THE REMOVAL OF ORGANIC WASTE MATTER FROM SECONDARY SEWAGE EFFLUENTS BY CHEMICAL COAGULATION

by

EMMANUEL MILIS

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ABSTRACT

The removal of organic waste matter was investigated:

a) On both a maturation pond effluent and a secondary clarifier effluent, collected from the same municipal sewage-treatment plant, and

b) On a maturation pond effluent collected from a different municipal sewage-treatment plant.

The inorganic coagulants alum, ferric chloride and lime as well as organic polyelectrolytes were tested for their ability to remove the organic waste matter from the above effluents under various conditions of pH and coagulant concentration.

The tests were on laboratory scale and were conducted under constant room temperature, mixing and stirring conditions. A standard laboratory technique was employed which approximately simulates the large scale operation.

Removal was evaluated in terms of Chemical Oxygen Demand (COD) of the wastewater.

It was found that, among the inorganic coagulants tested, ferric chloride was, in all cases, the most effective coagulant for COD removal. In general, the final COD achieved with ferric chloride was between 10 and 40 milligrams per litre, depending on the initial COD level of the raw effluent.

For the hydrolyzing metal coagulants a certain technique was employed which enabled the determination of the optimum conditions for COD removal - optimum pH and coagulant dosage - to be carried out quite accurately. This was done by means of graphs such as those shown on page 50. The optimum pH for COD removal was found to be between 5 and 5,5 for alum coagulation, and between 4 and 5 for ferric chloride coagulation, in all cases - see pages 112 and 113.

For lime it was found that the higher the lime dosage - and, consequently, the pH -, the higher the COD removal.

The organic polyelectrolytes were only slightly effective in removing the organic waste matter from the effluents. These were very effective, however, especially the non-ionic and anionic polymers, in improving the floc settling characteristics when they were employed as flocculant aids in conjunction with the inorganic coagulants.

The coagulation and/or flocculation mechanisms applicable to each inorganic coagulant or group of polymer flocculants for either COD, colour, or turbidity removals were discussed.

The effects of the main parameters controlling the removal of organic waste matter on coagulation was also discussed for each coagulant.

A plot was made for each coagulant from which the minimum residual COD that can be achieved by chemical coagulation may be predicted, if the initial colour concentration is determined - see page 129. These plots, however, would have to be established for different sewage effluents.

A plot was made for each hydrolyzing metal coagulant from which the residual turbidity after coagulation may be predicted under certain conditions - see page 131.

Recommendations were made about the best operating pH ranges for maximum COD, colour, and turbidity removals.

The cost of the chemicals required for good COD removal was estimated to be approximately equal to 5 cents per kilolitre for any coagulant and any of the effluents treated (1975 prices).

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CHAPTER 1

BACKGROUND

1.1 INTRODUCTION TO WATER POLLUTION

According to Fair, Geyer and Okun, (1), water pollution is the introduction into water of substances that impair its usefulness or make it offensive to the senses of sight, taste or smell.

In most cases of water pollution, the pollutants are introduced by means of a polluted stream. Their effects vary according to their concentration as well as their physical and chemical character. These effects can be fatal to the aquatic life.

The "natural waters" may be polluted or not. The "wastewaters" may be either municipal or industrial. The municipal wastewaters may consist of only "domestic sewage", or domestic sewage and "industrial wastes".

Nature does not remain apathetic to the effects of pollution. Phenomena such as rainfalls, evaporation, etc., act as self-defence mechanisms and manage to control the rate of pollution in natural waters. For wastewaters, however, these slow-response mechanisms prove to be ineffective, because they cannot cope with the increased requirements for purification (removal or inactivation of pollutants). Therefore, they should be treated before they reach the receiving bodies. This becomes more and more imperative day by day due to the growing population on earth and the increasing manufacturing variety and throughput. The presently acceptable water quality standards of the receiving bodies require that these must be free from substances which will: (a) settle to form putrescent or otherwise objectionable sludge deposits, (b) produce colour, odour or other conditions in such a degree as to create a nuisance, (c) be toxic or harmful to human, animal, plant, or aquatic life. The receiving bodies must also be free from floating debris, oil, scum or other floating materials in amounts sufficient to be deleterious or troublesome.

1.2 WASTEWATER TREATMENT

The treatment of wastewaters and especially of municipal wastewaters, with which the present thesis deals, will only be considered.

The municipal wastewaters are treated to make them suitable either for discharge into a receiving body or for subsequent re-use.

In the first case, the wastewaters are usually subject to the conventional primary and secondary biological treatments. These consist of the following processes: (a) Primary sedimentation of raw sewage, (b) Biological treatment of settled sewage (trickling filter or activated sludge processes), (c) Biological treatment of the sludge obtained from the above two steps (anerobic digestion process), and (d) Stabilization of treated wastewater through maturation ponds. The effluents from the plants where these processes occur are "secondary effluents".

In the second case, a tertiary treatment is necessary. This consists of application of physico-chemical processes and results in better quality water.

At present, however, a tertiary treatment is considered necessary even before the treated municipal wastewaters are discharged into a receiving body. The reason is that the extent of purification achieved by the application of biological treatment processes (90 to 95 per cent removal of suspended solids, COD, and BOD) is not considered acceptable. The resulting secondary effluents still contribute to the environmental pollution.

A common basic chain of unit physico-chemical processes in tertiary treatment consists of one or more of the following processes,(2)

(i) Chemical coagulation and flocculation followed by floc settling,

(ii) Filtration of the clarified effluent,

(iii) Activated-carbon adsorption treatment of the filtered effluent,

(iv) Filtration of the sludge obtained from Step (i).

These processes completely remove the suspended matter and most of the soluble organic matter from the wastewater, which then becomes acceptable for discharge into a receiving body.

However, for the wastewater to become suitable for subsequent re-use a further removal of a large portion of the inorganic soluble fraction of its total solids content is necessary. This may be achieved by the application of demineralization processes (e.g. reverse osmosis, ion-exchange, distillation, etc.).

A sterilization process (e.g. chlorination, ozonation, ultra-filtration, etc.) may be included in the final stages of treatment when the ultimate aim is the production of water for human consumption.

