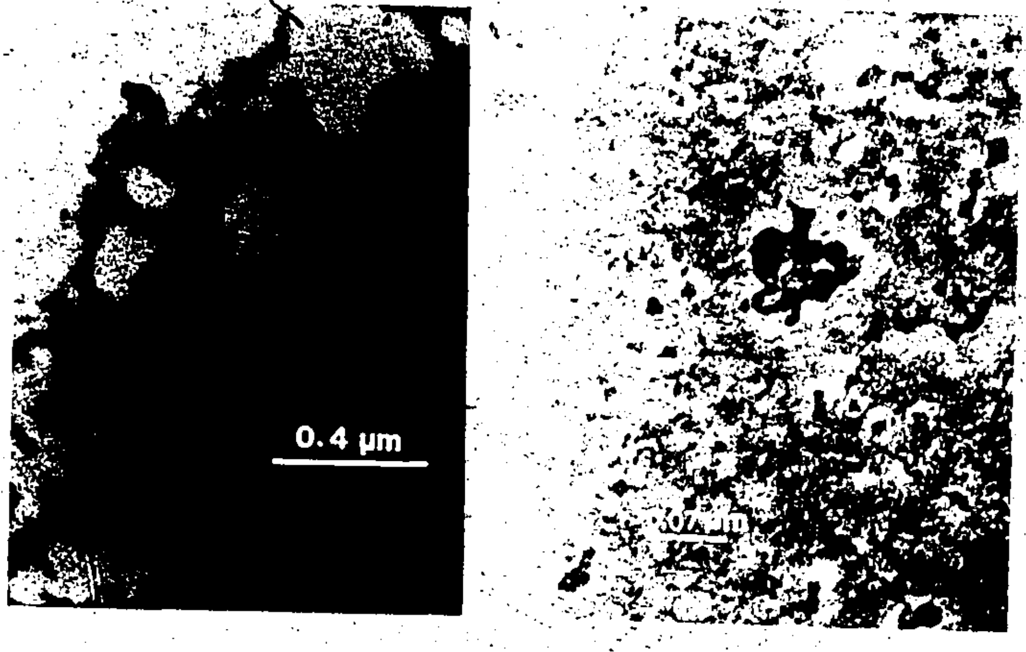
(a) 0.5×10^{-3} M (b) 0.188×10^{-3} M (c) 0.71×10^{-4} M (d) 10^{-5} M

FIGURE 5.2 Fulvic acid remaining in solution after the addition of aluminum sulfate (alum) chloride case (Figure 5.1a) only 40 percent of the initial fulvic acid remained in solution at the same pH when alum was used (Figure 5.2a). In addition to this, some restabilization of the particles occurred between pH 6 and 7 for the alum case. Particle stabilization, as was mentioned before, depends on the overall charge as a result of the individual charges of the ionic species which interact through reaction or adsorption. The sulfate ion can adsorb on aluminum hydroxide (DeHek et al., 1978) and depending on its concentration it can affect the settling of the particles through stabilization (Hayden and Rubin, 1976).

To investigate further the poor settleability of the aluminum-fulvic acid flocs, particles were examined under the electron microscope. The particles were found to contain a great deal of void space (Figure 5.3a) and some of the particles had sizes well below 0.5 μm (Figure 5.3b). These low-density, small-size particles do not settle very fast. This explains why, while the removal after filtration can be as high as 100 percent, the removal after settling is in general very low. Removals after settling higher than 50 percent were obtained only for the high aluminum dosage (0.5×10^{-3}M). In that case, the use of a large dosage of aluminum resulted in the formation of a large quantity of aluminum hydroxide and therefore in higher settling rates.

5.1.3 Turbidity measurements

It would be experimentally attractive if a measurement of turbidity could be a sensitive enough record of the coagulation/flocculation occurring. This would mean that on-line analysis and tracking of the process would be possible. Indeed, previous researchers used turbidity measurements to study the stabilization domain of colloidal particles coagulated with different aluminum salts (Rubin and Kovac, 1974) and



(a)   (b)

FIGURE 5.3 Electron micrographs of aluminum-fulvic acid particles

Aluminum concentration = 0.71×10^{-4} M

pH = 6.0

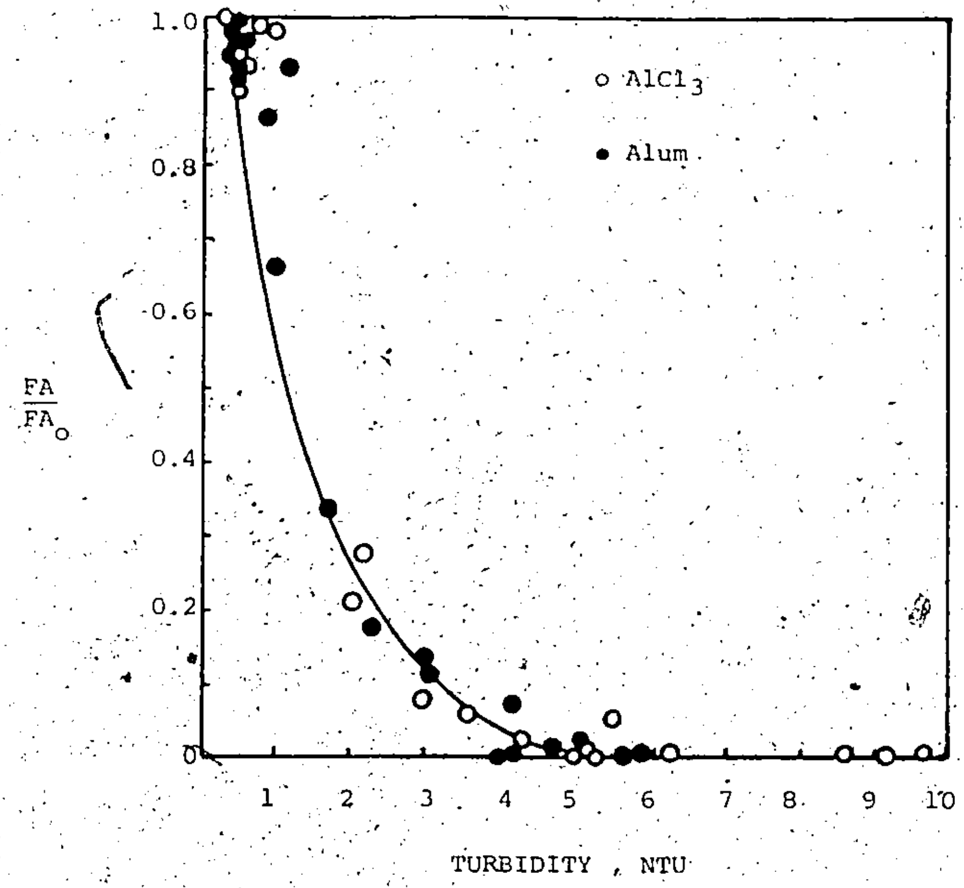


FIGURE 5.5 Fulvic acid remaining in solution after filtration through 0.10 μm filters as a function of the turbidity of the unsettled suspension

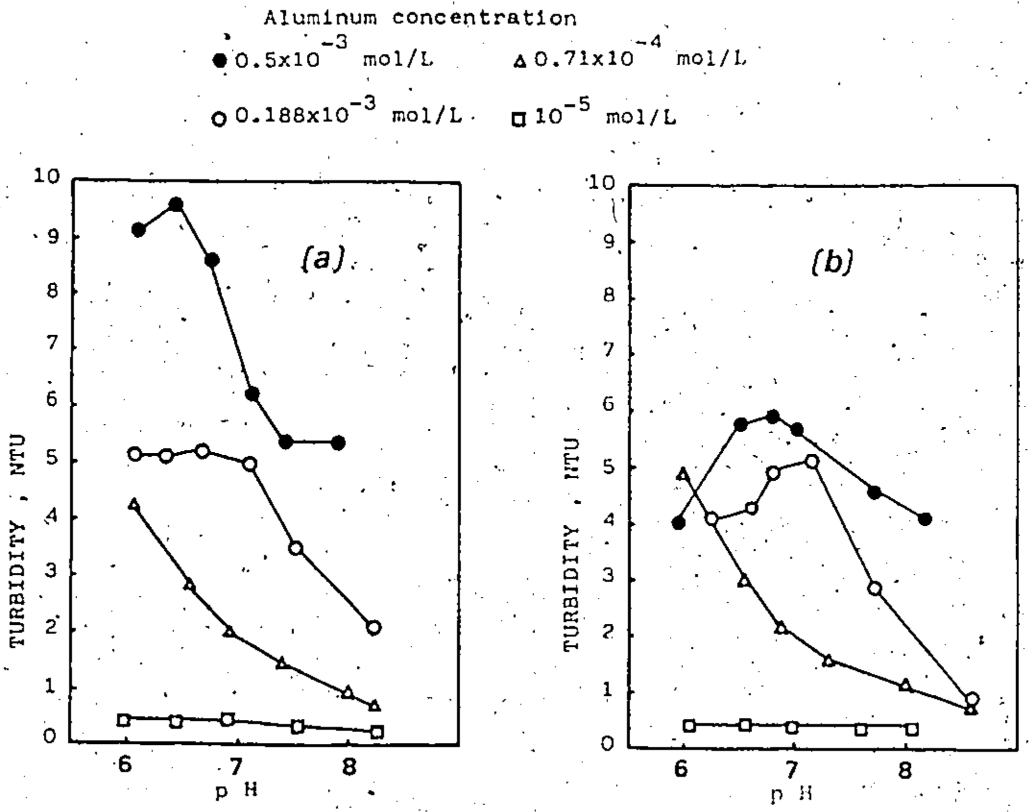


FIGURE 5.4 Turbidity of the aluminum-treated fulvic acid solution before settling

(a) Aluminum sulfate (b) Aluminum chloride

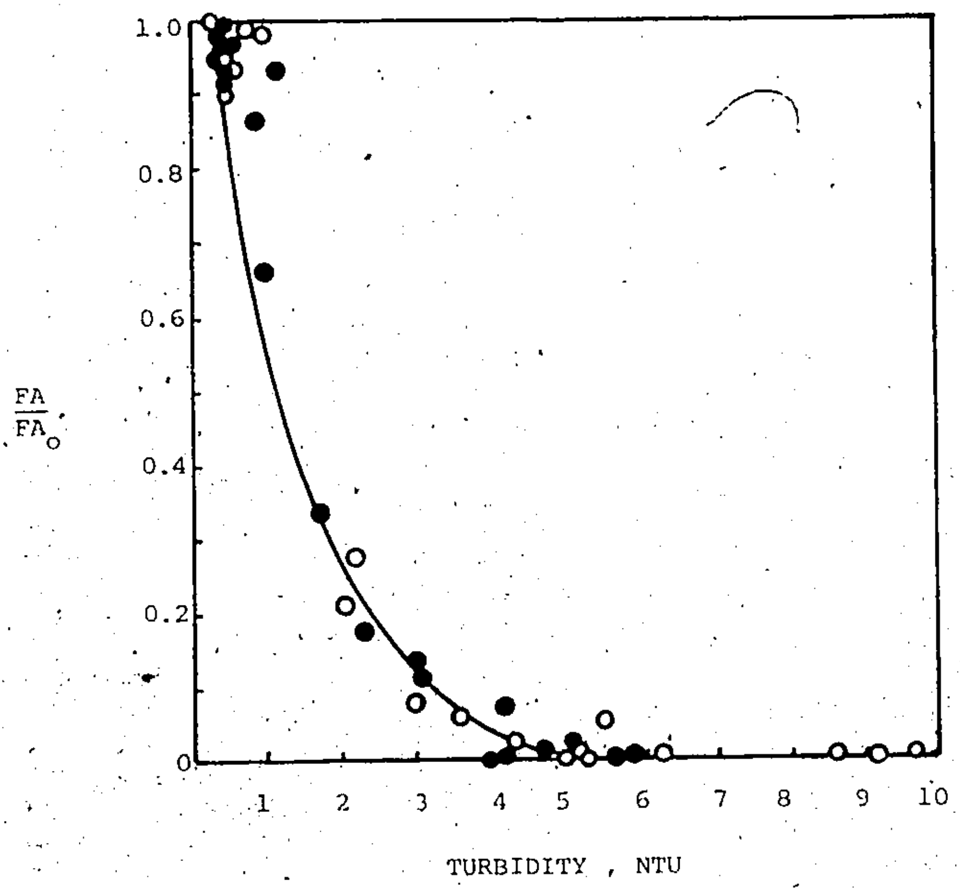


FIGURE 5.5 Fulvic acid remaining in solution after filtration through 0.10 μm filters as a function of the turbidity of the unsettled suspension

TABLE 5.1 Parameter estimates for the exponential decay model

Aluminum source	$AlCl_3$	Alum	Both
b_0	-0.31	-0.28	-0.29
b_1	0.87	0.78	0.82
Residual Sum of Squares	0.010	0.069	0.081
Correlation Coefficient	-0.82	-0.78	-0.80

the parameters b_0 and b_1 for the two aluminum salts. It is also important to note that the data points shown in Figure 5.5 were obtained at different pH values and aluminum concentrations. This means that the correlation found does not depend on the pH or the aluminum concentration. Therefore such a correlation may be used to monitor or control the removal of fulvic acid with aluminum at least in low turbidity waters. No correlation was found between the removal of fulvic acid after settling and the turbidity before settling. Equally unsuccessful was an attempt to relate refiltration-time measurements with removals after filtration or settling.

5.1.3 Effect of polymer addition

Removal After Settling

The rest of this study deals with the removal of fulvic acid from water by means of alum in the presence of nonionic polyacrylamide. Figure 5.6 shows the percentage fulvic acid remaining in solution after settling for an aluminum dose of 0.5×10^{-3}M and a polymer concentration of 0, 0.01 and 0.1 mg/L. The three curves exhibit the same general trends. Settling is less effective within pH 6.2 and 7.0 as well as above pH 7.5. The addition of the polymer improved the settling of the flocs. This improvement, however, was better at around pH 6.5. The fulvic acid which remained in solution at pH 6.5 in the presence of 0.1 mg/L polymer was approximately half of the fulvic acid level in the absence of the polymer. A smaller amount of polymer (0.01 mg/L) resulted in a smaller improvement; the fulvic acid concentration remaining in water was reduced to 50 percent of the initial concentration in the presence of 0.01 mg/L polymer from 65 percent in the absence of polymer. In the pH region between 7 and 8 the improvement was not

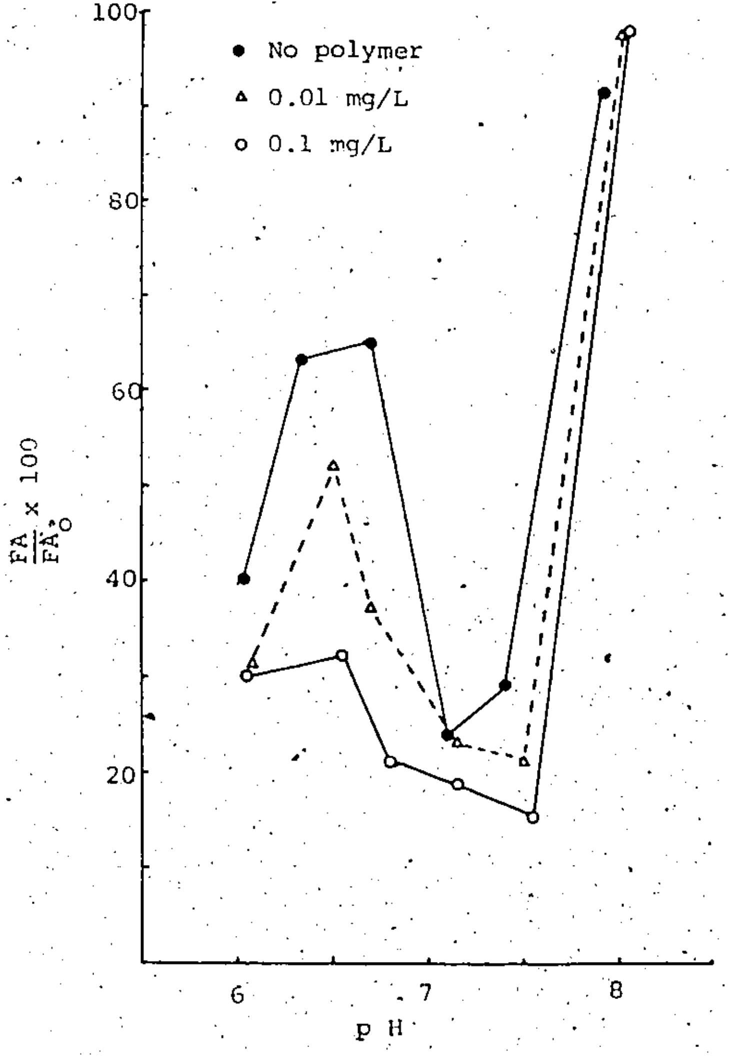


FIGURE 5.6 Fulvic acid remaining in solution after 20min of settling

Aluminum concentration = 0.5×10^{-3} M

very significant: about 15 percent improvement occurred. For a lower aluminum dosage (0.188 x 10^{-3} M) the presence of the polymer also enhanced the settling of the flocs (Figure 5.7). The highest polymer concentration of 0.1 mg/L resulted in great improvement while a polymer level of 0.01 mg/L polymer did not have any significant effect on the settling. The improvement demonstrated in the presence of 0.1 mg/L polymer occurred over the entire pH range studied, and it was more important at pH 7. While in the absence of polymer 85 percent of the initial fulvic acid remained in solution at pH 7.0, the addition of 0.1 mg/L polymer resulted in a residual fulvic acid level of 40 percent of the initial concentration.

For an aluminum dosage of 0.71 x 10^{-4} M the presence of polymer did not have any significant effect (Figure 5.8). The largest improvement was around 15 percent, and it occurred at pH 6 for 0.1 mg/L polymer.