A classification of the secondary effluent pollutants and contaminants and a selection of various tertiary unit processes for their removal is presented in Figure 1.1,(3). This Figure helps to evalu-

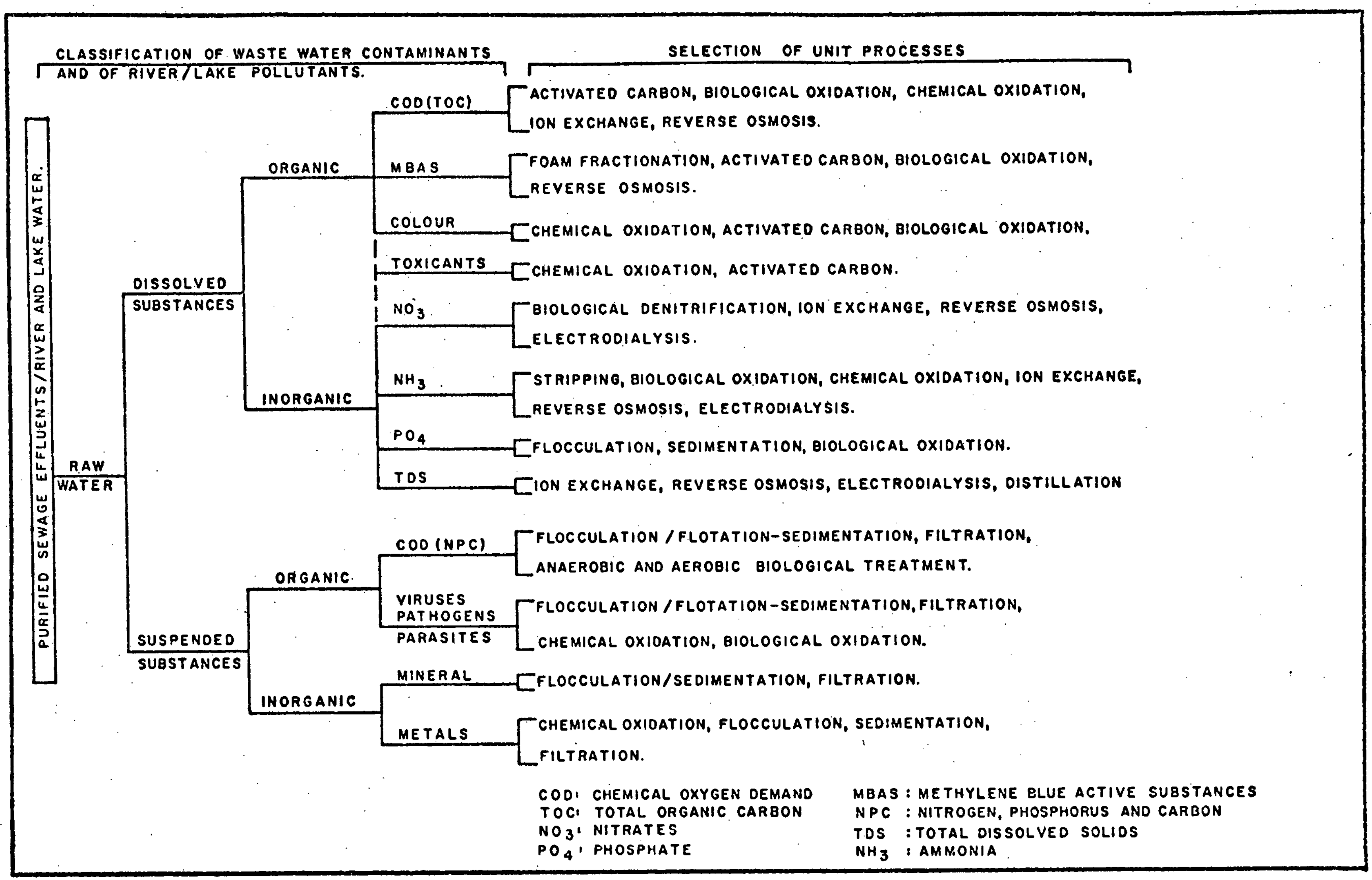


FIG. 1.1

CLASSIFICATION OF WASTEWATER CONTAMINANTS AND SELECTION OF PROCESS UNITS ate the potential of the chemical coagulation process, with which the present thesis deals, in removing contaminants and pollutants from wastewater. In Figure 1.1 chemical coagulation is referred to as "flocculation". This difference in terminology will be discussed in Section 2.1.

1.3 AIM AND OBJECTIVES OF THE PRESENT THESIS

The aim of this thesis was to investigate the efficiency of different chemical coagulants in removing suspended as well as dissolved organic impurities from secondary sewage effluents. From this, information could be provided on the feasibility of using chemical coagulation as an additional step in increasing the efficiency of existing treatment plants or, as a preliminary step, for the subsequent application of demineralization processes for the production of re-usable water. When applied on a large scale, the coagulation process would be the sole or the first step of the tertiary treatment stage in order to produce better quality water. If water recovery (that is purification for subsequent re-use) is envisaged, chemical coagulation may be a desirable preliminary step to reverse osmosis or ion-exchange. If water purification is only required, then chemical coagulation alone may be employed. The results reported in this thesis are applicable to the use of chemical coagulation for either purpose.

The chemical coagulation process was applied to samples of secondary sewage effluents on laboratory scale and under conditions such as to simulate the large-scale operation. A means of determining the extent of organics concentration was necessary. The entire range of organic compounds is most often represented by their COD, and the organic removal is best seen by the COD reduction. The COD and the total organic carbon (TOC) determinations may be the only methods for determining the organic load of certain wastwaters containing toxic substances, as the sewage effluents may do. Since the turbidity and colour of a sewage effluent are mostly produced by particles or substances of organic character - see Appendix D -,they each constitute a portion of the total COD level of the effluent. The change in COD, then, and not the turbidity or colour has been employed in this study to measure the removal of the organic waste matter.

The objectives of the present thesis were firstly, to investigate the potential of representative inorganic coagulants and organic polyelectrolyte flocculants in removing COD, either this was due to dissolved substances, suspended particles, or colour; secondly, to determine the process parameter which is primarily responsible for control of the removal of the organic matter from sewage effluents; and, thirdly, to examine the underlying coagulation and flocculation mechanisms applicable to each particular coagulant or flocculant under conditions of effective removal.

In order to do this, effluent samples from two sewage treatment plants were collected and treated in a similar manner.

1.4 ORIGIN OF THE TREATED EFFLUENTS - HISTORY OF TREATMENT

The one sewage purification plant is situated at Milnerton, Cape Town. From this plant effluent samples were collected from two different points along the effluent flow path:

(a) From the overflow of the secondary clarifiers (humus tanks), where settling of the suspended bacterial aggregates carried over from the trickling filters occurs, and

(b) From the overflow of the last maturation pond.

The effluent samples collected in this manner corresponded to a settled trickling filter effluent - or, humus tank effluent - and to a maturation pond effluent, respectively. Since the extent of their treatment was different, their composition and strength was also different. Therefore, the above two effluents may be considered as being unrelated sewage effluents of different origin. The first one is referred to as Milnerton Humus Tank (MHT) effluent, while the second one as Milnerton Maturation Pond (MMP) effluent.

The other treatment plant is situated at Athlone, Cape Town. From this plant samples were collected from the overflow of the last maturation pond only. The effluent sampled in this manner is referred to as Athlone Maturation Pond (AMP) effluent.

The treatment which the raw sewage had undergone in these two plants was similar. It consisted of primary sedimentation, followed by biological treatment through trickling filters, subsequent secondary clarification in humus tanks, and, finally, stabilization through a series of maturation ponds. No additional treatment was applied.

Thus, the raw sewage in both plants received conventional (primary physical and secondary biological) treatment, and each effluent was a secondary sewage effluent.

CHAPTER TWO

LITERATURE SURVEY

2.1 COAGULATION AND FLOCCULATION

According to Daniels, (4) the physical process of sedimentation of the suspended particles in raw waters and wastewaters is enhanced by coagulation and flocculation initiated by chemical and/or physical agents. The effect of coagulation and flocculation is the agglomeration of the fine and colloidal particles into larger and denser aggregates, which settle more rapidly and more completely. Coagulation and flocculation can occur simultaneously, and in most cases do, or occur with some degree of overlapping. They can be represented to occur sequentially as shown in Figure 2.1, (4).

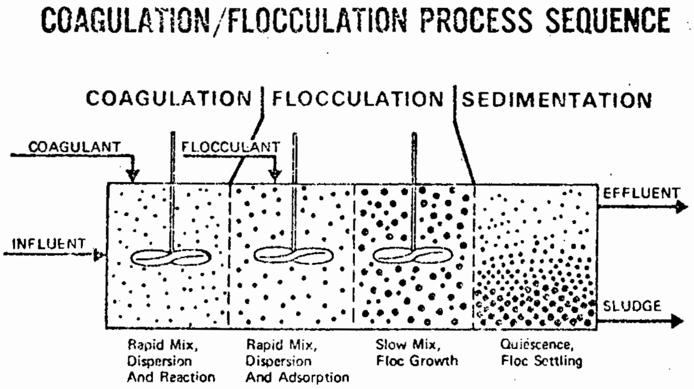


Figure 2.1

The two processes may be distinguished by their mechanisms of destabilization, the types of chemicals used to initiate them and the sizes of particles developed.

Generally, the aggregation of particles in a colloidal dispersion involves two distinct steps: (1) particle transport to effect particle contacts, and (2) particle destabilization to permit attachment when contact occurs. Particle transport in aqueous systems is essentially a physical process. Particle destabilization is a colloid-chemical process and is controlled by both chemical and physical factors.

La Mer, (5), (6) has distinguished between the terms "coagulation" and "flocculation". He describes coagulation as the process of destabilization by compression of the electrical double-layer that exists around each single particle, while flocculation as the process during which adsorption of large polymers and formation of bridges between the polymers and the particles occur, resulting in formation of a three-dimensional floc network.

Coackley and Wilson, (7) state that Gregory has pointed out that, as far as the cationic polyelectrolytes are concerned, no differentiation between coagulation and flocculation can be made in practice. They also state that Black has considered the coagulation and flocculation of suspensions with alum to proceed in three steps:

"(i) The rapid neutralization of the zeta potential of the particle,

(ii) The formation of positively charged microflocs, which can still remove negatively charged particles, and

(iii) A step involving the formation of a large well formed floc similar to that considered by La Mer to be true flocculation".

Coackley and Wilson avoid the use of the word coagulation and use only the term flocculation to describe visible size floc formation, according to La Mer's suggestion.

Daniels, (4) defines as coagulation the conversion of colloidal (< 0,001 mm) and dispersed (0,001 - 0,1 mm) particles into small visible floc (0,1 - 1 mm) upon the addition of a simple electrolyte. As flocculation he defines the further agglomeration into a small slowly-settling floc (1 - 10 mm) by an organic polyelectrolyte.

O'Melia, (8), however, terms as coagulation the overall process of particle destabilization and particle transport, while as flocculation the transport step only.

O'Melia's terminology is adopted and used in the present thesis, since the exact mechanisms of particle destabilization in water treatment are not completely clear, yet. The term "coagulant" refers here to a chemical that is involved in both the particle destabilization and particle transport steps, while the term "flocculant" refers to a chemical that is involved only in the transport step.

According to O'Melia, (8) coagulation may be brought about by chemical coagulants which are directly added to the system (e.g. synthetic polymers), or are produced within the system from other substances added to it (e.g. in the case of Al salts), or even are produced entirely within the system (e.g. in the case of bioflocculation, where destabilization is brought about by extracellular polymers secreted by micro-organisms). Furthermore, different coagulants may accomplish particle destabilization in different ways.

Many coagulants and flocculants exist - see references (4), (9) -, but those which have been most widely used in the wastewater treatment practice are the aluminum and ferric salts, lime - $Ca(OH)_2$ - and, recently, the synthetic organic polyelectrolytes. Therefore, this study will deal only with the destabilization mechanisms that are applicable upon use of these chemicals to bring about coagulation of the dispersed particles in water or wastewater. These mechanisms are similar for water and wastewater coagulations.