Removal After Filtration

The presence of polymer had no noticeable effect on the filterable fulvic acid concentration for an aluminum dosage of 0.5 x 10^{-3} M (Figure 5.9). This was expected since for this aluminum dosage practically all the fulvic acid had been removed from solution. The presence of the polymer becomes more significant at lower aluminum dosages and pH values higher than 7. Figure 5.10 shows that the presence of polymer resulted in lower fulvic acid concentrations at slightly alkaline pH for an aluminum concentration of 0.188 x 10^{-3} M. Even better improvements were obtained when the aluminum dose was 0.71 x 10^{-4} M. Figure 5.11 shows the fulvic acid remaining in solution after filtration through 0.45 μm pore-size filters. For pH 7 and for polymer levels of 0.01 and 0.1 mg/L, the filterable fulvic acid concentration was reduced by 35 and 94 percent

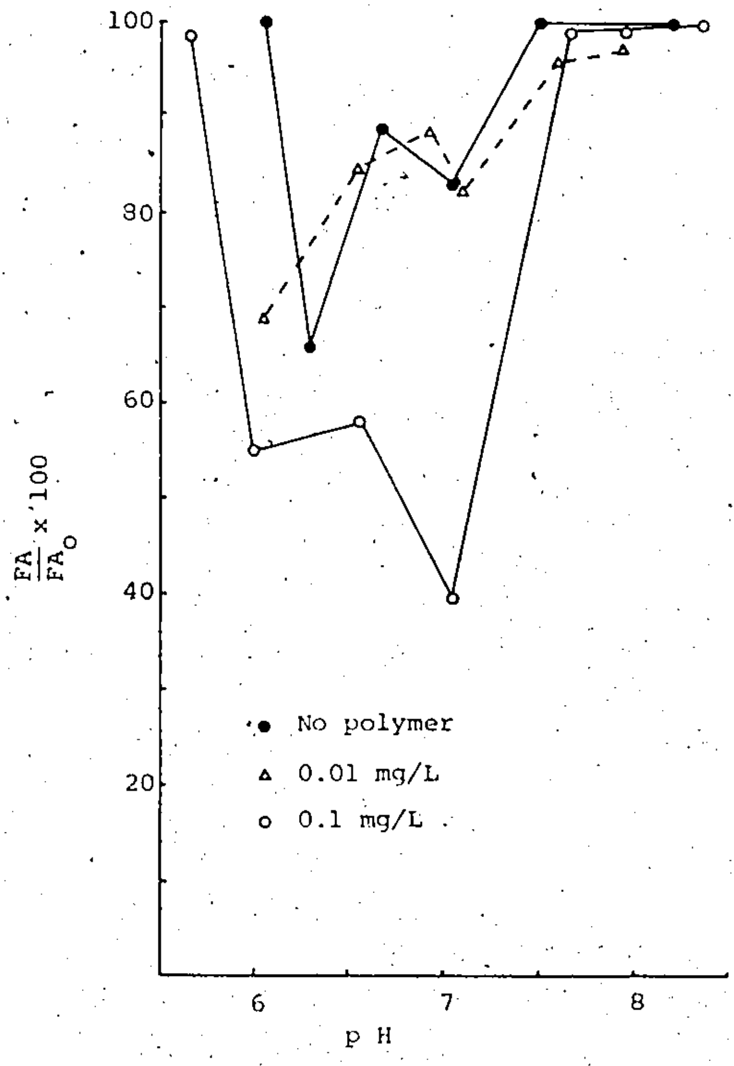


FIGURE 5.7 Fulvic acid remaining in solution after 20min of settling

Aluminum concentration = 0.188×10^{-3} M

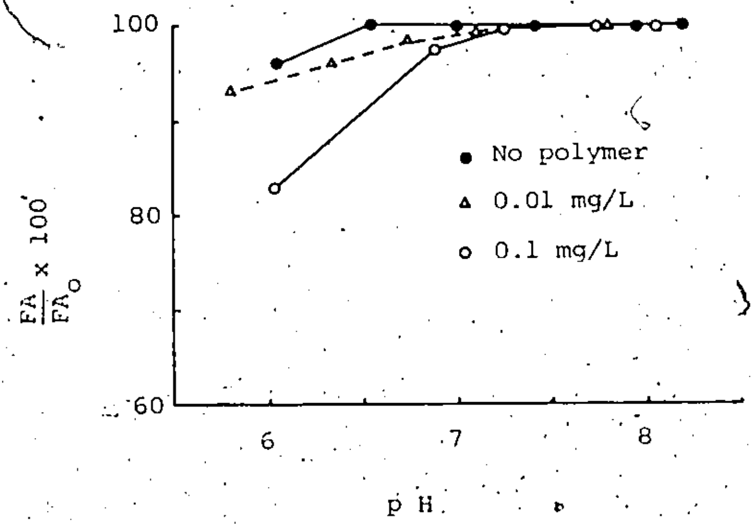


FIGURE 5.8 Fulvic acid remaining in solution after 20min of settling

Aluminum concentration = 0.71×10^{-4} M

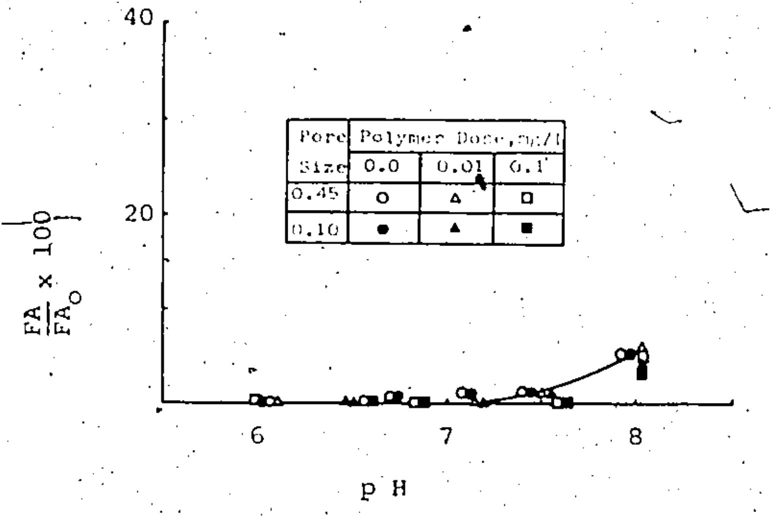


FIGURE 5.9 Fulvic acid remaining in solution after filtration

Aluminum concentration = 0.5×10^{-3} M

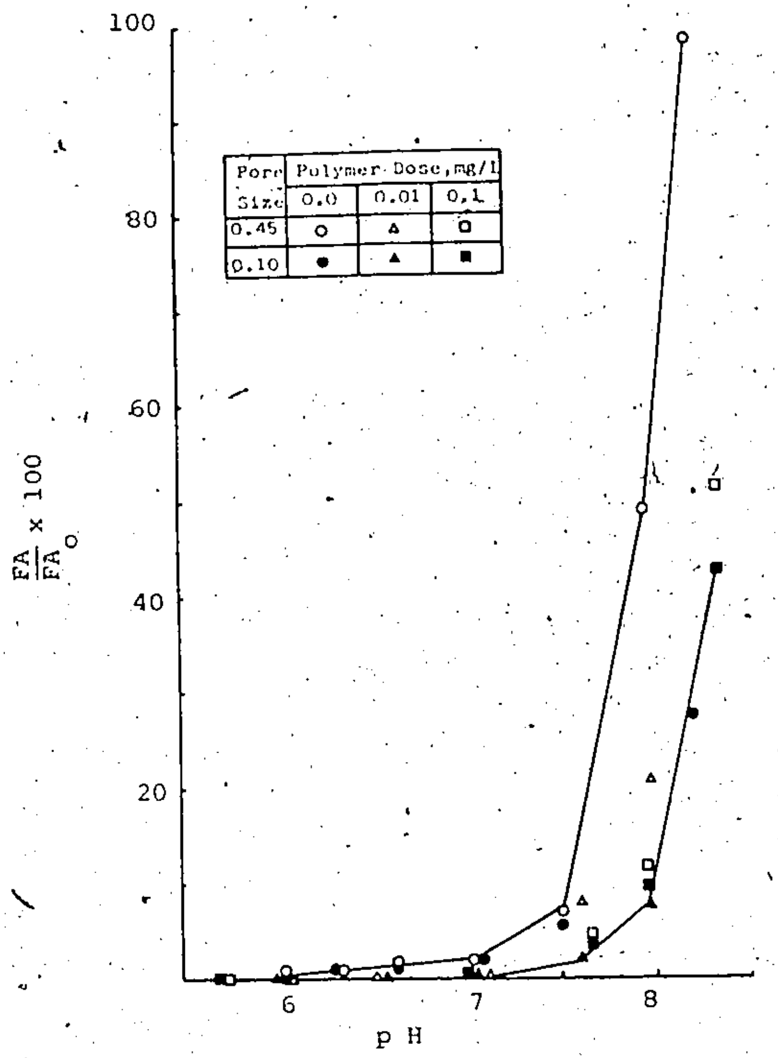


FIGURE 5.10 Fulvic acid remaining in solution after filtration

Aluminum concentration = 0.188×10^{-3} M

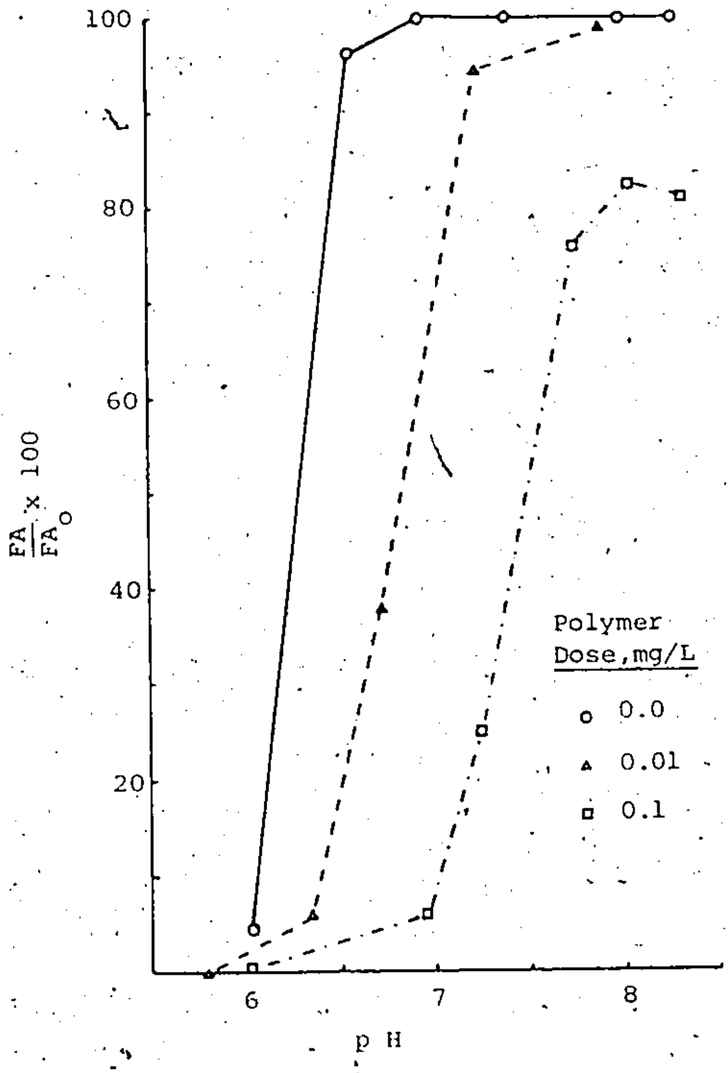


FIGURE 5.11 Fulvic acid remaining in solution after filtration

Aluminum concentration = 0.71×10^{-4} M

Filter pore size = 0.45 μm

respectively. Marked improvements were also observed when 0.1 µm filters were used for the solid-liquid separation (Figure 5.12). Although the presence of 0.01 mg/L polymer was not very beneficial, when the polymer dose was increased to 0.1 mg/L it resulted in further removal of fulvic acid from the water. One might try to identify the role of the polymer. Did the polymer flocculate the aluminum-fulvic acid particles and thus increase their size? or did the polymer adsorb onto the filter to serve as a precoat? To test the latter hypothesis, the polymer solution was filtered prior to the filtration of the aluminun-only-treated fulvic acid solution. Thus, by this action, the polymer was given a chance to precoat the filter. This polymer-treated filter was then used to filter an alum-fulvic acid solution (aluminum concentration 0.71×10^{-4} M). Negligible differences were obtained between the filtrate from this experiment and the filtrate obtained by filtering with untreated filter (Figure 5.2c). In a screening test, the ability of the nonionic polymer to remove fulvic acid was checked. In the absence of aluminum the polymer itself did not remove any fulvic acid from water. Hence it is concluded that the polymer brings together, by flocculation, the particles that are small enough to pass through the pores of the filter. This is further substantiated by comparison of the settling data and the filtration data. In this way the polymer not only promotes the settling of the flocs, but it also lowers the filterable fulvic acid concentration. This enhancement of the removal due to filtration can also be seen in Figure 5.13, where the filterable fulvic acid level has been plotted as a function of pH in the absence and presence of 0.1 mg/L polymer. Not only was much more fulvic acid removed from solution in the presence of polymer for both types of membrane filters, but even the fraction of the aluminum-fulvic

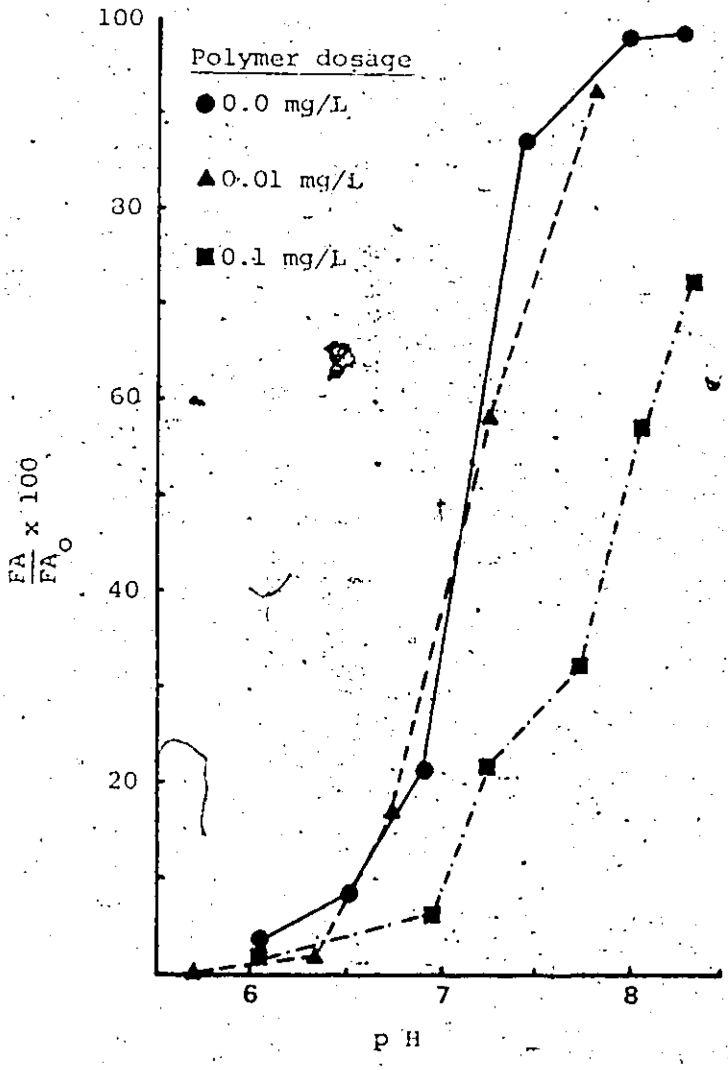


FIGURE 5.12 Fulvic acid remaining in solution after filtration

Filter pore size = 0.10 um

Aluminum concentration = $0.71x10^{-4}$ M

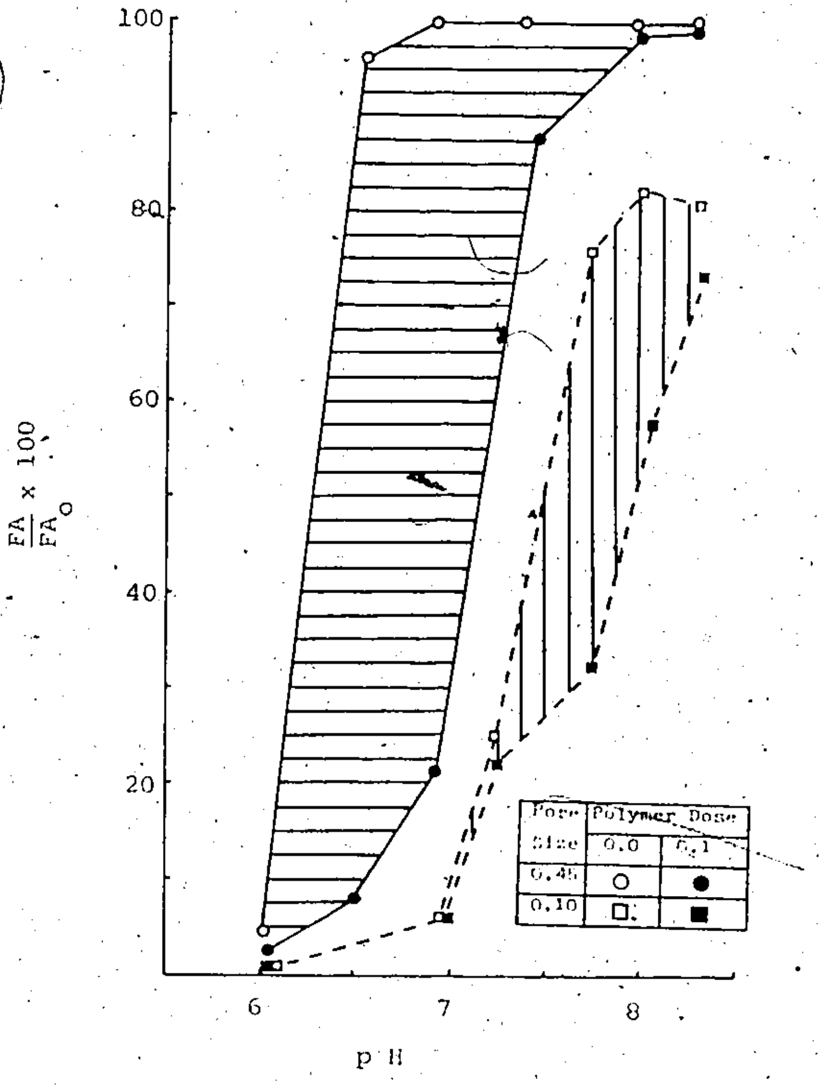


FIGURE 5.13 Fulvic acid remaining in solution after filtration

Aluminum concentration = 0.71×10^{-4} M

acid particles with approximate size between 0.45 μm and 0.10 μm became narrower in the presence of the polymer. It is apparent that in the ideal case where all these particles are removed from solution, the two curves will coincide.

Finally, for the lowest aluminum dosage of 10^{-5}M the presence of polymer had no noticeable effect on the filterable fulvic acid concentration. (Figure 5.14).

Although a study of the mechanism of the removal of fulvic acid with aluminum was outside the scope of this work, an interpretation of the observed trends and results is attempted below. It is believed that for the experimental conditions of this work, adsorption of fulvic acid molecules on the newly-formed aluminum hydroxide or aluminum fulvate (although we cannot operationally distinguish between these two solids) played an important role. There are two findings that provide evidence for this: first, the fact that the optimum pH for the removal after settling was different from the optimum pH for the removal after filtration, and second, the observed differences in the removal of fulvic acid when filters with different pore sizes were used. This latter finding indicates that a particle-size effect occurred particularly at intermediate aluminum concentrations. At intermediate aluminum to fulvic acid ratios, adsorption of fulvic acid molecules on the formed particles inhibits their growth to sizes removable by the 0.45 μm filters. This inhibition of growth is postulated to be similar to the inhibition of growth of iron hydroxide particles in natural waters which results in measurements of "soluble" iron higher than those predicted by equilibrium (Mill 1980). The added polymer interacts with the micro-colloidal aluminum-fulvic acid particles and not with the fulvic acid itself. In the presence of the

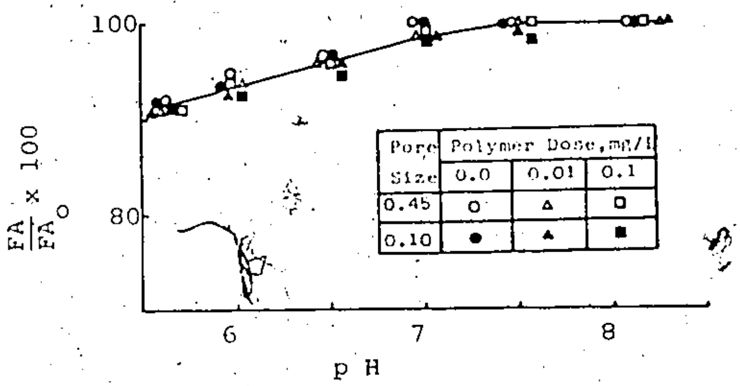


FIGURE 5.14 Fulvic acid remaining in solution after filtration

Aluminum concentration = 10^{-5} M

polymer, the size of the particles increases due to flocculation and therefore higher separation by filtration is achieved. This interaction between the polymer and the micro-colloidal particles may be the reason that in the presence of aluminum all types of polymer-cationic, anionic, nonionic- promoted the removal of humic matter from water (Edzwald et al. 1977). It may also explain why the effect of the polymer is larger at intermediate aluminum concentrations, such as 0.71×10^{-4} M, than at higher aluminum concentrations. When the aluminum concentration increases, coagulation and sweep-zone precipitation of the micro-colloidal particles by the additional aluminum species results in higher removals and consequently in lower flocculating efficiency of the polymer.