2.2 DESTABILIZATION MECHANISMS IN WATER AND WASTEWATER TREATMENTS

Generally speaking, there is no presently-available single theory of colloid behaviour that can account for and explain all the experimental findings in a quantitative manner. Different mechanisms have been proposed by different investigators to explain the destabilization phenomena. These phenomena are greatly influenced by the physical and chemical character of the dispersed phase, the physical and chemical reactions that are induced upon addition of the coagulants to water, and by the composition of the water medium. Therefore, the mechanism - or mechanisms - that applies when each particular coagulant - or group of coagulants showing similar behaviour upon their addition in water - is considered, will be dealt with separately.

2.2.1 Destabilization Mechanisms Applicable to Coagulation with Aluminum or Ferric Salts

The most important mechanisms or models which have been proposed to describe the mode of destabilization induced by the addition of Al or Fe(III) salts in water are discussed below:

(1) The double-layer model considers only one type of colloid-coagulant interactions (Coulombic forces) and neglects solvent interactions with the colloid and the coagulant. This model may be used to describe only a certain number of systems. It emphasizes the concept of the electrical double layer, and the significance of predominantly physical factors. In an oversimplified way it may be described as follows, (10):

"Foreign" ions are adsorbed on the surface of the dispersed particles and render them electrically charged. Upon addition of indifferent electrolytes - electrolytes whose ions do not interact chemically or are specifically adsorbed by the colloidal particles - coagulation is brought about by counter-ion adsorption and compaction of the diffuse part of the double layer while simultaneous charge neutralization takes place. Destabilization, according to this mechanism, is caused by the Al^{3+} or Fe^{3+} ions upon addition of the aluminum or ferric salts in water.

The double-layer model is based on the theoretical model developed by Verwey and Overbeek, (8) for the stability of colloids which predicts that destabilization is brought about by the counter ions and that the efficacy of these ions increases with the sixth power of their charge or valence. The Verwey-Overbeek theoretical model was experimentally verified when Hardy, using observations of Schulze, formulated the Schulze-Hardy rule. This rule states that coagulation is brought about by the ion of opposite charge to that of the colloid, and that the efficacy of this ion increases markedly with its charge or valance. It is in agreement with the Verwey-Overbeek model.

The double-layer model is not considered capable of explaining the coagulation phenomena appearing upon addition of Al or Fe(III) salts in natural waters or wastewaters, at present.

(2) Packham (11), (12), has done a literature survey on the coagulation process and has discussed the various mechanisms which have been proposed by different investigators at times to explain the coagulation phenomena.

Mattson was the first to suggest that the positively charged hydrolysis products of aluminum are more effective for the coagulation of negatively charged clay suspensions than the aluminum ion itself. Investigating the coagulation of mineral suspensions with aluminum sulphate, Packham, (13) verified the finding of Mattson and other investigators that the hydrolysis products of aluminum rather than the aluminum ion are responsible for coagulation. Based on his own experimental findings, (14) he established other previous findings, that the turbidity removal occurs by "enmeshment" in a "mass of rapidly precipitating and flocculating aluminum hydroxide", when aluminum sulphate is used as coagulant. This rapid precipitation is most complete at about pH 7, which is the isoelectric point of aluminum hydroxide.

The behaviour of ferric salts, when used as coagulants, has been shown to be similar to that of aluminum salts - see Section 2.4.

(3) As a result of alkalimetric titration experiments, Stumm and Morgan, (10) have concluded that the effect of aluminum or ferric ions is brought about not by these ions, but by their polymeric hydrolysis

products upon coagulation.

They have presented evidence that confirmed the importance of chemical forces in the destabilization of colloids in water treatment, and have suggested and demonstrated that "specific chemical interactions" between the hydrolysis species of the coagulant metal ions and carboxylic, phosphato, sulphato, or aromatic hydroxy functional groups, existing in solution or on the surface of colloidal particles, are primarily responsible for the removal of dissolved and colloidal impurities such as colour, proteins and carbohydrate materials. Alkalimetric titration experiments revealed that co-ordinating anions displace the aquo groups of the coagulant metal ions. In the absence of complex forming anions other than OH^-, hydroxyl ions will tend to satisfy the co-ordinative requirements of the metal ion. Other complex forming anions, when present, may compete with OH^- ions for the co-ordinative sites and may completely or partially substitute for OH^- ions in the charge neutralization reaction of the metal cations.

(5) Stumm and O'Melia, (15) have presented a simple "adsorption model" that, in principle, permits a quantitative description of the interrelationships between the coagulant dosage, pH, and the surface area concentration of the dispersed phase. They emphasized the chemical factors that are effective in the destabilization of colloids, without ignoring the significance of mass transport in the overall process of particle aggregation. They reasoned that in view of the accepted theory of hydrolysis of metal ions, polynulcear hydrolysis products may occur as soluble kinetic intermediates in a transition stage before the precipitation of the metal hydroxide occurs. They suggested that coagulation is a time-dependent process including the following steps, (15):

"(1) Hydrolysis of multivalent metal ions and subsequent polymerization to multinuclear hydrolysis species, (2) Adsorption of hydrolysis species at the solid-solution interface to accomplish destabilization of colloids, (3) Aggregation of destabilized particles by interparticle bridging involving particle transport and chemical interactions, (4) Aggregation of destabilized particles by particle transport and van der Waal forces, (5) Ageing of flocs, accompanied by chemical changes in the structure of Me-OH-Me linkages, concurrent change in floc sorbability and in the extent of floc hydration, and (6) Precipitation of the metal hydroxide".

Stumm and O'Melia, (15) have supported the view that the hydrolysis products of ferric and aluminum ions have a different charge than the metal ions themselves, and are adsorbed more readily at particle-water interfaces than nonhydrolyzed metal ions. This tendency to be adsorbed is especially pronounced for polynuclear polyhydroxo species.

According to the same investigators, the attraction of the surface for the adsorbate may also result from chemical interactions such as hydrogen bonding, co-ordination reactions, covalent bonding, ion-exchange reactions, and electrostatic effects.

2.2.2 Destabilization Mechanism Applicable to Coagulation or Flocculation with Organic Polyelectrolytes

La Mer and co-workers, (16) have developed a "bridging theory", which provides an acceptable qualitative model for the ability of polymers to destabilize colloidal dispersions, (8). To be effective in destabilization, a polymer molecule must contain chemical groups which can interact with sites on the surface of the colloidal particles. This interaction is an adsorption reaction that results in charge neutralization. When a polymer molecule comes into contact with a colloidal particle, some of the chemical groups adsorb at the particle interface leaving the remainder of the molecule extending out into the solution. If a second particle with some vacant adsorption sites contacts these extended segments, attachment can occur. A particle-polymer-particle complex is thus formed in which the polymer serves as a bridge. If a second particle is not available, in time the extended segments may eventually adsorb on other sites of the original particle, so that it is no longer capable of serving as a bridge, (8).

The kinetics of the adsorption are assumed to follow a Langmuir isotherm, where the surface coverage is a function of a polymer concentration in the electrolyte and a parameter b, analogous to the equilibrium constant used in gas adsorption theory, (7).

According to this model the following requirements are necessary for coagulation or flocculation to occur, (7):

(1) that extended polymer segments are available for interparticle bridging,

(2) that the segments are of sufficient length and number, and

(3) that free surface sites are available.

2.2.3 Destabilization Mechanism Applicable when Lime is Used as Coagulant

Lime has been used extensively for the coagulation of sewage and industrial wastes and, in general, has not given as good results as aluminum or ferric salts.

Once lime is added to water or sewage, the calcium hydroxide reacts with bicarbonates to precipitate calcium carbonate. It also reacts with phosphates precipitating calcium phosphates. Although neither of these precipitates forms flocs, the addition of lime beyond the amount required to precipitate the carbonate and phosphate (the bulk of phosphates is already removed at pH 9 to 9,5, but above pH 10,5 a very low residual amount remains, (17)) will lead to calcium hydroxide going into solution, (2). Consequently, the pH will rise above 9,5 and magnesium present initially as bicarbonate, carbonate, sulphate, or chloride will precipitate as a gelatinous floc, (17), (18).

The magnesium hydroxide floc is a voluminous coagulant with relatively high specific surface area, and it is a good adsorber of contaminants. Magnesium hydroxide is removed completely from solution only when a pH as high as 12 or higher prevails, (18). Usually, there is sufficient magnesium present in the water for enough of it to be precipitated to ensure good clarification of the waste at pH levels below 11,5. The calcium carbonate is enmeshed in the floc formed by the magnesium hydroxide and tends to act as a weighing agent.

Folkman and Wachs, (19) state that it has been shown that the positively charged magnesium hydroxide rather than the negative calcium carbonate floc is the main agent for removal of negative colloids in sewage. The removal mechanism functions via charge neutralization and subsequent adsorption of the colloidal particles on the magnesium hydroxide floc.

2.3 PARTICLE TRANSPORT (FLOCCULATION)

According to O'Melia, (8) interparticle contacts can be caused by the functioning of three particle contact mechanisms. These are: (a) Brownian diffusion (thermal motion) of particles, (b) Bulk-fluid motion (mechanical motion), and (c) Differential settling (gravity motion) - in which a rapidly settling particle overtakes and collides with another settling at slower rate.

O'Melia, (8) has briefly discussed the basic theories which apply in particle transport and have been the product of work of Smoluchowski who distinguished between two kinds of flocculation. When interparticle contacts are produced by Brownian motion, the transport process is called "perikinetic flocculation". When these contacts are caused by fluid motion, the process is called "orthokinetic flocculation".

Fair and Gemmell, (20) have developed a simplified mathematical model of floc growth in a stirred suspension with the aid of Smoluchowski's equation for orthokinetic flocculation. These authors have numerically solved Smoluchowski's equation.

Harris, Kaufman and Krone, (21) have studied the effects of fluid-flow patterns in continuous flow processes on flocculation efficiency. They state that the degree of completion of the flocculation reaction contained in continuous flow or batch reactors is a function of the product of a rate constant, the mean velocity gradient, the retention period, the quantity of floc in the system, and a parameter characterizing the floc size distribution. According to these investigators, the flocculation rate constant is a function of the physico-chemical parameters generally associated with coagulation.

Herbert and Hudson, (22) have derived a mathematical relationship describing the kinetics of flocculation. This takes into account the flocculating time and intensity, the coagulant dosage, the volume of the floc, and the solids content of the floc. It indicates that the entrapment of suspended matter by floc is influenced by the volume of the floc produced rather than by the size or appearance of the floc particles. Experiments have indicated that the floc can be made ten times more compact by extended agitation than by limited agitation, without imparing its settling characteristics.

It would be useful to define the meaning of some terms used in the particle transport field. The initial step in chemical coagulation as soon as the coagulant is added is called "mixing", if considered alone. "Mixing" describes the specific blending of coagulating chemicals with water in order to create a more or less homogeneous single or milti-phase system. "Stirring", by contrast, describes the disturbing of the flow pattern of a fluid in a mechanically orderly way for the purpose of effecting a dynamic redistribution of particles by the induced turbulence. Random rather than orderly turbulence can be distinguished by the term "agitation". Mixing is a brief operation seeking a quick response, often in advance of stirring or agitation. Stirring or agitation aim usually at the conjunction of suspended particles or flocs. From another viewpoint flocculation may be regarded as the combination of mixing and stirring or agitation that produces aggregation.

2.4 EXPERIMENTAL FINDINGS IN RELATION TO BOTH THE HYDROLYSIS OF Al OR Fe(III) IONS AND THE THEORIES OF DESTABILIZATION

2.4.1 Hydrolysis of Ferric Ion

Stumm and Morgan, (10) have stated that in dilute solutions of ferric ion the species Fe^{3+}, $Fe(OH)^{2+}$, $Fe(OH)_2^{+}$ and $Fe_2(OH)_2^{4+}$ are present. In more concentrated solutions they claim that the tetrapositive-dimeric species is the most important protolysis product. At higher pH the species $Fe(OH)_4^{-}$ predominates. Since cationic ferric hydroxocomplexes prevail in slightly acidic or neutral solutions, positively charged ferric hydroxide colloids are expected to be formed in this pH range. Under alkaline conditions, the polymerization of $Fe(OH)_4^{-}$ species leads to the formation of negatively charged colloids.