Since the polymer is most beneficial at intermediate aluminum concentrations, it is possible that, by adding small quantities of polymer, desired levels of removal may be achieved at aluminum dosages smaller than those required in the absence of the polymer. This may lead to an optimized combination of aluminum and polymer concentrations that results in desired removals with the minimum cost of chemicals. In addition to this, further optimization of the process may be possible by finding the optimum polymer properties, such as molar mass and degree of hydrolysis. These considerations will be dealt with in the following chapters.

5-2 CONCLUSIONS

For the conditions studied in this work the following conclusions can be drawn:

1. The aluminum dosage and the pH were the most important variables affecting the removal of fulvic acid from water. The more aluminum added to the water, the higher the removal of fulvic acid. Slightly

acidic pH values (around 6) aided the removal of fulvic acid. Complete removal of fulvic acid can be achieved, but aluminum dosages as high as 0.5×10^{-3}M (about 13 mg/L A) and pH 6 are necessary.

2. Differences exist in the separation efficiencies of membrane filters of varying pore size. Filters with 0.10 μm pore size were in general more efficient than were the 0.45 μm filters. These differences became significant at intermediate aluminum concentrations (0.71×10^{-4}M).
3. Aluminum chloride and aluminum sulfate (alum) demonstrated similar efficiencies in terms of filterable fulvic acid remaining in solution. This is in partial agreement with the findings by Bersillon (1983) who reported that while the presence of the sulfate ion resulted in deterioration of the removal by approximately 2 removal percentage points at pH 6, no noticeable difference was observed at higher pH values.
4. Settling of the flocs was very slow. Only in the case of the highest aluminum concentration (0.5×10^{-3} M) the settleable portion of the treated fulvic acid exceeded 50 percent of the initial concentration.
5. The optimum pH when removal was measured by filtration was different from the optimum pH when removal was measured by settling.
6. Some differences existed in the settling of the flocs when different aluminum salts were used. Partial stabilization of the particles was postulated to have occurred between pH 6 and 7 in the presence of the sulfate ion. Similar effects of the sulfate ion have also been reported by Hayden and Rubin (1976).
7. The turbidity of the treated unsettled solution depended on the

aluminum concentration and the pH. The fulvic acid remaining in solution after filtration was found to correlate well with the turbidity before settling. An exponential decay model was fitted to the data. It is therefore possible that the turbidity before settling be used to monitor or control the removal after filtration.

8. The presence of the nonionic polyacrylamide enhanced the settling of the particles, particularly when poor settling had been observed. The higher the polymer dosage, the higher the removal due to settling.
9. In the presence of the polymer the filterable fulvic acid concentration was reduced even further, particularly when intermediate aluminum dosages were used. This was attributed to the flocculation of the micro-colloidal particles which, in the absence of the polymer, pass through the pores of the filter.
10. In the presence of the polymer the pH range for effective removal of fulvic acid by filtration was extended towards higher pH values. This agrees with the previous observations by Edzwald et al. (1977).

CHAPTER SIX

MODELLING THE REMOVAL OF FULVIC ACID FROM WATER WITH ALUMINUM

This chapter presents the application of the modelling technique developed in section 3.5 of this thesis. Because of the empirical nature of the technique, two criteria for removal are used, removal after filtration and removal after settling. In addition, two aluminum salts have been studied, aluminum chloride and aluminum sulfate (alum).

6.1 RESULTS AND DISCUSSION

6.1.1 Removal after filtration

The quadratic model of the removal after filtration was tested first for the region defined by pH values ranging from 6 to 8 and aluminum concentration from 0.71×10^{-4} M to 0.5×10^{-3} M. No transformation of the observations was performed. The estimated values of the model parameters for the removal by filtration for aluminum chloride and aluminum sulfate are presented in Table 6.1. The model predictions along with the experimental data are shown in Figures 6.1 and 6.2 for aluminum chloride and aluminum sulfate respectively. The parameter estimates for the two models lie very close, which indicates that there are no significant differences in the two models. In other words, both aluminum chloride and aluminum sulfate demonstrated similar efficiencies in removing fulvic acid from water. The model also predicts the effect of the pH and the aluminum concentration. As can be seen in Figures 6.1

TABLE 6.1 Parameter estimation for the modelling of the removal after filtration without transformation of the observations

Al source	$AlCl_3$	Alum
b_0	96.04	96.13
b_1	-20.83	-20.17
b_2	18.17	20.50
b_{12}	21.75	22.50
b_{11}	-12.12	-8.37
b_{22}	-8.12	-13.38
Residual Sum of Squares	370.2	478.5
Pure Error Sum of Squares	10.75	10.75
Lack of Fit Sum of Squares	359.45	467.8
Calculated F-value	33.4	43.5
$F_{0.05}(3,3)$	9.28	9.28

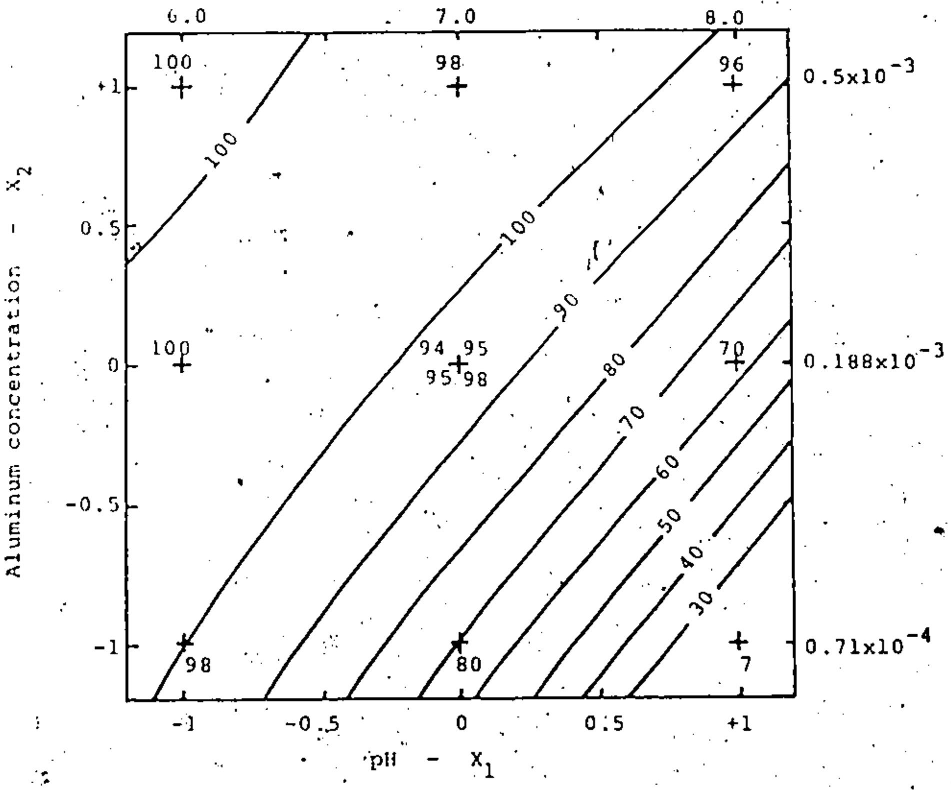


FIGURE 6.1 Removal after filtration for the $AlCl_3$ study without transformation of the observations
The left-hand ordinate and the bottom abscissa are given in coded form as used in the model. The right-hand ordinate gives the Al dosage in mol/L and the top abscissa gives the pH as was actually measured.

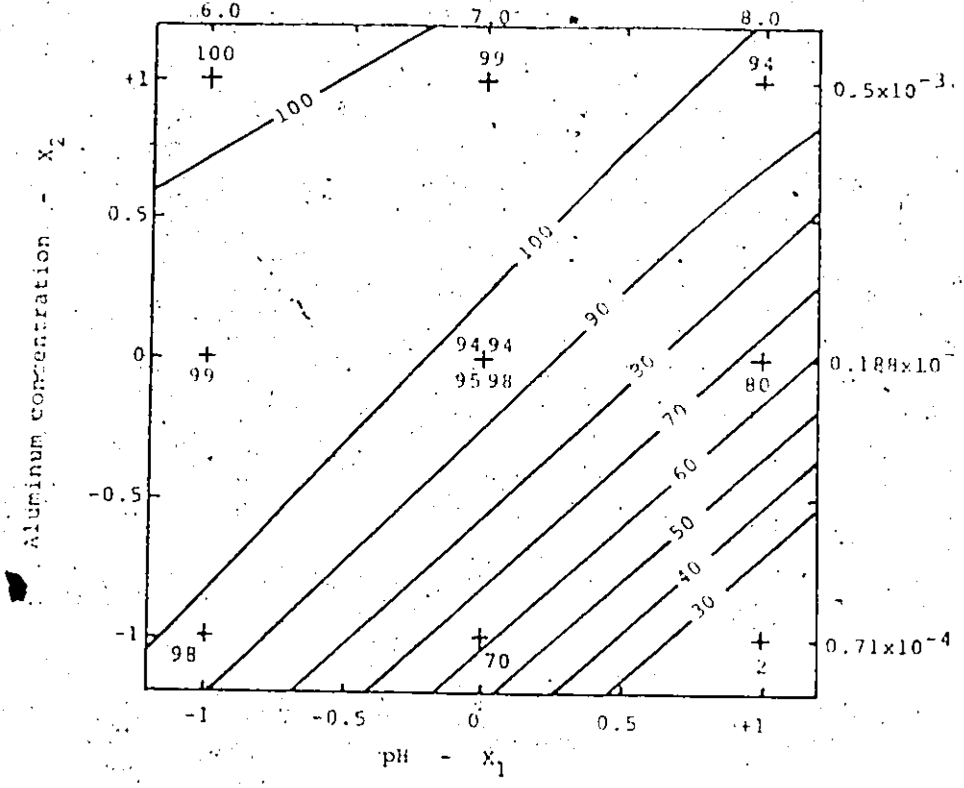


FIGURE 6.2 Removal after filtration for the Alum study without transfomation of the observations

and 6.2, increasing the aluminum dosage or lowering the pH resulted in higher removals.

The analysis of variance for these two studies is shown in Table 6.1. For both models, the calculated F value was higher than the value that would permit 95 percent confidence for good fit. This lack of fit resulted from the fact that the discrepancies between the explained and predicted response values could not be explained in terms of experimental error, since the pure error sum of squares was relatively small (accounting for less than three percent of the residual sum of squares). Repeat runs at the centre of the square experimental region resulted in consistent response values as it can be seen in Figures 6.1 and 6.2. It should be mentioned, however, that despite the lack of fit indicated by the F-test, the average difference between the observed and the predicted values was around 6 removal percentages.

The lack of fit indicates that the quadratic model was not flexible enough to account for the high degree of non-linearity of the experimental region. There are two ways that one can proceed: either to increase the complexity of the model, by including higher order terms for instance, or to apply a suitable transformation to the observations. This latter technique was used in this work, as described in a previous section. Figure 6.3 shows the residual sum of squares and the maximized likelihood function as a function of the transformation parameter λ for both a linear (with respect to the variables) and a quadratic model for the $AlCl_3$ case. For each model, there was an optimum value of λ which minimized the residual sum of squares or equivalently maximized the maximized likelihood function. For the linear model, this value was 3.5, while for the quadratic model, it was 2.1. Similar results were obtained in the alum case. For the linear model, the optimum value of λ was 2.8,

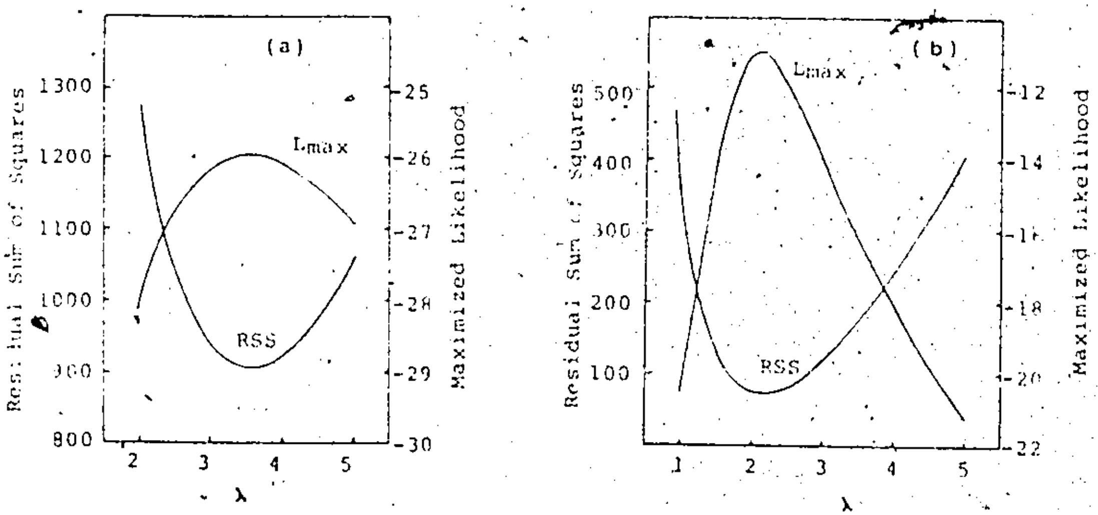


FIGURE 6.3 Maximized Likelihood Function and Residual Sum of Squares as functions of the transformation parameter

(a) Linear model (b) Quadratic model

while for the quadratic model, it was 2.0. A detailed analysis of variance for both models before and after transformation of the observations is given in Table 6.2 for aluminum chloride and Table 6.3 for alum. Linear models were inadequate even after the appropriate transformation. The inclusion of the quadratic terms in the model reduced substantially the residual sum of squares, but the model indicated sufficient fit only after an appropriate transformation of the observations. At the optimum λ (approximately equal to 2), the calculated F value was well below the level which would indicate lack of fit. Hence, a very good model has been developed.

Visual examination of the models before and after the optimum transformation is presented in Figures 6.4 and 6.5 for aluminum chloride and alum, respectively. Although both models follow the trends, the model derived after the optimum transformation appears to give much better predictions. An interesting point in Figures 6.4 and 6.5 is that the models, and particularly those before any transformation, can predict removals slightly higher than 100 percent. This overshoot occurs because a quadratic equation is used in the model, although there is no physical meaning for removals higher than 100 percent.

In the previous analysis, the suggested modelling technique was applied to a large experimental region. In practice, however, variation in the independent variables is not as large as it was used in this work. Coagulant concentrations are usually constant and variations in pH are in general less than 1 pH unit. A smaller experimental or operational region is, in general, less non-linear and therefore this modelling technique would be more efficient even without the appropriate transformation. To demonstrate this, a new region was defined by keeping the same range of

TABLE 6.2 ANOVA Table for the $AlCl_3$ case

	Untransformed		Transformed	
	Linear	Quadratic	Linear	Quadratic
λ	1	1	3.5	2.1
d.o.f.	9	6	9	6
R.S.S.	3098.6	370.2	910.2	74.6
M.S.	344.3	61.7	101.1	12.4
F	-	33.4	28.5	3.75

$F_{0.05}(3,3) = 9.28$

TABLE 6.3 ANOVA Table for the Alum case

	Untransformed		Transformed	
	Linear	Quadratic	Linear	Quadratic
λ	1	1	2.8	2.0
d.o.f.	9	6	9	6
R.S.S.	3474.6	478.5	1383.7	116.2
M.S.	386.1	79.8	153.7	19.4
F	-	43.5	24.9	4.26

$F_{0.05}(3,3) = 9.28$

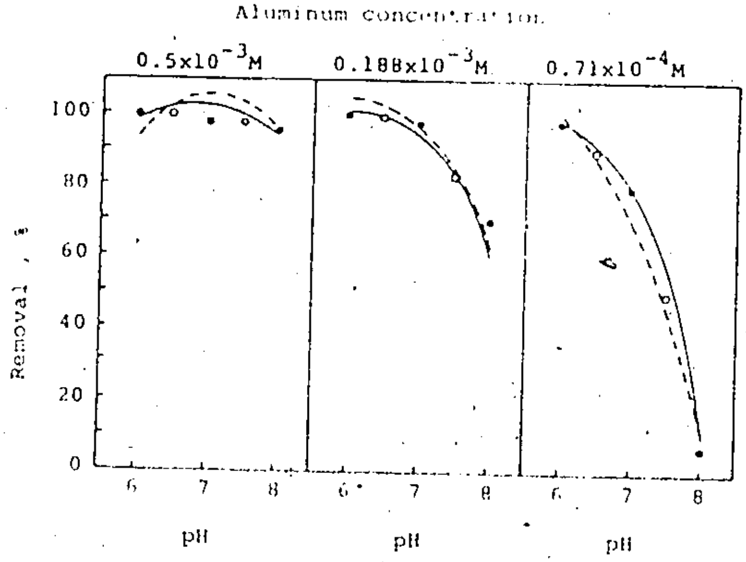


FIGURE 6.4 Model predictions for the removal after filtration for the $AlCl_3$ study.

——— with transformations of the observations

----- without transformation of the observations

Only the data points represented by the dots were used in the regression analysis

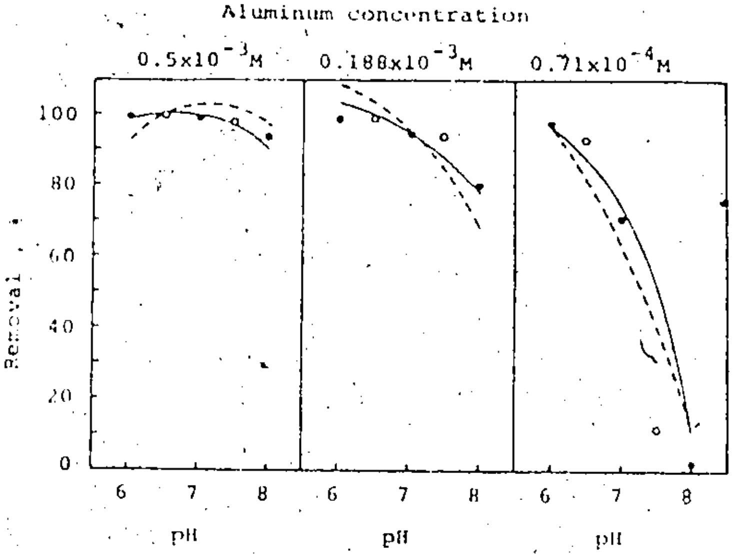


FIGURE 6.5 Model predictions for the removal after filtration for the Alum study

——— with transformation of the observations

----- without transformation of the observations

Only the data points represented by the dots were used in the regression analysis the pH as before (6-8) and by varying the aluminum concentration from 0.188×10^{-3} M to 0.5×10^{-3}M. The model predictions along with the experimental observations are illustrated in Figure 6.6 for aluminum chloride and in Figure 6.7 for alum. The estimates of the parameters and the analysis of variance are presented in Table 6.4. Once again, the parameters of the two models were very close, which indicates that there was not significant difference in the removal efficiencies of aluminum chloride and aluminum sulfate. Another important observation is that with the exception of the constant parameter, b_0, all other parameters were largely reduced. This demonstrates that the response surface has become less non-linear for the new experimental region. Despite their small numerical values, however, all parameters but b_{22} were significantly different from zero, since the zero value was not included within their confidence intervals. The calculated F values indicated that a statistically acceptable fit had been achieved. Some overshooting also occurred in this case as can be seen by the appearance of two 100 percent-isoremoval curves in Figures 6.6 and 6.7. This, however, did not result in any significant increase in the residual sum of squares. Because of the good fit, transformation of the observations is not necessary in these two cases.

6:1.2 Removal After Settling

A similar approach was followed to model the removal of fulvic acid after settling. Settling of the flocs was in general very slow and the removal curves were highly non-linear . Therefore, modelling of the removal after settling without a significant lack of fit based on the untransformed data can only be applied to a rather small experimental region. Such a region was defined by the pH ranging from 6.5 to 7.5 and the aluminum concentration ranging from 0.188×10^{-3}M to 0.5×10^{-3} M.

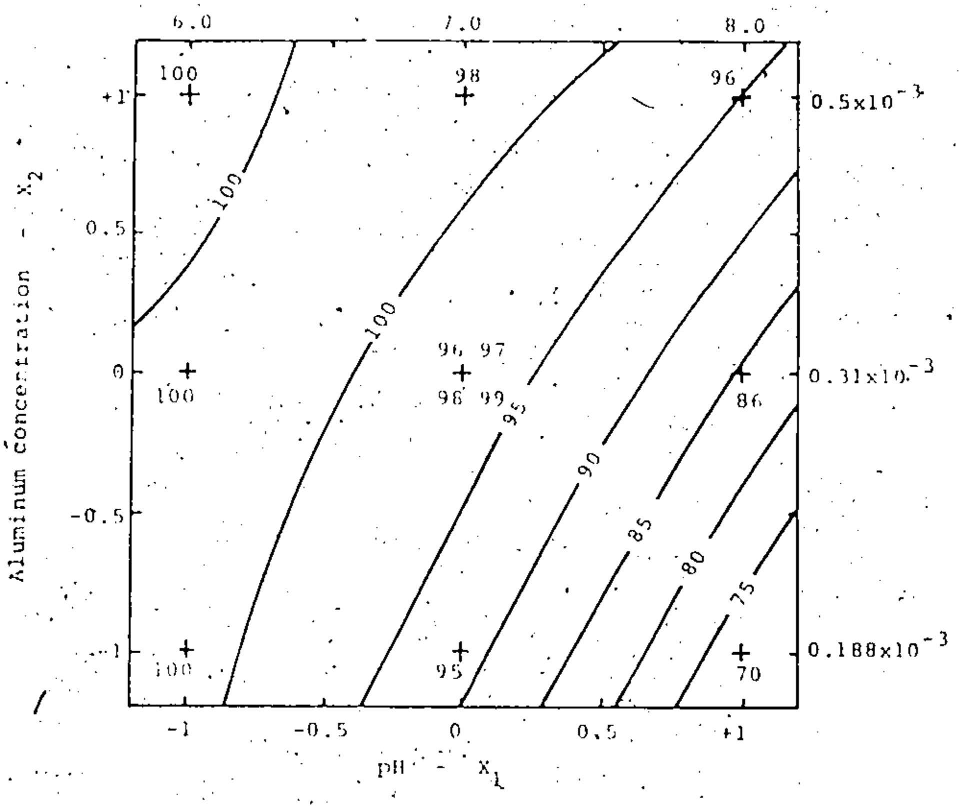


FIGURE 6.6 Removal after filtration for the $AlCl_3$ study of the reduced region

Residual Sum of Squqres = 41.6

F-value = 7.3

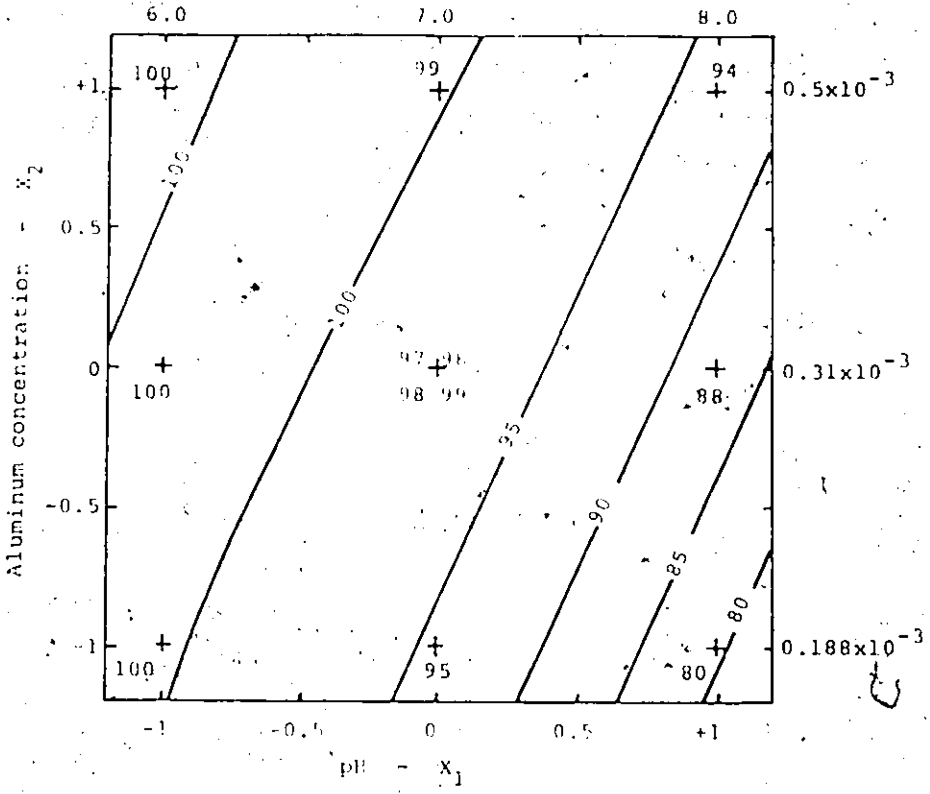


FIGURE 6.7 Removal after filtration for the Alum study of the reduced region

Residual Sum of Squares = 5.5

F-value = 1.75

TABLE 6.4 Parameter estimation in the modelling of the reduced experimental region without transformation of the observations

Al source	$AlCl_3$	Alum
b_o	97.58	97.92
b_1	-8.00	-6.33
b_2	4.83	3.00
b_{12}	6.50	3.50
b_{11}	-4.75	-3.75
b_{22}	-1.25	-0.75
Residual Sum of Squares	41.50	5.5
Pure Error Sum of Squares	5.0	2.0
Lack of Fit Sum of Squares	36.5	3.5
Calculated F-value	7.3	1.75
$F_{0.05}(3,3)$	9.28	9.28

The predicted and the observed response values are shown in Figure 6.8 for aluminum chloride and Figure 6.9 for aluminum sufate. Table 6.5 presents the estimates of the model parameters along with the analysis of variance for both cases. The parameters estimated in the aluminum chloride study were significantly different from those in the alum case. This indicates that the two models are significantly different. This can also be seen by inspection of the isoremoval lines in Figures 6.8 and 6.9. Aluminum chloride demonstrated higher removals at pH 6.5 than at pH 7.5, while flocs in the case of alum seemed to settle faster at intermediate or higher pH (7.0 to 7.5). The low settleability of the flocs in the case of alum at pH values between 6 and 7 was attributed to the adsorption of sulfate ions . For both studies, the model demonstrated sufficient fit in accordance to the F-test (Table 6.5). Larger experimental regions were also examined. Depending on the specific region, some models demonstrated good fit, while others were characterized by significant lack of fit. In general, however, the removal after filtration was modelled more effectively for a wider experimental region than the removal after settling, while transformation of the observations helped to overcome the difficulties introduced by the non-linearity.

Another difference in the modelling of the removal after filtration and settling is that the pure error sum of squares in the case of settling was in general larger than the pure error sum of squares in the case of filtration. This arose from the fact that the removal as measured by filtration gave more consistent and repeatable results than when the removal was measured after settling. This means that there is a larger experimental error associated with the settling rather than with the filtration.

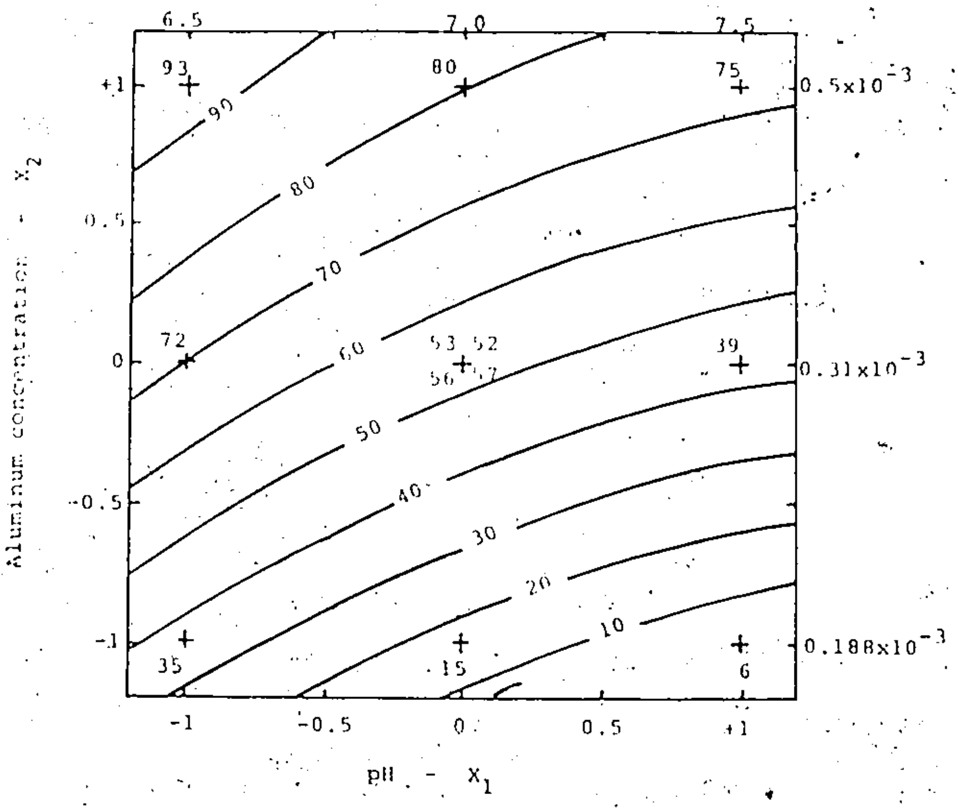


FIGURE 6.8 Removal after 20 min of settling for the $AlCl_3$ study

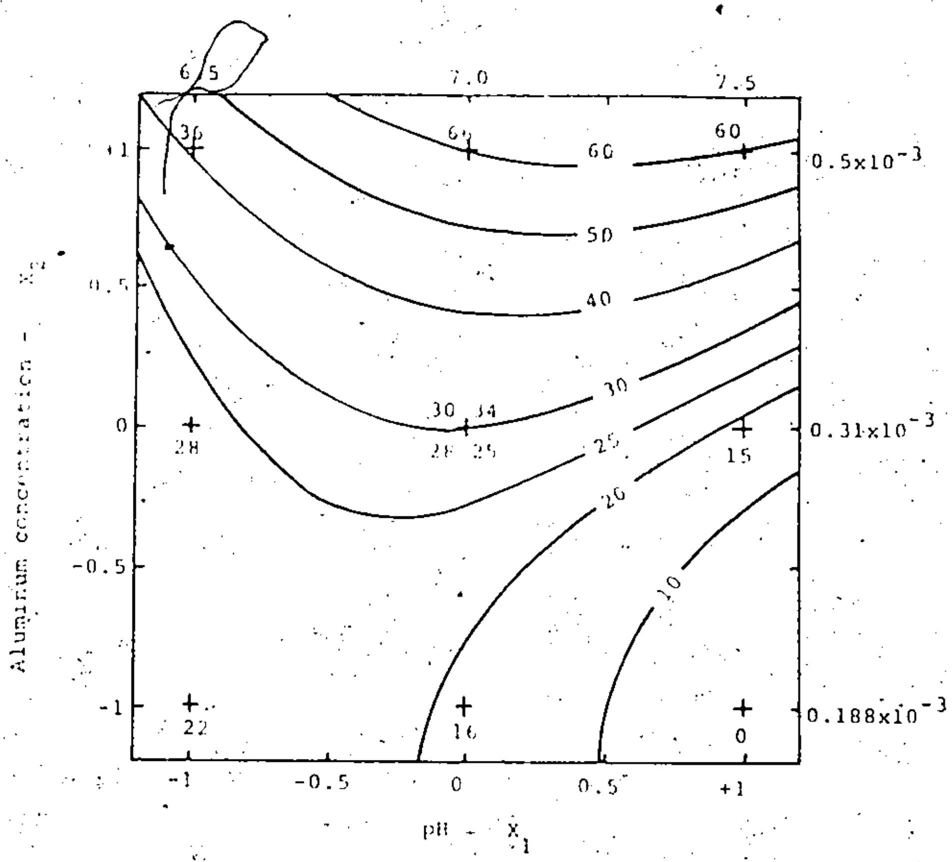


FIGURE 6.9 Removal after 20 min of settling for the Alum study

TABLE 6.5 Parameter estimation in the modelling of the removal after settling without transformation of the observations

Al source	$AlCl_3$	Alum
b_o	53.88	29.88
b_1	-13.33	-1.83
b_2	32.00	20.67
b_{12}	2.75	11.50
b_{11}	2.88	-9.62
b_{22}	-5.13	9.88
Residual Sum of Squares	57.2	173.8
Pure Error Sum of Squares	17.0	42.7
Lack of Fit Sum of Squares	40.2	131.1
Calculated F-value	2.36	3.07
$F_{0.05}(3,3)$	9.28	9.28

In general, it can be concluded that the modelling technique demonstrated in this chapter can be applied effectively to monitor and control the removal of fulvic acid with aluminum. The technique does not require an understanding of the natural phenomena per se, and therefore, it can be used in the modelling of diverse operations, such as settling or filtration. While only two independent variables were considered in this chapter, namely the pH and the aluminum concentration, the model can be expanded to study as many variables as possible. Such model expansion can include variations in the fulvic acid concentration, addition of polymer and so on. The model is calibrated by means of an orthogonal factorial experimental design. This allows the calculation of uncorrelated estimates of the parameters, using a minimum number of experimental runs. However, because the model is empirical, it cannot be applied to substantially different conditions. This can only be possible when a model incorporates the understanding of the natural phenomena.

6.2 CONCLUSIONS

Upon conditions relevant to this work, the following conclusions are drawn:

For removal after filtration

1. For pH range 6 to 8, and aluminum concentration range 0.71×10^{-4} M to 0.5×10^{-3} M:

   1.1 No significant difference was found between coefficients in the quadratic models in the aluminum chloride study as compared with the aluminum sulfate.

   1.2 The quadratic models could not satisfy a 95 percent significance F-test. This was attributed to a lack of fit and not to experimental error. The models, however, could predict removals to within 6 percent.

1.3 Transforming the observed data (according to the Box and Cox method and for $\lambda = 2$) yielded quadratic models that easily satisfied a 95 percent significance F-test. The transformation eliminated the need for more complicated mathematical models.

1.4 The models predicted quantitatively the effect of the aluminum dosage and the pH. For some conditions, all models predicted removals slightly greater than 100 percent. This overshoot is inherent in the quadratic models.

2. For pH range 6 to 8 and aluminum concentration 0.188×10^{-3} M to 0.5×10^{-3}M:

2.1 No significant difference was found between coefficients in the quadratic models for the two aluminum salts.

2.2 The quadratic models satisfied a 95 percent significance F-test. Transformation of the observations for this experimental region was not necessary.

For removal after settling

1. Modelling of the removal after settling was less effective as compared to the modelling of the removal after filtration. This was attributed to the fact that the response surface in the case of settling was highly non-linear.

2. For pH range 6.5 to 7.5 and aluminum concentration range 0.188×10^{-3}M to 0.5×10^{-3} M, the quadratic model adequately described the removal after settling for the two aluminum salts, satisfying a 95 percent significance F-test. For this experimental region,

however, significant differences were found between coefficients of the quadratic model in the aluminum chloride study as compared with the aluminum sulfate.

3. There were larger variations in the response in the case of settling than in the case of filtration. This indicated that the reproducibility in the case of settling was not as good as in the case of filtration, and it resulted in higher values of the pure error sum of squares during the statistical evaluation of the settling models.

CHAPTER SEVEN

FULVIC ACID REMOVAL WITH ALUMINUM AND A NONIONIC POLYMER: MODELLING AND OPTIMIZATION

In the previous chapter the use of the quadratic models has been demonstrated on the removal of fulvic acid with aluminum. In this chapter the polymer dosage becomes an additional variable in the experimental system.

The objectives of this part of the work were:

1. to model the removal of fulvic acid with aluminum in the presence of nonionic polyacrylamide, and
2. to identify optimum combinations of aluminum and polymer concentrations that minimize the cost of the chemicals for specified fulvic removals.

7.1 RESULTS AND DISCUSSION

This section concentrates on the modelling and the optimization of the removal of fulvic acid with aluminum and nonionic polyacrylamide after filtration. The first experimental region where the modelling technique was tested was defined by the pH ranging from 7 to 8, the aluminum concentration from 0.71×10^{-4} M to 0.5×10^{-3} M and the polymer concentration from 0.001 to 0.1 mg/L. This experimental region will be referred to as Region I. The least-square estimates of the model parameters are given in Table 7.1. The most significant parameter was b which is an average effect. Among the parameters that characterize the

TABLE 7.1 Parameter estimation and statistical evaluation of the model for Region I for the removal of fulvic acid by filtration

Variable	i	b_i	b_{ii}	b_{ij} $(j=i+1,3)$	
-	0	94.31	-	-	
pH	1	-9.48	0.75	9.68	-2.79
Al conc.	2	29.78	-27.65	-12.51	
Polymer	3	9.09	1.93	-	

Residual Sum of Squares	1328.98
Pure Error Sum of Squares	10.86
Calculated F-value	42.8
$F_{0.05}(17,6)$	3.9
Average Difference	5.91

variables all parameters associated with the aluminum concentration appeared to be of major significance. This indicates that for this experimental region the aluminum concentration was the major factor affecting the removal of fulvic acid from water. Three of the parameters, namely $b_{11} = 0.75$, $b_{13} = 2.79$ and $b_{33} = 1.93$ were not significantly different from zero, since an examination of their confidence intervals revealed that the zero value was included within their confidence intervals.