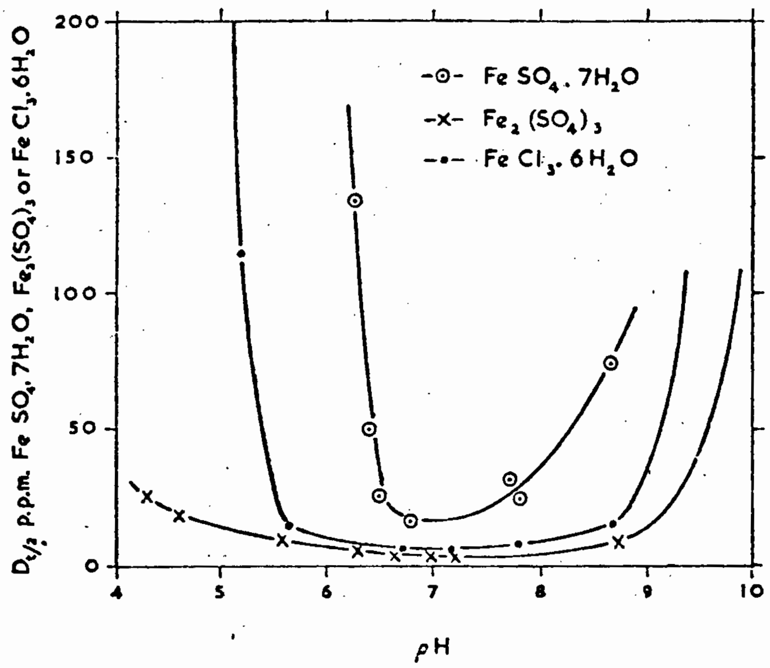
Packham, (11) mentions that Bartow, Black and Sansbury have found that with ferric salts, floc formation and coagulation takes place within a zone between pH 5 and 7, pH 6,1 being the optimum. The optimum pH range for coagulation with ferric salts given by these authors differs from the findings of Hopkins and Whitmore, who have found that coagulation with ferric salts was satisfactory at all pH levels above pH 3,5.

Zhukova *et al.*, (23) studying the precipitation of ferric hydroxide at constant ionic strength 0,5 M, have found that ferric hydroxide was precipitated above pH 6, under these conditions, that the minimum solubility of the hydroxide was (1,5 ± 0,1) × 10^{-5} M, and that maximum precipitation of ferric hydroxide was obtained at pH between 6,5 and 12.

Stumm and Morgan, (10) have reported that Lengweiler and co-workers gave as the isoelectric point of the Fe^{3+} ion hydrolysis species pH 6,7. Webb, (24) mentions that the isoelectric point of ferric hydroxide is approximately pH 8 (minimum solubility and highest rate of precipitation are usually observed at the isoelectric point). Stumm and Morgan, (10) have demonstrated via alkalimetric titrations, that rapid coagulation with ferric coagulant is only possible between approximately pH 4 and 6. Lengweiler and co-workers were led to the abovementioned conclusion by determining at which pH equal quantities of ion species move to the anode and to the cathode. Stumm and Morgan, however, have considered that such a method for the determination of the isoelectric point does not take into account the effect of hydrogen and hydroxyl ions, which are potential determining ions upon hydrolysis. They were led to their own conclusion not by performing electrophoretic measurements, but by conducting alkalimetric titration experiments.

The results of coagulation tests carried out at the Water Research Association on 50 ppm Kaolin suspensions using ferric salts are shown in Figure 2.2, (12). From this Figure it is apparent that most effective coagulation occurred at about neutral pH values, where ferric hydroxide seemed to have precipitated most rapidly, and that the effect of anions was important in precipitation.*

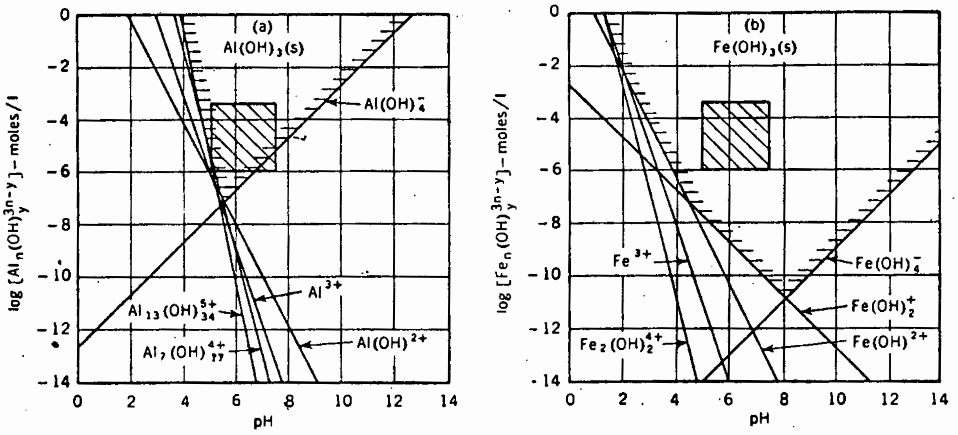
Stumm and O'Melia, (15) have presented the results of calculations for the solubility of "freshly precipitated" ferric hydroxide. These results are shown in Figure 2.3-(b), where the equilibrium concentrations of iron hydrolysis species in solution in contact with freshly precipitated ferric hydroxide are given as a function of pH.



Coagulation of 50 ppm kaolin with iron compounds

Figure 2.2

*$D_{t/2}$ in Figure 2.2 is the coagulant dosage required to halve the initial turbidity.



Equilibrium Composition of Solutions in Contact With Freshly Precipitated $Al(OH)_3$ and $Fe(OH)_3$

Figure 2.3

2.4.2 Hydrolysis of Aluminum Ion

The hydrolysis of aluminum ion is more complicated than that of ferric ion. The main hydrolysis product is a soluble polymeric aluminum hydroxo-complex with a stoichiometric ratio of OH^- to Al^{3+} of 2,5 : 1, (10). According to Stumm and Morgan, (10), Brosset has suggested $Al_2(OH)_{15}^{3+}$ as the most likely structure. Matijevic and co-workers, on the other hand, have concluded that the hydrolysis of aluminum ion in the pH range 4-7 leads rather to the formation of $Al_8(OH)_{20}^{4+}$. Hall and Packham, (25) state that Beiderman has suggested the formulations $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$. Stumm and O'Melia, (15) have supported these formulations. According to Hall and Packham, (25) there seems to be a general agreement that polynuclear complexes are formed, which can reverse the charge of negative colloidal particles and which have the approximate composition $Al(OH)_{2,5}$.