A statistical evaluation of the model for this region is also shown in Table 7.1. According to the F-test at the 95 percent confidence level the model indicated lack of fit. The reason was twofold: the high value of the residual sum of squares (1328.98) and the low value of the pure error sum of squares. The latter contributed by less than one percent to the residual sum of squares. This was the result of the high degree of reproducibility for the same experimental conditions. Despite this lack of fit, however, the average difference between predicted and observed values was less than 6 removal percentages. This is equivalent to an error of less than 10 percent for the high removals that are of interest in water treatment.

Visual representation of the model predictions along with the experimental observations for pH 7.0 and 8.0 are shown in Figures 7.1 and 7.2, respectively. The removal of fulvic acid increased dramatically with increase in the aluminum dosage, while the effect of the polymer concentration was not as large. The effect of the polymer, however, was more significant at pH 7.0 rather than at pH 8.0. The effect of the polymer depended also on the aluminum dosage. At lower aluminum concentrations the polymer promoted the removal of fulvic acid to a

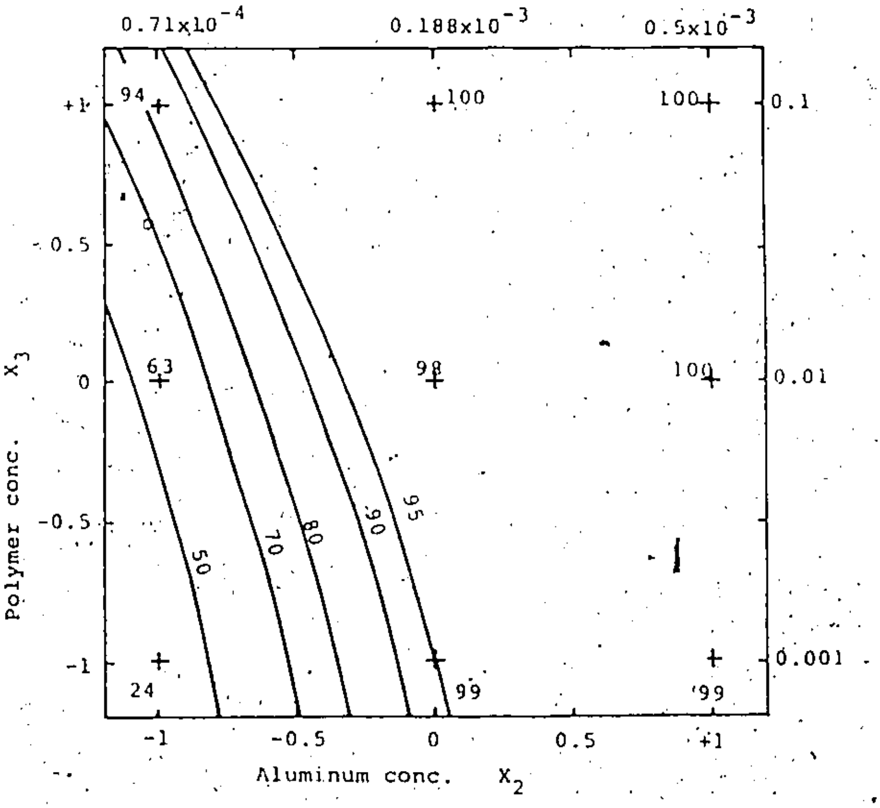


FIGURE 7.1 Removal predictions for Region I

pH = 7.0

The left-hand ordinate and the bottom abscissa are given in coded form as were used in the model.The right-hand ordinate gives the polymer concentration in mg/L and the top abscissa gives the aluminum dosage in mol/L.

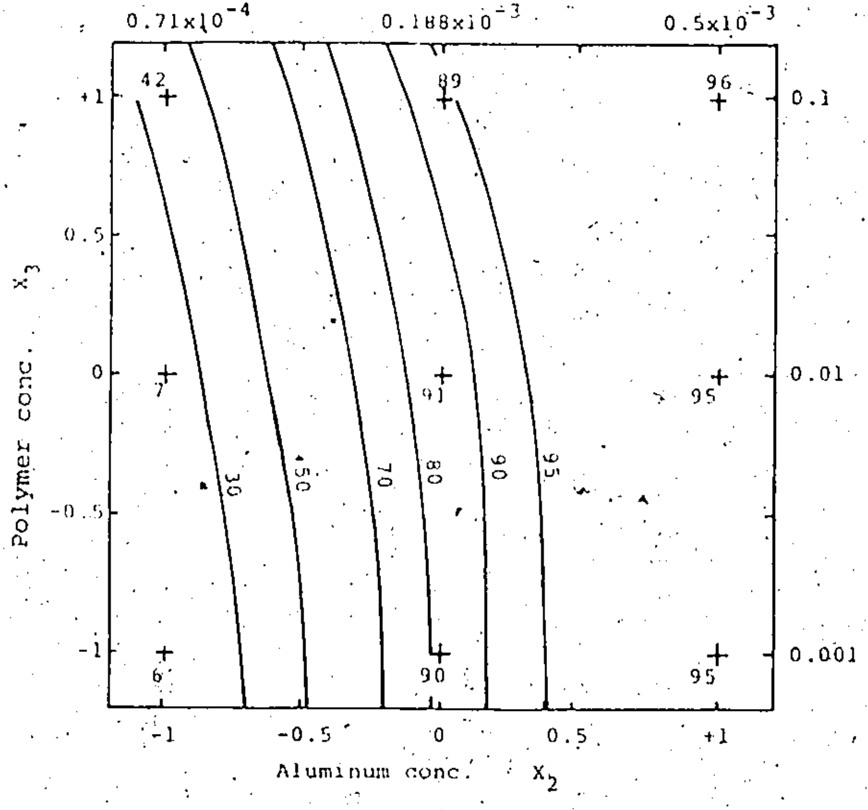


FIGURE 7.2 Removal predictions for Region II

pH = 8.0

larger extent than at higher aluminum concentrations. At pH 7.0 and an aluminum dosage of 0.71×10^{-4} M the observed removals were 24, 63 and 94 percent for 0.001, 0.01 and 0.1 mg/L polymer respectively, while for an aluminum concentration of 0.188×10^{-3} M the polymer did not demonstrate any significant effect. In that case the removals ranged between 98 and 100 percent. This behavior of the polymer at the lower aluminum concentrations and consequently low or moderate removals may be explained as the result of the interaction between the polymer and the aluminum-fulvic acid particles. It has been demonstrated in Chapter 5 that the polymer does not interact directly with the fulvic acid molecules, but with the particles formed as a result of the interaction between the organic matter and the aluminum. At lower aluminum concentrations a significant portion of the formed particles is very small in size (less than 0.1 µm). In the presence of the polymer the size of the particles increases due to flocculation and therefore higher separation by filtration is accomplished. When the aluminum concentration increases, coagulation and sweep-zone precipitation of the micro-colloidal particles by the aluminum species results in higher removals and consequently in lower flocculating efficiency of the polymer. Another important observation was that less aluminum was required to achieve a specific removal at the lower pH (pH = 7.0) than at pH 8.0.

Figures 7.1 and 7.2 give suitable combinations of aluminum and polymer dosages to achieve a desired fulvic acid removal. The combined cost of the chemicals, however, differs along the iso-removal lines. While the cost of polymer is higher than the cost of alum, much smaller dosages were required. Figures 7.3 and 7.4 show the combined cost of chemicals as a function of the polymer concentration for various removal

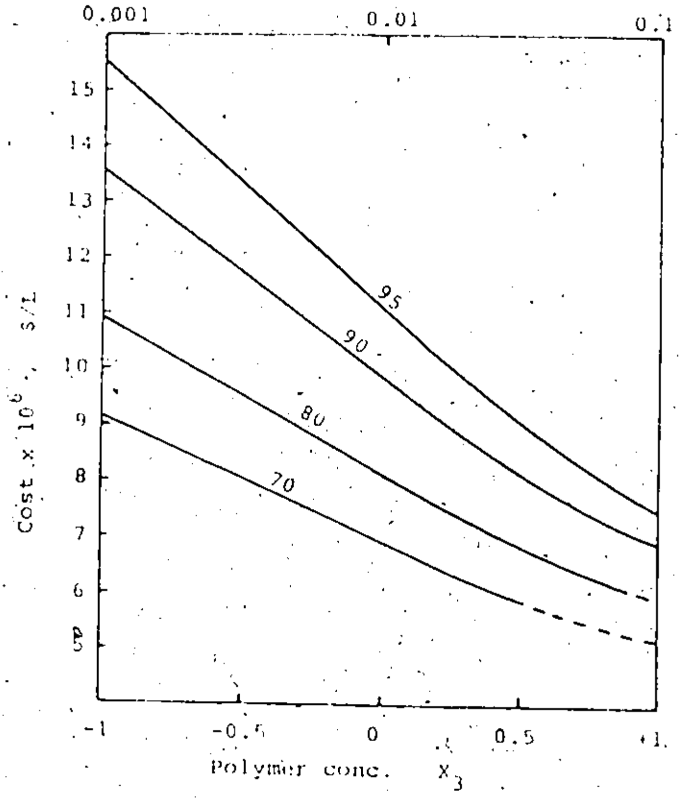


FIGURE 7.3 Combined cost of chemicals for different degrees of removal for Region I

pH = 7.0

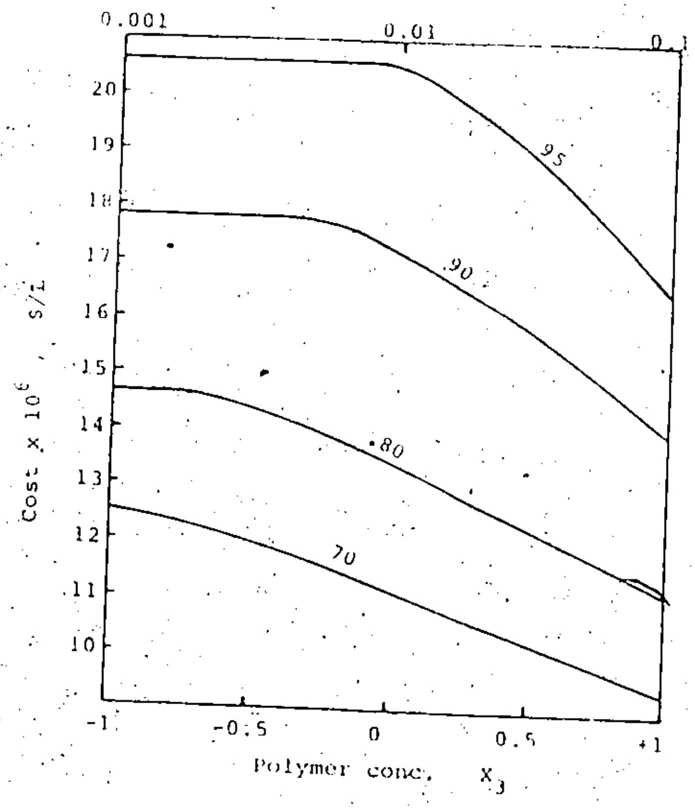


FIGURE 7.4 Combined cost of chemicals for different degrees of removal for Region I

pH = 8.0

levels at pH 7.0 and 8.0 respectively. The cost was based on the 1983 market prices for alum and water-soluble polymers. These prices were (in Canadian dollars):

Aluminum = \$0.081 per mol Al, and

Polymer = \$5.2 per kg

Figures 7.3 and 7.4 demonstrate that as the polymer concentration increased, the combined cost of the chemicals decreased. In addition to this, the cost of the chemicals for achieving a specific removal depended also on the pH. For a high desired removal level, such as 90 or 95 percent, it would cost almost twice as much to remove fulvic acid from water at pH 8.0 than at pH 7.0. It should be mentioned that in Figure 7.3 the dotted line represents the model predictions at aluminum concentrations that were outside the experimental region. Although the error associated with the removal or cost may be as high as 10 percent, these figures clearly indicate that the addition of nonionic polyacrylamide had a beneficial effect on the removal of fulvic acid with aluminum.

Since there was a reduction in the combined cost with increasing polymer concentrations and judging from Figures 7.3 and 7.4, the next experimental region that was tested was defined by:

pH :7 to 8

aluminum concentration: 0.71×10^{-4} M to 0.188×10^{-3} M

polymer concentration: 0.01 to 1.0 mg/L

This experimental region is denoted as Region II. The parameter estimates for this region are presented in Table 7.2, along with the statistical evaluation of the model. Once again the most significant parameter was b_o, which is an average effect. The next most important parameters were b_2(associated with the aluminum concentration) and b_1

TABLE 7.2 Parameter estimation and statistical evaluation of the model for Region II for the removal of fulvic acid by filtration

Variable	i	b_i	b_{ii}	b_{ij} (j=i+1,3)	
-	0	89.24	-	-	
pH	1	-14.38	-2.62	9.15	2.31
Al conc.	2	18.84	-7.81	-9.31	
Polymer	3	4.57	-8.26	-	

Residual Sum of Squares	543.20
Pure Error Sum of Squares	15.38
Calculated F-value	12.1
$F_{0.05}(17,6)$	3.9
Average Difference	3.64

(associated with the pH). In general, however, there has been a significance reduction in the values of the parameters that characterize the effect of the aluminum concentration, as can be seen by comparing Tables 7.1 and 7.2. This was the result of a less non-linear response surface, which in general occurs when the experimental region is reduced in size. This reduction of the non-linearity of the response surface had a most profound effect on the aluminum concentration. The parameter which characterized the second-order term (b_{22}) was reduced from -27.65 to -7.81 when the higher aluminum concentration limit was reduced from 0.5×10^{-3} M to 0.188×10^{-3} M. Two of the parameters that were not significantly different from zero in Region I also had the zero value included in their confidence intervals. These parameters were b_{11} =-2.62 and b_{13}= 2.31. The third one, however, namely b_{22},increased significantly which indicates that in Region II the effect of the polymer concentration was more non-linear.

Statistically the model demonstrated better fit in Region II. There was a reduction in the residual sum of squares by almost 60 percent, while the pure error sum of squares indicated again a high degree of reproducibility. The model, however, failed to satisfy the F-test despite a significant reduction in the calculated F value. On the other hand the average difference between the observed and the predicted values was 3.7 removal percentages. This translates into an error of less than five percent for high removal levels. Such a relatively small error is acceptable for most engineering applications.

To assess further the adequacy of the model the residuals were plotted on normal probability paper. As is shown in Figure 7.5, all the residuals lie close to a straight line. This confirms that the observed

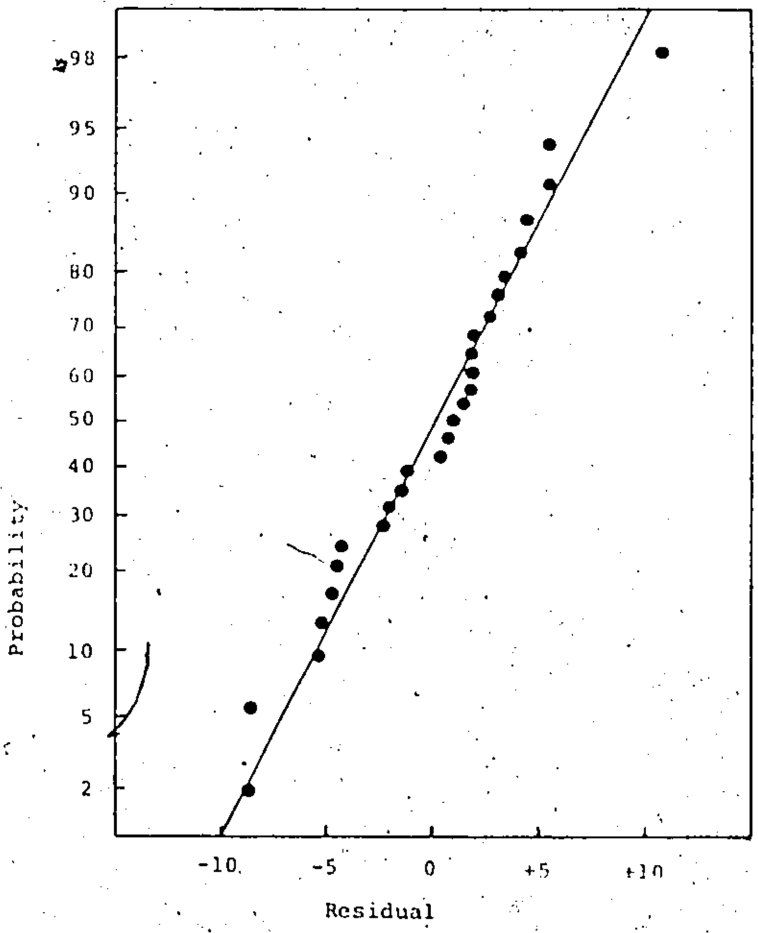


FIGURE 7.5 Plot of the residuals on probability paper

residuals may be explained as a result of random noise.

Plots of the predicted response and the experimental data are shown in Figures 7.6 and 7.7 for pH 7.0 and 8.0 respectively. The iso-removal curves for Region II are quite different from the iso-removal curves for Region I. The curves in Region II are characterized by the appearance of minima with respect to the polymer concentration. This was the result of particle restabilization in the presence of 1.0 mg/L polymer which caused the removal efficiency to deteriorate. The restabilization of the particles was more significant at pH 7.0 than at pH 8.0. The tendency for the polymer to have a larger effect on the removal at pH 7.0 (than at pH 8.0) had been previously observed for Region I.

The combined cost of the chemicals along the iso-removal curves for pH 7.0 and 8.0 is given in Figures 7.8 and 7.9 respectively. Both figures clearly demonstrate that the cost curves passed through a minimum. This minimum occurred at a polymer concentration of 0.1 mg/L, and it was the same for both pH levels. The optimum aluminum concentration, however, depended on the pH. At pH 7.0 the optimum aluminum concentration for 95 percent removal was 0.9 x 10^{-4} M (corresponding to X_2 = -0.5 on Figure 6), while at pH 8.0 was around 0.2 x 10^{-3} M for equivalent removal (Figure 7.7). The minimum combined cost at pH 7.0 was found to be approximately half of the cost at pH 8.0 for the same removal levels.