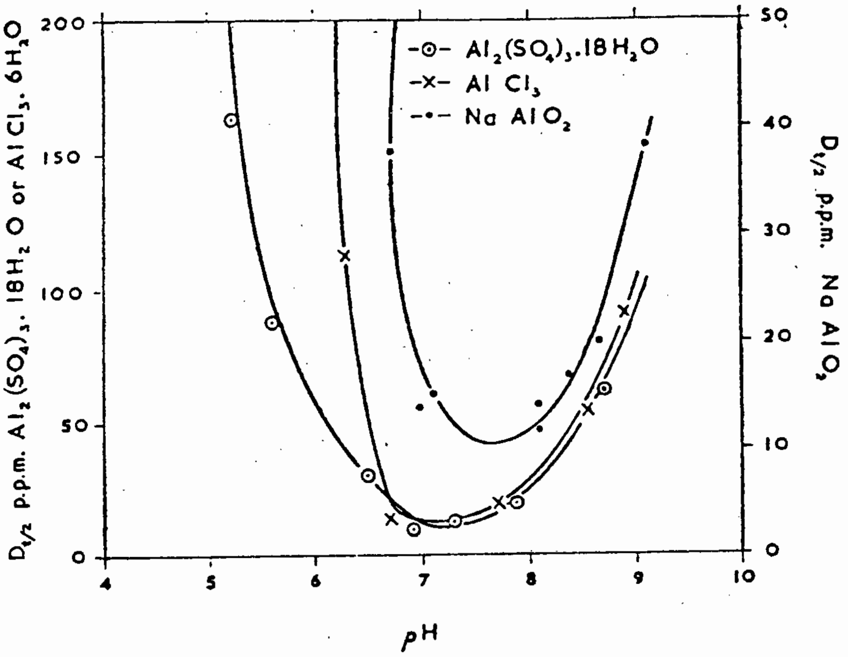
Stumm and Morgan, (10) have proposed a stepwise conversion of the Al^{3+} species via the intermediate hydrolysis species to eventual formation of $Al(OH)_4^-$, which predominates at basic pH values.

According to Packham, (11) Wolman and Hannan, in their review of the reactions of aluminum sulphate, state that efficient coagulation takes place only in the isoelectric range where the maximum quantity of aluminum hydroxide is formed. At too high a pH the aluminum hydroxide disappears, either due to peptisation in alkaline media or aluminate formation. At too high or too low pH values residual aluminum appears in solution. Hatfield has found that optimum coagulation and minimum residual aluminum were obtained within the range 5,8 to 7,5 pH. Blum has shown that precipitation of aluminum hydroxide commences at pH 3 and is complete prior to pH 7. Dissolution of the hydroxide begins at pH 7 and is complete at pH 10,5. Buswell and Edwards have shown that the solubility of aluminum hydroxide is at a minimum between 5,5 and 7,8 pH. Theriault and Clark have concluded that the isoelectric point of aluminum hydroxide is at pH 5,6, but they have observed that optimum coagulation occurred between pH 4,95 and 5,4. This indicates that most rapid coagulation takes place slightly below the isoelectric point of aluminum hydroxide. Miller has found that the solubility of aluminum hydrolysis products was least between pH 6,7 and 7. Peterson and Bartow have shown that coagulation was most rapid in a narrow zone between pH 7,3 and 7,4. Packham has found, (14) that maximum precipitation of aluminum occurs between pH 5,5 and 7,2, but that the highest rate of precipitation of aluminum hydroxide occurs at pH 7.

Zhukova *et al.*, (23) have found that aluminum hydroxide precipitated between pH 4,2 and 12 (at constant ionic strength 0,5M), that the minimum solubility of the hydroxide was equal to $(0,2 \pm 0,01) \times 10^{-3}M$, and that maximum precipitation of $Al(OH)_3$ was obtained between pH 6 and 9,5. Stumm and Morgan, (11) have shown that rapid precipitation of aluminum hydroxide occurs between about pH 5 and 7. This result is in agreement with Packham's, (14).

The results of coagulation tests carried out at the Water Research Association on 50 ppm Kaolin suspensions using aluminum salts are shown in Figure 2.4, (12). From this Figure it is observed that most effective coagulation occurred at about neutral pH values, where the aluminum hydroxide precipitated most completely.

Stumm and O'Melia, (15) have presented the results of calculations of the equilibrium concentrations of the aluminum ion hydrolysis species in solution in contact with freshly precipitated aluminum hydroxide. These are shown as a function of solution pH in Figure 2.3-(a).



Coagulation of 50 ppm kaolin with aluminium compounds

Figure 2.4

From the experimental findings presented in Section 2.4.1 and the present Section it may be concluded that the isoelectric point of aluminum hydroxide is at about pH 7. In the case of ferric hydroxide the results are rather inconclusive. Accepting Stumm and Morgan's results it should be at about 5 pH. Accepting the rest of the results it should be at about neutral pH. The results shown in Figure 2.4 support the finding according to which pH 7 is the isoelectric point of aluminum hydroxide. Those shown in Figure 2.2 suggest a similar isoelectric point for ferric hydroxide. (It is assumed that the removal of the Kaolin dispersion occurred by enmeshment, and that it is optimum at the pH at which the corresponding metal precipitate precipitates most rapidly in the absence of Kaolin - See Appendix A).

2.4.3 Experimental Findings Related to the Mechanisms of Coagulation or Flocculation with Al or Fe(III) Salts, Lime, and Organic Polyelectrolytes

The present stage of development of the theories of destabilization and particle aggregation is described in Appendices A, B and C.

2.4.4 Conclusions on the Potential of Chemical Coagulation

From what has been mentioned in the present Chapter, as well as in Appendices A, B and C it is concluded that chemical coagulation can, under certain conditions, remove suspended organic and inorganic waste matter, soluble organic and inorganic waste matter, and viable bacteria and algae from water. Similar conclusions apply to wastewaters. The removal of the organic suspended and soluble waste matter, as well as of algae, bacteria, and viruses from wastewaters - or, more specifically, from municipal sewage effluents - by chemical coagulation is discussed in detail in Appendix E.