Overall it can be concluded that the addition of 0.1 mg/L of nonionic polyacrylamide with equivalent reductions in the aluminum dosages resulted in optimum combinations of these two chemicals. If one considers the cost of accomplishing 90 to 95 percent removal of fulvic acid solely with aluminum as being practically the same as in the presence of 0.001 mg/L polymer, then under optimum conditions the overall

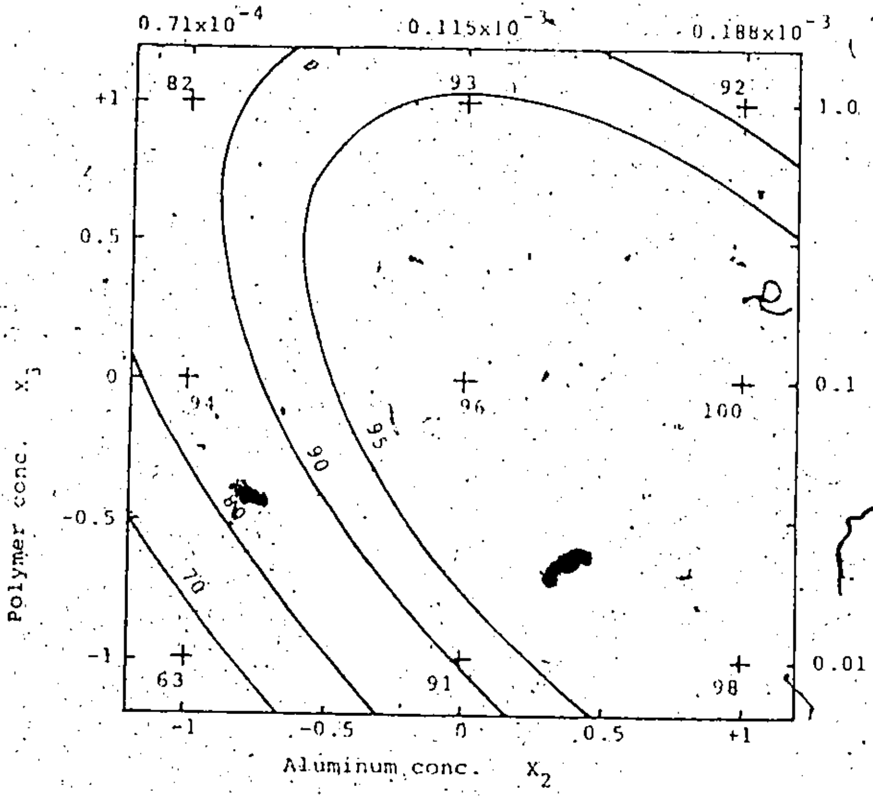


FIGURE 7.6 Removal predictions for Region II

pH = 7.0

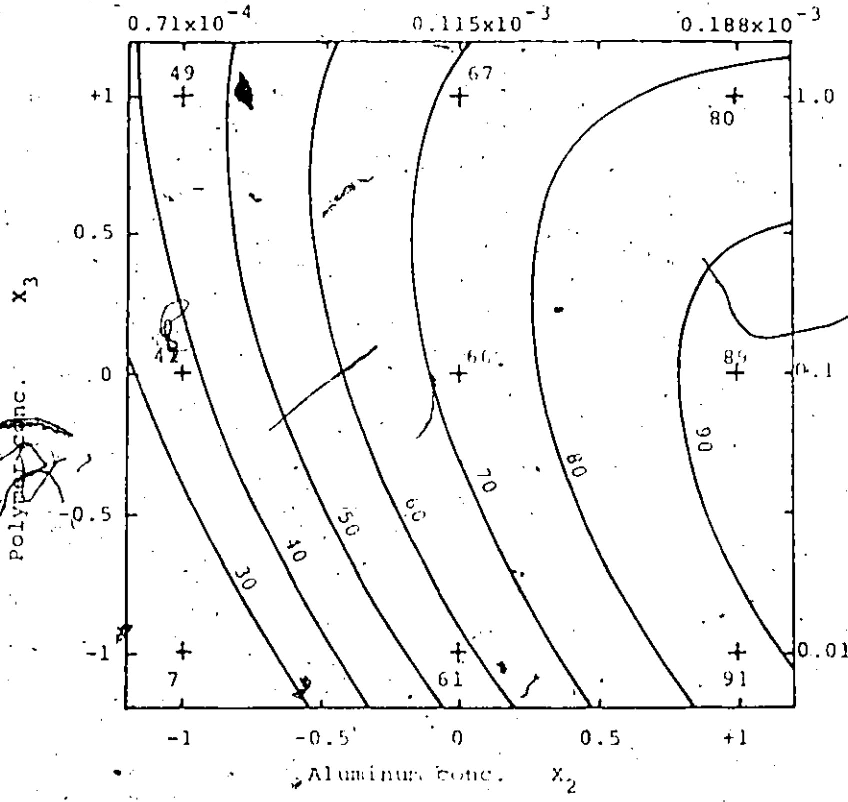


FIGURE 7.7 Removal predictions for Region II

pH = 8.0

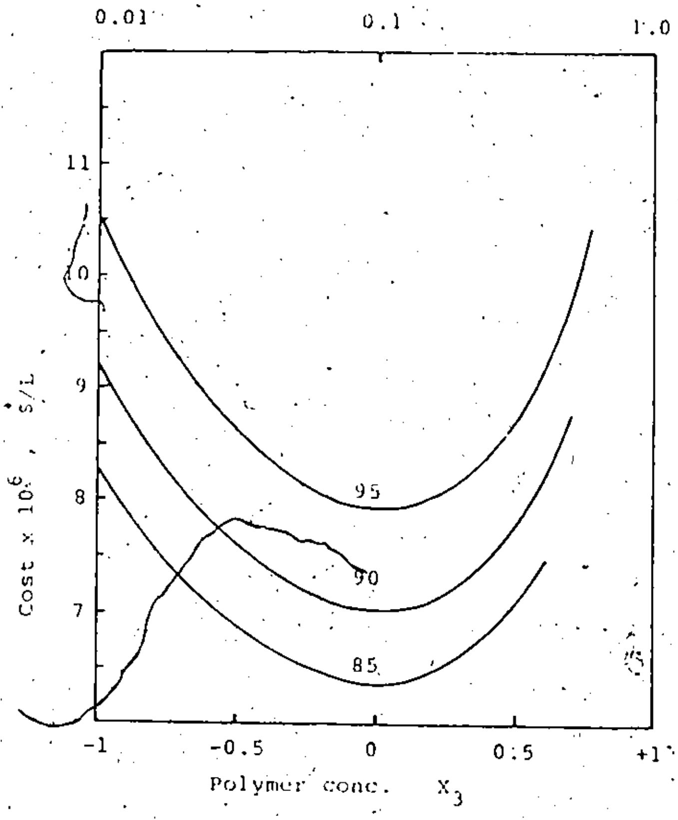


FIGURE 7.8 Combined cost of chemicals for different degrees of removal for Region II

pH = 7.0

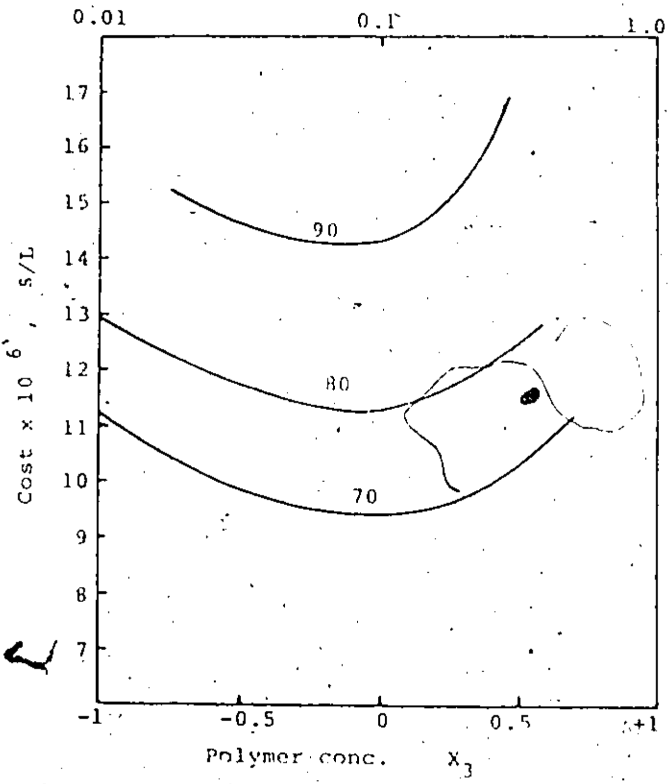


FIGURE 7.9 Combined cost of chemicals for different degrees of removal for Region II

pH = 8.0

reduction in the cost of chemicals was as high as 50 percent depending on the pH, with the higher reduction occurring at pH 7.0.

Further improvement of the model is also possible, either through an appropriate transformation of the observations, or by applying the modelling technique around the optimum. The latter is of significance from an operational point of view, since during normal operation it is very unlikely that changes in the aluminum and polymer concentrations would be of the magnitude studied in this work.

Finally, a point should be made about the measurement of the removal. The concept of "removal" usually depends on the separation of the solid from the liquid phase. In this work membrane filters with a pore size of 0.10 μm were employed. It has been shown in Chapter 4 that filters with different pore sizes may have different separating efficiencies. On the other hand, deep-bed filters used in water treatment plants do not necessarily behave like the membrane filters in the lab. Nevertheless, the procedures and ideas presented in this chapter should provide guidance for the optimization of the removal of fulvic acid using polymers in full scale operation with deep-bed filters.

7.2 CONCLUSIONS

The following conclusions can be drawn from this work:

1. The removal by filtration of fulvic acid with aluminum and nonionic polyacrylamide was successfully modelled by a quadratic polynomial based on a three-level factorial design. For experimental regions of practical significance the error between observed and predicted values was less than five percent.

2. The aluminum concentration had the most significant effect on the removal, pH was the next most significant and the polymer concentration was the least significant for the pH range from 7.0 to 8.0.
3. The presence of the polymer at concentrations below 0.1 mg/L facilitated the removal. The effect of the polymer was more significant at pH 7.0 than at pH 8.0 and at lower aluminum concentrations.
4. Concentrations of polymer around 1.0 mg/L resulted in restabilization of the particles and subsequently in deterioration of the removals. The particle restabilization was more significant at pH 7.0 than at pH 8.0. Particle restabilization has also been observed by Edzwald et al. (1977).
5. The combined cost of the chemicals (alum and polymer) was minimum at a polymer dosage of 0.1 mg/L for the entire pH range studied. The optimum aluminum concentration, however, was a function of the pH.
6. The combined cost of the chemicals at pH 7.0 was approximately half of the cost at pH 8.0 for the same degree of removal.
7. Under optimum removal conditions, with respect to the polymer and aluminum concentrations, an overall reduction in the cost of the chemicals of up to 50 percent was estimated as compared to the cost in the absence of the polymer for the same high level of removal. This reduction depended on the pH, with the higher reduction occurring at pH 7.0.

CHAPTER EIGHT

AN INVESTIGATION OF THE FACTORS AFFECTING THE REMOVAL OF FULVIC ACID FROM WATER BY ALUMINUM AND POLYMERS

In the previo[illegible] effect of nonionic polyacrylamide on the removal of fulvic a[illegible] aluminum was elucidated. There has been no effort to optimize the polymer properties, such as the molar mass and the degree of hydrolysis. In practice, the application of polymers in water treatment is contingent upon their commercial availability rather than a thorough examination of their properties.

This chapter attempts to clarify the effect that the molar mass and the degree of hydrolysis of polyacrylamide have on the removal of fulvic acid from water in the presence of aluminum. This is done in relation to various experimental conditions with regards to the pH, the polymer dosage and the concentration of calcium present in the water. The five variables (calcium concentration, polymer degree of hydrolysis, polymer molar mass, pH and polymer dosage) were studied in accordance to a 2^{5-1} Resolution V fractional factorial experimental design (Box and Hunter, 1961 b). In the Resolution V design no main effect or two-factor interaction is confounded with any other main effect or two-factor interactions. In this work it was assumed that three - (or more) factor interactions were negligible and therefore unconfounded estimates of the main effects and the two-factor interactions could be obtained.

8.1. RESULTS AND DISCUSSION

The design matrix of the 2^{5-1} experimental design is shown in Table 8.1. The defining relation of this design is given by I=12345. The versions of the fifth variable (plus or minus) are equal to the product of the versions of the other four variables. All the main effects are, therefore, confounded with four-factor interactions, while all two-factor interactions are confounded with the three-factor interactions. If three and four-factor interactions are negligible, then one can estimate the average, the five main effects and the ten two-factor interactions with the sixteen runs of the design. Each effect equals one eighth of the summation of the response values with each value being multiplied with the corresponding sign in the column of the effect. The average is a mean value of the response. The response was the percentage of fulvic acid that was removed as determined by the residue obtained by filtration.

The estimates of the effects along with the confounding patterns are presented in Table 8.2. The magnitude of each effect indicates its relative significance in the process. The effect of pH, for instance, with a value I_4=-16.85 is more significant than the effect of polymer concentration I_5 = 0.55. The sign of each estimated effect is also very important. It indicates which level of the variable affects the response more. In the case of pH, the negative sign shows that the low setting of pH (pH =7) yielded higher removals than the high setting of pH (pH = 8).

To assess the significance of the effects, an estimate of the standard error is required. This is equivalent to the square root of the variance of the effect. The variance can be obtained by (Box et al, 1978):

TABLE 8.1 Design matrix of the study and observed removals

X	1	2	3	4	5	12	13	14	15	23	24	25	34	35	45	Removal after filtration
1	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	80.9
2	+	+	+	-	-	+	+	-	-	+	-	-	-	-	+	94.3
3	+	+	-	+	-	+	-	+	-	-	+	-	-	+	-	83.0
4	+	+	-	-	+	+	-	-	+	-	-	+	+	-	-	96.0
5	+	-	+	+	-	-	+	+	-	-	-	+	+	-	-	83.0
6	+	-	+	-	+	-	+	-	+	-	+	-	-	+	-	96.0
7	+	-	-	+	+	-	-	+	+	+	-	-	-	-	+	83.6
8	+	-	-	-	-	-	-	-	-	+	+	+	+	+	+	96.0
9	-	+	+	+	-	-	-	-	+	+	+	-	+	-	-	71.0
10	-	+	+	-	+	-	-	+	-	+	-	+	-	+	-	92.5
11	-	+	-	+	+	-	+	-	-	-	+	+	-	-	+	74.0
12	-	+	-	-	-	-	+	+	+	-	-	-	+	+	+	93.1
13	-	-	+	+	+	+	-	-	-	-	-	-	+	+	+	72.2
14	-	-	+	-	-	+	-	+	+	-	+	+	-	-	+	92.5
15	-	-	-	+	-	+	+	-	+	+	-	+	-	+	-	72.5
16	-	-	-	-	+	+	+	+	-	+	+	-	+	-	-	94.6

TABLE 8.2 Effect estimates from the 2^{5-1} factorial design

Variable	Confounding pattern	Effect
Average	$l_I \rightarrow$ average$+\frac{1}{2}(12345)$	$l_I = 85.95 \pm 0.12$
Calcium conc.	$l_1 \rightarrow 1 + 2345$	$l_1 = 6.3 \pm 0.24$
DOH	$l_2 \rightarrow 2 + 1345$	$l_2 = -0.7$
MM	$l_3 \rightarrow 3 + 1245$	$l_3 = -1.3$
pH	$l_4 \rightarrow 4 + 1235$	$l_4 = -16.85$
Polymer conc.	$l_5 \rightarrow 5 + 1234$	$l_5 = 0.55$
Ca x DOH	$l_{12} \rightarrow 12 + 345$	$l_{12} = -0.4$
Ca x MM	$l_{13} \rightarrow 13 + 245$	$l_{13} = 0.2$
Ca x pH	$l_{14} \rightarrow 14 + 235$	$l_{14} = 3.9$
Ca x Polymer	$l_{15} \rightarrow 15 + 234$	$l_{15} = -0.5$
DOH x MM	$l_{23} \rightarrow 23 + 145$	$l_{23} = -0.55$
DOH x pH	$l_{24} \rightarrow 24 + 135$	$l_{24} = 0.1$
DOH x Polymer	$l_{25} \rightarrow 25 + 134$	$l_{25} = -0.05$
MM x pH	$l_{34} \rightarrow 34 + 125$	$l_{34} = -0.2$
MM x Polymer	$l_{35} \rightarrow 35 + 124$	$l_{35} = -0.35$
pH x Polymer	$l_{45} \rightarrow 45 + 123$	$l_{45} = -0.25$

$$V\text{ (effect)} = 4\sigma^2/N \qquad (1)$$

where N = number of runs

σ^2 = the variance of the observations

An estimate of σ^2 can be obtained by performing repeat runs, usually at the centre point of the design. In the present work, this was practically impossible, since no polymer with molar mass at the intermediate level of those of the two polymers was commercially available and its production in the lab was deemed unfeasible relative to the research objectives. Therefore, the repeat runs were performed at one of the experimental points of the design matrix. In order to ensure that the estimated variance did not have a conservative value, the repeat runs were done at a point where the reproducibility was considered to be relatively small. The experimental run 7 (Table 8.1) was selected as such. This run was done at pH 8 where, for the aluminum concentration used, the removal was not close to 100 percent. The six replicate runs gave the following removals (in percentages): 83.0, 83.0, 83.9, 83.6, 84.2, 83.0. The reported value of 83.6 for run 7 in Table 2 is the average of these six values. An estimate of the variance can, then, be calculated from (Box et al, 1978):

$$s^2 = \frac{1}{5} \sum_{i=1}^{6} (y_i - \bar{y}_i)^2 \qquad (2)$$

where s^2 = an estimate of the variance

y_i = the removal values, and

$\bar{y}_i$ = the average removal of the six runs

Substituting in Eq. (2), an estimate of the variance equal to 0.231 was obtained. From Eq. (1) the variance of the effect was, then, calculated and was found to be 0.05775. Therefore, the standard error of each effect was 0.24. The standard error of the average was half that, ie. 0.12.

These two values are shown in Table 8.2. Most of the effect estimates are different from zero. The contribution of a variable, however, whose effect appeared to be different from zero, is not necessarily very large. The effect of the polymer concentration, for instance, has a value $l_5 =$ 0.55. Eventhough it is larger than the standard error, 0.24, its contribution to the removal is not very large. One way to distinguish the most important effects is to plot these on normal probability paper (Daniel, 1976; Box et al, 1978). All effects that are small can be explained as random noise, following a normal distribution. On normal probability paper these effects would, then, appear on a straight line. Any effects with a significant contribution would not be on the line. The plot of the effects is shown in Figure 8.1. There are three effects that are located away from the line, $l_4 = -16.85$, $l_{14} = 3.9$ and $l_1 = 6.3$, while $l_3 =$ -1.3 lies close to the line but not on it. We conclude, therefore, that the most significant fraction that affected the removal of fulvic acid from water with aluminum and polymers were the pH, the calcium concentration, the interaction between pH and calcium, and the polymer molar mass.

The effect of pH has been adequately described in the literature (Edzwald, 1979; Hall and Packham, 1965). Although in this section the lowest pH employed was 7.0, the optimum pH for most efficient removal has been found between 5 and 6. The pH affects both the ionization of the functional groups on the fulvic or humic molecules and the hydrolysis of the aluminum ions. Increased ionization of the fulvic functional groups results in lower aluminum efficiencies or, in other words, it requires higher aluminum dosages for effective coagulation.

The presence of calcium in the standard test water was also very significant, as was concluded above. In this study, however, that the pH

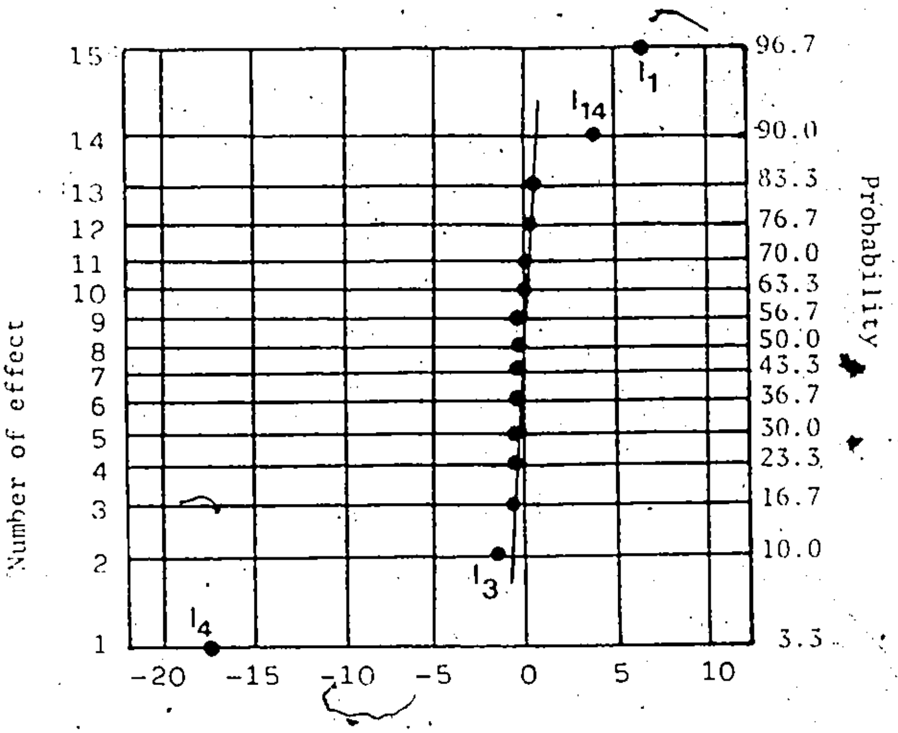


FIGURE 8.1 Normal plot of effects

was also a variable, the effect of calcium should be studied in connection with the pH. This is indicated by the significantly large value of the interaction effect $I_{14} = 3.9$. This means that the presence of calcium influences the removal of fulvic acid with aluminum and its influence depends on the pH. Both the calcium main effect and the pH - calcium interaction are positive. This indicates that higher removals were obtained at 40 mg/L calcium (higher calcium level) than at 4 mg/L (low calcium level) for both pH levels. The effect of the calcium, however, was different at pH 7 from that at pH 8. An estimate of the difference may be obtained by considering the average removals which were achieved at pH 7 and 8 for the two calcium levels. This may be done by blocking the experimental design. The average removals from runs 1,3,5, and 7, and 9, 11, 13, and 15 characterize the effect of calcium at pH 8 for 40 mg/L and 4 mg/L calcium, respectively, while the average removals from runs 2,4,6, and 8, and 10, 12, 14, and 1[illegible] characterize the effect of the same calcium levels at pH 7. The presence of 40 mg/L calcium at pH 8 resulted in an increase in removal by 10.2 percentage points, while at pH 7 this increase amounted to only 2.4 percentage points. Therefore, the beneficial effect of calcium was four times as large at pH 8 as at pH 7. This estimate, however, is an approximate one, since blocking of a 2^{5-1} Resolution V design is not possible without associating one or more main effects or two factor interactions with the block variables. In the above estimation, this does not constitute a serious error, because the effect of the calcium and the pH are far more significant than the effect of any other variable.

The beneficial role of calcium is in agreement with the findings by Randtke and Jepsen (1981). They found that at pH 6 the addition of calcium chloride in the water resulted in lower alum requirements for effective removals of peat fulvic acid. A similar effect has also been demonstrated for ferric sulfate, a coagulant with a chemical behavior similar to alum (Maulding and Harris, 1968). It was found that the presence of calcium increased the effectiveness of color removal and extended the pH range of good coagulation to higher pH values.

The role of calcium seems to be two fold: first, it can interact directly with the fulvic (or humic) molecules, and second, it can interact with the aluminum-fulvic acid particles. Dempsey (1981) has shown that the calcium-fulvic acid interaction was strong enough to neutralize over 50 percent of the fulvic acid charge, while the extent of association between calcium and fulvic acid increased with increasing pH for the most fulvic acid fractions. On the other hand, high levels of calcium can coagulate the colloidal particles that are formed from the interaction between aluminum and fulvic acid. In the absence of aluminum no removal of the organic matter has been observed with the calcium alone at and around neutral pH (Maulding and Harris, 1968; Shapiro, 1964). The larger interaction between calcium and fulvic acid at higher pH and the coagulation of the micro-colloidal particles (associated with reduced removals) may explain the more significant role of calcium at pH 8 than at pH 7. This is also an indication that the removal of fulvic acid with aluminum would be larger in hard waters than in soft waters.

The polymer properties had a smaller effect on the removal than did the pH and the calcium concentration. Of the polymer properties the molar mass was more significant than the degree of hydrolysis. The polymer with the molar mass of 5 to 6 million was more effective than that of 13 million as indicated by the negative estimated effect $I_3 = 41.3$.

The low effect of the polymer charge, as characterized by the degree of hydrolysis, may be attributed to the interaction of the polymer with the aluminum-fulvic acid colloidal particles and not with the fulvic acid molecules. The same reason was also used to explain the increased removals after filtration observed in the presence of the polymer (Chapter 5).

8.2. CONCLUSIONS

Those that confirm previous results:

1. A combination of aluminum and polyacrylamide can be used to remove fulvic acid from water. This agrees with the findings of Edzwald and coworkers.

New conclusions:

2. The applicability of a 16-experiment, fractional factorial experimental design could efficiently resolve the effect on removal of fulvic acid of the variables pH, calcium concentration, polymer concentration, polymer molar mass and degree of hydrolysis.
3. For a fixed concentration of fulvic acid and aluminum dosage the most significant effects were the pH, the calcium concentration, the effect of the calcium-pH interaction and the polymer molar mass. The effect of the pH was larger at pH 7, the lowest pH used, than at pH 8.
4. The presence of calcium increased the efficiency of the aluminum-polymer combination to remove fulvic acid from water. This is in agreement with the findings of Randtke and Jepsen (1981). The effect of calcium was more significant at pH 8 than at pH 7.
5. The polymer molar mass was the most important of the polymer properties, although its effect was less significant than that of the

pH or the calcium. The most effective molar mass was around 5 million.

6. For the experimental conditions of the research, all second order interactions between the pH, the calcium concentration, the polymer dosage, the polymer molar mass and the polymer degree of hydrolysis were negligible, with the exception of the interaction between the pH and the calcium concentration.

CHAPTER NINE

CONCLUSIONS AND RECOMMENDATIONS

9.1 CONCLUSIONS

The conclusions of the research are as follows:

1. The efficiency of aluminum coagulants to remove fulvic acid from water after filtration depended on the pore size of the membrane filter. Differences in the removal of up to 80 percent were observed between filters with pore sizes 0.45 μm and 0.10 μm with the latter being in general more efficient. Partial clogging of the filter pores resulted in improved separation of the flocs from the liquid phase in the case of 0.45 μm filters. Because this effect is so significant, care should be taken in interpreting data where removal has been measured on the filtrate through membranes or filters of pore sizes greater than 0.10 μm.
2. The removal of fulvic acid with aluminum salts was a strong function of the pH and the aluminum dosage. Complete removals by filtration were achieved at the lowest pH used (pH 6.0) and for the highest aluminum concentration (0.5×10^{-3} M) for both aluminum chloride and aluminum sulfate. Although the optimum pH range as reported by Hall and Packham (1965) (optimum pH 4.5 - 6.0) is outside the experimental region in this work, the removals obtained in this work at pH 6 agree within 5 percent with the removals reported by Edzwald (1979) and Dempsey et al (1984).

3. Both aluminum sulfate (alum) and aluminum chloride demonstrated similar efficiencies in removing fulvic acid from water after filtration for the pH range 6.0 to 8.0. Bersillon (1983), in his study of the removal of TOC from natural water, found at pH 6.0 about 2 percent difference in removal between alum and aluminum chloride and he reported that at higher pH the two aluminum salts behaved similarly. Thus, this work agrees with Bersillon (1983). (The Maulding and Harris (1968) study contrasting ferric chloride with ferric sulfate concluded that the presence of sulfate had a detrimental effect on the color removal by ferric coagulation. Their work, however, was done at pH 3 to 4. Hence, they were studying a different system and used a different pH range. Therefore, their conclusion that the chloride salt was more effective a coagulant should not be pertinent to this work.).

4. The removal of fulvic acid after settling was always smaller than the removal after filtration. Removals higher than 50 percent were only obtained for the highest aluminum dosage (0.5×10^{-3} M). Some differences existed in the settling of the flocs for the two aluminum salts for an aluminum concentration of 0.5×10^{-3} M. Partial stabilization of the particles was postulated to have taken place between pH 5 and 6 in the presence of the sulfate ion.

5. The turbidity of the treated unsettled solution depended on the aluminum concentration and the pH. The fulvic acid remaining in solution after filtration was found to correlate with the turbidity before settling following an exponential decay model. No significant differences were observed in the exponential decay models derived in the case of alum and aluminum chloride.

6. The presence of the nonionic polyacrylamide enhanced both the settling of the flocs and the removal after filtration. The maximum increase in the removal after settling was around 40 removal percentages while the maximum increase in the removal after filtration was as high as 95 removal percentages. This increase in the removal due to the presence of nonionic polyacrylamide is in general agreement with the findings by Edzwald et al (1977). The improvement in the removal after filtration was more significant at intermediate aluminum concentrations (0.71×10^{-4} M) and it was attributed to the flocculation of the micro-colloidal particles which, in the absence of the polymer, passed through the pores of the filter.
7. A mathematical model was developed to quantitatively describe the effect of the pH, the aluminum concentration and the polymer concentration on the removal of fulvic acid. The model was based on the idea that for a small experimental (or operating) region the response surface could be adequately modelled with a quadratic equation with respect to the variables. Further improvement of the model was also possible after an appropriate transformation of the observations. The adequacy of the model along with the statistical evaluation of the processes was easily checked by performing well accepted statistical tests, such as the F-test.
8. Because the model was empirical, both the removal after filtration and the removal after settling were modelled. The removal after settling was characterized by larger non-linearities as well as smaller reproducibility as compared to the removal after filtration.

9. A concentration of nonionic polyacrylamide of 0.1 mg/L had the maximum effect on the removal of fulvic acid with aluminum after filtration. The effect of the polymer addition was more significant at pH 7.0 than at pH 8.0 and at lower aluminum concentrations. Polymer concentrations larger than 0.1 mg/L resulted in restabilization of the micro-colloidal particles and consequently in deterioration of the removals. The particle restabilization was also more significant at pH 7.0 than at pH 8.0. The results by Edzwald et al (1977) also suggest some particle restabilization at polymer levels higher than the optimum.

10. At the optimum dosage of nonionic polyacrylamide of 0.1 mg/L the combined cost of chemicals for effective removal was minimal. Under optimum conditions an overall reduction in the combined cost of chemicals of up to 50 percent was estimated as compared to the cost in the absence of polymer. The cost reduction was also higher at pH 7.0 than at pH 8.0.

11. An investigation of factors that affect the removal of fulvic acid with aluminum after filtration indicated that the calcium present in the fulvic water had a larger effect on the removal than the polymer properties. Increased removals were observed in the presence of calcium, while the improvement was more significant at pH 8.0 than at pH 7.0. Among the polymer properties, the molar mass was more important than the degree of hydrolysis. The most effective molar mass was around 5 million.

9.2 RECOMMENDATIONS

The following suggestions are recommended for future research:

1. A study of the effect of cationic polymer in the presence of aluminum and comparison with the nonionic and anionic polymers. Optimization of the removal in the presence of the cationic polymer, which can interact directly with the fulvic material.
2. A study of the turbidity before settling - removal after filtration correlation. An investigation of the existence of the correlation and explanation of the exponential decay model. Does the same correlation hold in the presence of polymer or for various fulvic acid concentrations?
3. A more thorough investigation of the effect of calcium on the removal of fulvic acid with aluminum. Can we optimize the removal by adding calcium and aluminum together?
4. Optimization of a water treatment system using three criteria: removal of fulvic acid, removal of turbidity and sludge production. Modelling of each of these quantities will be done by the response surface method.

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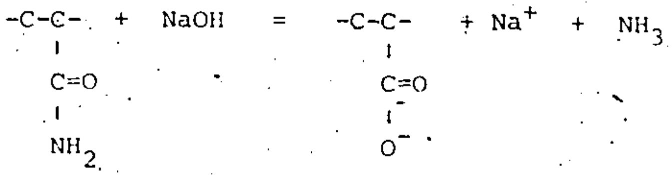
APPENDIX 1

HYDROLYSIS OF POLYACRYLAMIDE

The preparation of anionic polyacrylamide by hydrolyzing nonionic polyacrylamide can be represented by the following reaction



$$-C-\underset{\substack{|\\ C=O\\ |\\ NH_2}}{C}- \;+\; NaOH \;=\; -C-\underset{\substack{|\\ C=O\\ |\\ O^-}}{C}- \;+\; Na^+ \;+\; NH_3$$

During the hydrolysis, the $-NH_2$ group is substituted with a -OH group at alkaline pH. The reaction can be monitored by measuring the amount of ammonia released. The degree of hydrolysis is defined as the mass of monomer units hydrolyzed divided by the total mass of the polymer, and it is usually expressed as a percentage.

The hydrolysis was performed in the apparatus shown in Figure A.1. The experimental procedure was similar to that followed by Huck (1977). Some minor modifications were made, primarily in the amount of polymer used, in order to speed up dissolution and to ensure that no polymer was lost during the transfer of the viscous polymer solution. 100 mL of 1g/L nonionic polymer solution was transferred to flask A, and its temperature was raised to 50°C. During the entire process ultrapure nitrogen gas was bubbled through to inhibit any degradation of the polymer chains caused by oxygen at this elevated temperature. 50 mL of 0.01 N hydrochloric acid solution was placed in flask B. The hydrolysis reaction started when

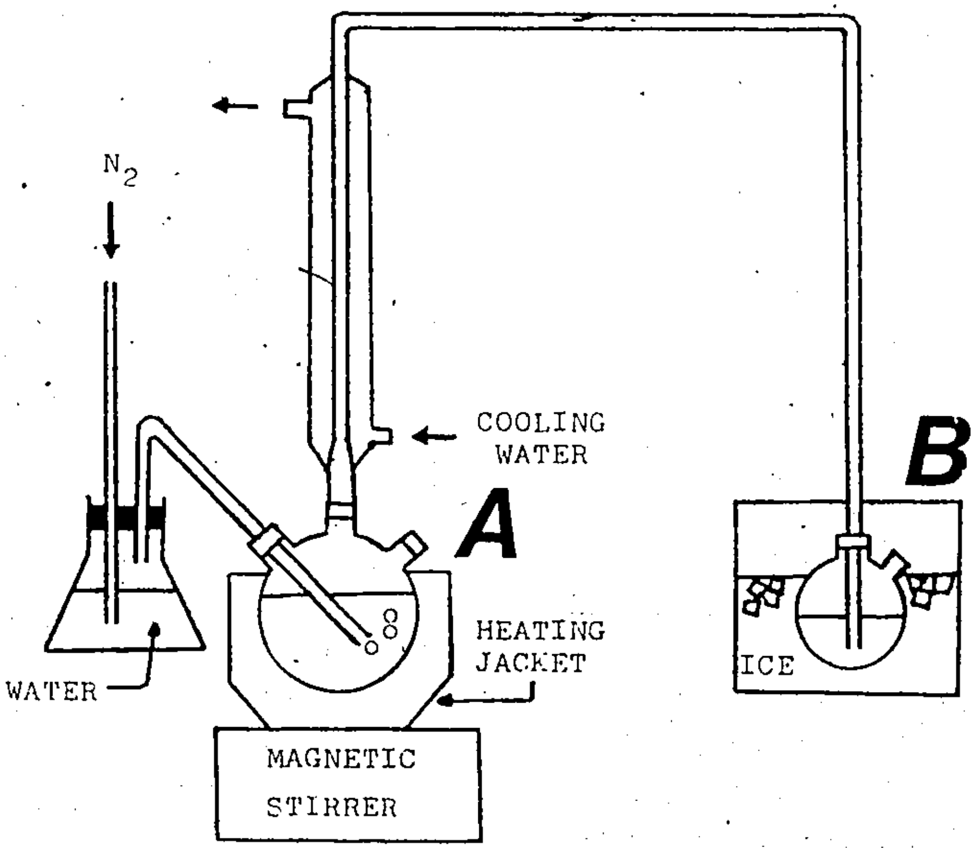


FIGURE A.1 Apparatus for the hydrolysis of the polymer

50 mL of 0.01 N sodium hydroxide solution was added to flask A. The ammonia produced was driven out of the polymer solution by the nitrogen gas and it was trapped into the hydrochloric acid solution in flask B. The amount of ammonia released could be quantitatively analyzed by measuring the change in the normality of the hydrochloric acid solution. When the desired degree of hydrolysis had been postulated to be reached, the reaction was stopped by immersing flask A in iced water. The polymer was precipitated by the slow addition of propanol up to a total volume of 1L, while the hydrochloric acid solution was titrated to pH 7.0 in order to determine the new normality of the solution and subsequently the precise degree of hydrolysis. The duration of the hydrolysis reaction was quite large. For the desired degree of hydrolysis of 25 percent, the duration of the reaction was approximately 16h. Despite the care taken to keep all experimental conditions consistent, the results of the hydrolysis reaction were not very reproducible. This was attributed to the heterogeneity of the hydrolysis reaction. Poor reproducibility was also a problem with previous studies that used similar schemes of hydrolysis (Benedek et al, 1976; Huck, 1977). Getting the exact degree of hydrolysis depended on developing the experience and by trial and error.

APPENDIX 2

EXPERIMENTAL DATA

A2.1 FILTRATION STUDY

Leaching of UV-contributing organics

mL of distilled water	Absorbance							
	0.45				0.10			
25	0.012	0.012	0.005	0.006	0.006	0.004	0.004	0.002
50	0.005	0.003	0.001	0.005	0.002	0.002	0.000	0.001
75	0.000	0.000	0.000	0.002	0.002	0.000	0.000	0.000
100	0.000	0.000	0.000	0.002	0.001	0.000	0.000	0.000
125	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
150	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
200	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
250	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000

Absorbance of untreated fulvic acid solution
Fulvic acid concentration= 10.0 mg/L

mL of fulvic water	Absorbance							
	0.45				0.10			
10	0.340	0.340	0.343	0.347	0.332	0.348	0.347	0.352
20	0.370	0.366	0.368	0.370	0.371	0.368	0.369	0.371
40	0.372	0.367	0.368	0.369	0.371	0.367	0.367	0.375
60	0.372	0.369	0.369	0.368	0.369	0.370	0.371	0.369
80	0.373	0.370	0.372	0.370	0.367	0.368	0.365	0.372
100	0.371	0.370	0.371	0.368	0.369	0.366	0.366	0.366
125	0.372	0.369	0.368	0.367	0.369	0.368	0.368	0.366
150	0.369	0.365	0.367	0.368	0.368	0.366	0.366	0.368

Absorbance of untreated fulvic acid solution
Fulvic acid concentration = 25.0 mg/L

mL of fulvic water	Absorbance							
	0.45				0.10			
10	0.758	0.746	0.754	0.767	0.778	0.774	0.773	0.783
20	0.856	0.850	0.846	0.849	0.858	0.849	0.851	0.851
40	0.863	0.855	0.850	0.859	0.856	0.856	0.853	0.855
60	0.879	0.855	0.855	0.857	0.855	0.855	0.854	0.856
80	0.864	0.859	0.858	0.856	0.853	0.856	0.856	0.855
100	0.861	0.858	0.855	0.855	0.853	0.856	0.854	0.855
125	0.859	0.858	0.858	0.854	0.861	0.858	0.856	0.856
150	0.862	0.857	0.855	0.859	0.856	0.855	0.858	0.853

Absorbance of the filtrate of aluminum-treated fulvic solution
Aluminum concentration = 0.5×10^{-3} M pH = 5.96

mL of filtrate	Absorbance					
	0.45			0.10		
10	0.010	0.008	0.000	0.008	0.008	0.001
20	0.000	-0.002	-0.002	0.000	0.000	0.000
40	0.001	-0.005	-0.003	0.004	0.004	-0.003
60	0.000	0.000	-0.006	0.000	0.001	-0.001
80	0.002	0.002	0.002	0.000	-0.002	0.000
100	0.000	0.000	0.000	-0.005	0.000	0.000
125	0.001	0.000	0.001	0.001	0.002	0.005
150	0.001	-0.003	0.001	0.001	-0.003	-0.005

Absorbance of the filtrate of aluminum-treated fulvic solution
Aluminum concentration = 0.5×10^{-3} M pH = 8.13

mL of filtrate	Absorbance					
	0.45			0.10		
10	0.239	0.258	0.267	0.058	0.060	0.055
20	0.109	0.290	0.296	0.042	0.041	0.038
40	0.045	0.266	0.292	0.041	0.036	0.032
60	0.040	0.115	0.239	0.038	0.030	0.032
80	0.040	0.060	0.085	0.038	0.030	0.036
100	0.042	0.041	0.048	0.038	0.028	0.032
125	0.041	0.038	0.041	0.036	0.030	0.030
150	0.040	0.037	0.042	0.038	0.030	0.027

Absorbance of the filtrate of aluminum-treated fulvic solution
Aluminum concentration = 0.71×10^{-4} M pH = 6.02

mL of filtrate	Absorbance						
	0.45				0.10		
10	0.020	0.020	0.025	0.036	0.025	0.028	0.029
20	0.055	0.038	0.068	0.078	0.024	0.025	0.032
40	0.134	0.024	0.167	0.178	0.021	0.023	0.022
60	0.120	0.018	0.197	0.194	0.021	0.022	0.022
80	0.049	0.020	0.166	0.145	0.023	0.024	0.024
100	0.019	0.021	0.060	0.081	0.017	0.019	0.020
125	0.017	0.016	0.031	0.027	0.019	0.021	0.022
150	0.017	0.018	0.024	0.021	0.020	0.019	0.024

Absorbance of the filtrate of aluminum-treated fulvic solution
Aluminum concentration = 0.71×10^{-4} M pH = 7.97

mL of filtrate	Absorbance					
	0.45			0.10		
10	0.311	0.320	0.315	0.261	0.271	0.265
20	0.356	0.352	0.350	0.318	0.322	0.320
40	0.360	0.357	0.356	0.343	0.338	0.339
60	0.359	0.359	0.358	0.351	0.347	0.345
80	0.359	0.360	0.358	0.347	0.349	0.346
100	0.359	0.353	0.360	0.344	0.349	0.345
125	0.364	0.362	0.358	0.345	0.344	0.344
150	0.364	0.365	0.359	0.343	0.340	0.345

Absorbance of the filtrate of aluminum-treated fulvic solution
Aluminum concentration = 10^{-5} M pH = 6.04

mL of filtrate	Absorbance					
	0.45			0.10		
10	0.337	0.339	0.353	0.351	0.348	0.339
20	0.371	0.372	0.369	0.371	0.369	0.363
40	0.377	0.369	0.370	0.369	0.369	0.367
60	0.371	0.369	0.373	0.369	0.366	0.366
80	0.374	0.371	0.372	0.367	0.368	0.367
100	0.373	0.369	0.368	0.369	0.367	0.365
125	0.370	0.372	0.370	0.366	0.370	0.369
150	0.369	0.370	0.375	0.369	0.367	0.369

A2.2 FULVIC ACID REMAINING IN SOLUTION AFTER TREATMENT WITH ALUMINUM

ALUMINUM SOURCE : $AlCl_3$

Aluminum concentration = 0.5×10^{-3} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
5.56	0.30	0.30	10.00	-
5.96	0.00	0.00	8.71	4.0
6.49	0.00	0.00	0.69	5.8
6.82	0.16	0.10	1.22	5.9
6.99	0.28	0.16	1.96	5.7
7.51	0.22	0.20	2.52	-
7.72	0.21	0.21	2.72	4.6
8.05	0.42	0.41	-	-
8.13	0.89	0.74	9.73	4.1

Aluminum concentration = 0.31×10^{-3} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.01		0.01	-	
6.55		0.20	2.81	
6.96		0.42	4.34	
		0.30	4.38	
		0.21	4.71	
		0.09	4.82	
7.51		0.80	6.11	
7.98		1.43	-	

Aluminum concentration = 10^{-5} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.04	9.39	9.28	10.0	0.4
6.54	9.57	9.57	10.0	0.4
6.97	9.68	9.66	10.0	0.4
7.62	9.88	9.73	10.0	0.4
8.09	10.00	10.00	10.0	0.4

Aluminum concentration = 0.188×10^{-3} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.05	0.05	0.02	10.00	-
6.26	0.17	0.07	10.0	4.1
6.49	-	0.11	6.48	-
6.59	0.18	0.16	5.63	4.3
6.78	0.18	0.18	8.27	4.9
7.01	0.23	0.22	8.49	-
		0.50		
		0.49		
		0.58		
7.16	0.37	0.38	8.76	5.1
7.49	-	0.98	9.40	-
7.70	1.68	1.41	9.79	2.9
8.02	-	3.04	9.96	-
8.59	9.01	6.42	10.00	0.9

Aluminum concentration = 0.71×10^{-4} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.02	0.23	0.24	9.22	4.9
6.55	7.44	1.13	10.00	3.0
6.95	9.97	1.95	10.00	2.2
7.28	10.00	3.34	10.00	1.6
7.97	9.84	9.27	10.00	1.2
8.29	9.70	8.65	10.00	0.8

ALUMINUM SOURCE : Alum

Aluminum concentration = 0.5×10^{-3} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.05	0.03	0.00	3.93	9.1
6.45	0.04	0.04	6.36	9.6
6.72	0.08	0.08	6.72	8.6
6.99	-	0.10	3.40	-
7.12	0.12	0.12	2.36	6.2
7.39	0.14	0.14	2.38	5.4
7.52		0.22	4.02	-
7.95	0.54	0.50	9.20	5.4

Aluminum concentration = 0.31×10^{-3} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.00		0.01	-	
6.55		0.04	7.20	
7.01		0.14	6.62	
		0.13	7.00	
		0.21	7.19	
		0.28	7.49	
7.55		0.48	8.51	
7.98		1.19	-	

Aluminum concentration = 0.188×10^{-3} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.05	0.09	0.05	10.00	5.1
6.32	0.08	0.08	6.63	5.1
6.49	0.09	0.08	7.77	-
6.64	0.10	0.08	8.87	5.2
7.04	0.24	0.22	8.39	5.0
		0.46		
		0.56		
		0.59		
7.50	0.69	0.57	10.00	4.9
8.01	5.02	2.00	10.00	-
8.19	9.88	2.76	10.00	5.1

Aluminum concentration = 0.71×10^{-4} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.05	0.44	0.23	9.69	4.2
6.55	9.63	0.77	10.00	2.9
6.96	10.00	2.02	9.98	2.0
7.45	10.00	8.75	10.00	1.4
7.99	10.00	9.34	10.00	0.9
8.28	10.00	9.89	10.00	0.7

Aluminum concentration = 10^{-5} M

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
5.52	9.19	9.12	9.81	0.4
5.95	9.50	9.44	9.80	0.4
6.53	9.80	9.75	9.87	0.4
6.95	9.84	9.85	9.98	0.4
7.53	10.00	9.98	10.00	0.3
8.02	10.00	10.00	10.00	-
8.26	10.00	10.00	10.00	-

A2.3 FULVIC ACID REMAINING IN SOLUTION AFTER TREATMENT WITH ALUMINUM AND POLYMER

ALUMINUM SOURCE : ALUM ONLY

ALUMINUM CONCENTRATION = 0.5×10^{-3} M

Polymer concentration = 0.001 mg/L

pH	FA-0.45	FA-0.10	FA-20min
7.12		0.15	
7.40		0.20	
7.92		0.55	

Polymer concentration = 0.01 mg/L

pH	FA-0.45	FA-0.10	FA-20min
6.08	0.00	0.00	3.10
6.49	0.00	0.00	5.17
6.69	0.00	0.00	3.67
7.16	0.02	0.00	2.27
7.50	0.10	0.10	2.09
8.03	0.63	0.48	9.75

Polymer concentration = 0.1 mg/L

pH	FA-0.45	FA-0.10	FA-20min
6.03	0.00	0.00	2.96
6.55	0.00	0.00	3.19
6.80	0.00	0.00	2.09
7.16	0.00	0.00	1.85
7.55	0.00	0.00	1.48
8.03	0.51	0.36	9.84

ALUMINUM CONCENTRATION = $0.188\text{x}10^{-3}$ M

Polymer concentration = 0.001 mg/L

pH	FA-0.45	FA-0.10	FA-20min
6.12	0.00	0.00	8.78
6.57	0.00	0.00	7.71
6.89	0.04	0.01	8.50
7.16	0.14	0.11	8.80
7.58	0.84	0.27	9.65
7.85	2.98	0.98	9.74

Polymer concentration = 0.01 mg/L

pH	FA-0.45	FA-0.10	FA-20min
6.05	0.00	0.00	6.90
6.55	0.00	0.00	8.44
6.89	0.12	0.16	8.83
7.10	0.17	0.10	8.24
7.60	0.81	0.60	9.61
		0.60	
		0.80	
		0.70	
		0.50	
		0.40	
		0.50	
7.97	2.05	0.84	9.64

Polymer concentration = 0.1 mg/L

pH	FA-0.45	FA-0.10	FA-20min
5.70	0.00	0.00	9.83
6.01	0.00	0.00	5.51
6.53	0.01	0.00	5.82
7.06	0.05	0.03	3.95
7.66	0.44	0.37	9.93
7.95	1.22	1.07	9.88
8.33	5.15	4.27	10.00

Polymer concentration = 1.0 mg/L

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
7.05		0.79	1.34	5.2
7.53		0.77	10.00	3.8
8.04		1.98	9.87	2.5

ALUMINUM CONCENTRATION = 0.115×10^{-3} M

Polymer concentration = 0.01 mg/L

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
7.08		0.92	7.42	3.7
7.48		1.76	-	3.2
7.98		3.30	-	1.6

Polymer concentration = 0.1 mg/L

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
7.03		0.41	9.26	3.8
7.47		1.09	10.00	3.1
		1.10		
		0.80		
		1.00		
		1.30		
		1.00		
		1.20		
7.98		3.93	-	1.7
8.15		5.64	10.00	1.4

Polymer concentration = 1.0 mg/L

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
7.02		0.71	8.36	3.5
7.45		1.18	9.94	3.2
7.98		3.32	10.00	1.6

ALUMINUM CONCENTRATION = 0.71×10^{-4} M

Polymer concentration = 0.001 mg/L

pH	FA-0.45	FA-0.10	FA-20min
6.14	0.21	0.09	9.35
6.38	2.84	0.28	9.74
6.68	9.75	0.50	9.89
7.07	9.65	7.58	9.99
7.50	9.82	9.05	10.00
8.28	9.79	9.40	10.00

Polymer concentration = 0.01 mg/L

pH	FA-0.45	FA-0.10	FA-20min
5.79	0.04	0.01	9.32
6.34	0.57	0.12	9.57
6.72	3.83	1.50	9.85
6.98	6.79	3.68	9.90
7.23	9.45	5.84	9.93
7.49	9.62	5.88	10.00
7.90	9.94	9.26	10.00

Polymer concentration = 0.1 mg/L

pH	FA-0.45	FA-0.10	FA-20min
6.03	0.08	0.10	8.20
6.94	0.59	0.61	9.81
7.25	2.51	2.16	9.91
7.50	5.73	3.67	9.96
7.75	7.58	3.27	9.98
8.05	8.25	5.78	10.00
8.32	8.11	7.28	10.00

Polymer concentration = 1.0 mg/L

pH	FA-0.45	FA-0.10	FA-20min	Turbidity
6.98		1.78	10.00	1.8
7.46		3.2	10.00	1.5
7.95		5.08	10.00	0.9

ALUMINUM CONCENTRATION = 10^{-5} M

Polymer concentration = 0.1 mg/L

pH	FA-0.45	FA-0.10	FA-20min
5.65	9.27	9.16	9.73
6.06	9.42	9.36	9.88
6.58	9.56	9.51	10.00
6.99	9.62	9.63	10.00
7.50	9.78	9.73	10.00
7.97	9.88	9.85	10.00

ALUMINUM CONCENTRATION = 0.0 M

Polymer concentration = 0.1 mg/L

pH	FA-0.10
6.09	10.00
6.98	9.99
7.43	10.00

FILTER CONDITIONING BY PRE-FILTRATION OF THE POLYMER SOLUTION

Aluminum concentration = 0.71×10^{-4} M

Polymer concentration in the jars = 0.0 mg/L

pH	FA-0.45	FA-0.10
6.57	9.06	0.15
7.09	10.00	3.27
7.46	9.92	8.23
7.92	9.83	9.50

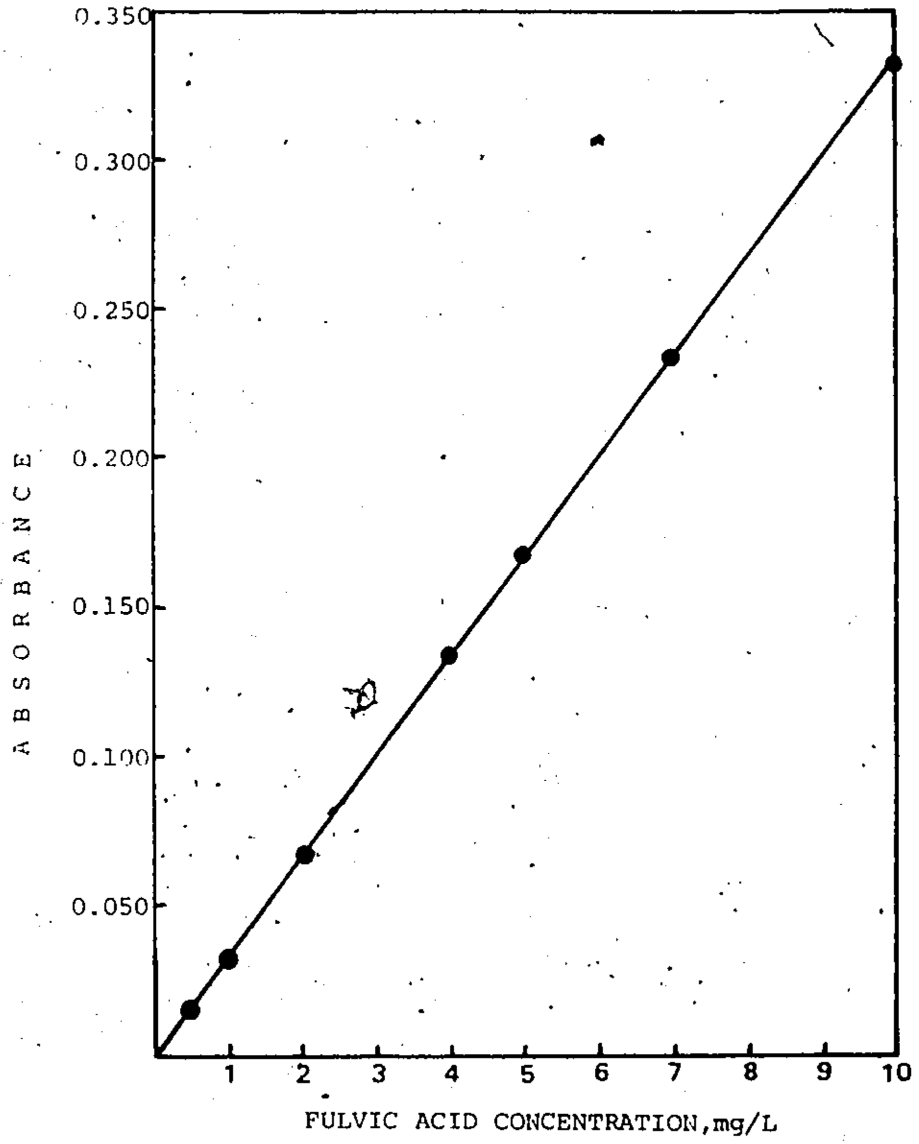
A2.4 RESULTS OF THE FRACTIONAL FACTORIAL EXPERIMENTAL DESIGN

FULVIC ACID REMAINING IN SOLUTION

Run Number	Fulvic Acid Concentration
1	1.91
2	0.57
3	1.70
4	0.40
5	1.70
6	0.40
7	1.70
7	1.61
7	1.64
7	1.64
7	1.58
7	1.70
8	0.40
9	2.90
10	0.75
11	2.60
12	0.69
13	2.78
14	0.75
15	2.75
16	0.54

APPENDIX 3

CALIBRATION OF THE SPECTROPHOTOMETER AT 254 nm



APPENDIX 4

pH MEASUREMENTS

A list of the pH electrodes tested is given below :

No	TYPE OF ELECTRODE	MANUFACTURER	CATALOG No	JUNCTION
1	Glass/Reference pair	FISHER	13-639-3 13-639-51	- porous ceramic
2	Combination,Glass body solution-filled	FISHER	13-639-91	porous ceramic
3	Combination,polymer body,solution-filled	FISHER	13-639-97	-"-
4	Combination,flat surface,solution-filled	CORNING	476216	-"-
5	Combination,polymer body,gel-filled	ORION	91-05	porous plastic
6	Combination,polymer body,gel-filled	FISHER	13-639-104	porous plastic
7	Combination Ross	ORION	81-02	porous ceramic

A problem associated with the measurement of the pH was caused by the release of CO_2 from solution due to carbonate equilibrium.When the response of the electrode was slow,the pH of the solution was increasing with time.Slow electrode response was the result of partially clogged junction due to KCl deposition.The electrode used was No 1.Its selection was based on the ability to clean the porous junction faster and more efficiently.The reference electrode is a calomel reference.

APPENDIX 5

ERROR ANALYSIS

For the statistical components of this thesis, the errors have been evaluated by the replicate runs and this information was used inherently in the statistical tests that discriminate between random error and significant effects of the variables.

A list of the variability of the measurements for the variables of this work is compiled below:

VARIABLE	REPRODUCIBILITY
pH	0.02 pH units
Absorbance	0.002
Turbidity	0.1 NTU
Removal after filtration	4 removal percentage points
Removal after settling	10 removal percentage points
Al dosage or polymer dosage	Very high, due to accurate measurement of the weight or volume