2.5 NATURE OF SUSPENDED AND DISSOLVED ORGANIC IMPURITIES IN SEWAGE EFFLUENTS

This subject is discussed in Appendix D.

2.5.1 Conclusions Drawn from the Survey of the Nature of Organic Impurities in Sewage Effluents

From the discussion presented in Appendix D it becomes apparent that the results which have been reported by different investigators concerning the composition of organic substances in sewage effluents have been influenced by the origin of the individual effluent, its extent and history of treatment, and the method of analysis applied for the isolation of the organic substances. It seems, however, that, in the majority of cases, the colloidal and soluble fractions - as defined by Ricker and Hunter, (26), (27) - are the fractions which contain most of the organic waste matter in a sewage effluent.

It is useful to note that the treatment of the sewage effluents through stabilization ponds reduces the concentration of bacteria and biodegradable organic matter, but the effluents become populated with algae.

In summary, the organic waste matter in secondary sewage effluents is present in both soluble and suspended - settleable as well as non-settleable - forms. The fractions which are responsible for turbidity, colour, and odours consist predominantly of substances of organic character which are amenable to removal by coagulation up to a certain extent - see also Appendix E.

2.6 PREVIOUS RESEARCH ON THE REMOVAL OF ORGANIC WASTE MATTER FROM SECONDARY EFFLUENTS BY CHEMICAL COAGULATION

The above subject is discussed in Appendix E.

CHAPTER 3

EXPERIMENTAL AND METHODS

3.1 EXPERIMENTAL TECHNIQUE AND CRITERIA FOR LABORATORY EVALUATION

The conventional jar test technique was employed throughout this study for laboratory evaluation of the coagulation process. This technique is represented graphically in Figure 3.1 below, (4):

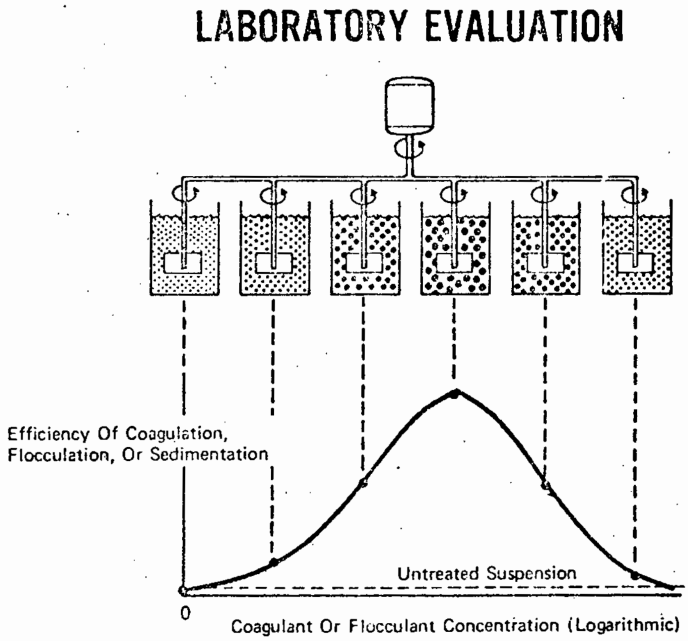


Figure 3.1

The application of the jar test technique is carried out in three stages. The first stage involves a short initial dispersion period with vigorous mixing, during which the coagulant is dispersed uniformly throughout the suspension. During this period the destabilization mechanisms act. The second stage involves a longer period of mild stirring during which flocculation occurs. The degree of stirring should be such as to result in contacts between destabilized particles, which in turn result in floc formation, and such that the velocity gradients induced by stirring do not result in floc break-down to smaller flocs due to excessive floc shear. The third stage involves a period of sedimentation with minimum or no agitation. During this period the flocs are allowed to settle.

The technique simulates the dynamic coagulation and sedimentation patterns that appear in full scale operation, while simultaneously avoiding the problems encountered in the full scale flow-through units.

The criteria used to evaluate the settled effluent quality and, hence, the efficacy of coagulation were as follows:

(1) COD of the supernatant after coagulation and settling,

(2) Remaining turbidity measured after the lapse of a specified settling time period,

(3) Remaining colour after settling (this was measured occasionally).

Of these, the first is the most important requirement. While COD is closely related to the organic load of the effluent - either in suspended or soluble form - turbidity is an expression of the optical property of a sample. Attempts to correlate turbidity with the weight concentration of the suspended matter are impractical, as the size, shape and refractive index of the particulate materials are of great importance optically, but bear little direct relationship to the concentration and specific gravity of the suspended matter, (28).

Among the techniques of potentiometric titration, electrokinetic measurement, and turbidity measurement, the technique of turbidity measurement represents the most convenient experimental procedure for the determination of sol stability (Matijevic, (29)). This procedure is based upon the fact that in the particle size range most commonly found in colloidal systems, the turbidity, or the scattering intensity, increases rapidly with particle size, in most cases. Occasionally, turbidity measurements in coagulation experiments are conducted after considerable time has elapsed from the addition of the coagulant. The coagulant sols have usually settled, and the supernatant has a very low turbidity. Stable sols, however, remain turbid. In the latter case, a stabilized sol will have a higher turbidity than a coagulated sol. Therefore, it is important to record the settling period allowed for the flocs to settle when either reporting or evaluating turbidity data.

The colour measurements will be limited to the characteristics of light transmitted by clarified effluents. Suspended materials should be removed by filtration and not by centrifigation, (28). The colour of a filtered sample is also characterized, besides the transmitted light characteristics, by its hue, degree of luminance, and saturation, (28).

3.2 THE EXPERIMENTAL APPARATUS

The jar test multiple stirrer apparatus, shown in Figure 3.2, was used throughout this study (Coffman, Model 73). This apparatus consists of six magnetic stirrers mechanically coupled so as to operate at the same speed, which may be varied from 5 to 100 rpm. The speed is controlled by a tachometer that gives manual stirrer control. The magnetic stirrers are enclosed in a fibre-glass case on which six square 2 litre capacity jars are placed, each equipped with one magnetic stirrer-bar. Each of these magnetic stirrer-bars is permanently attached to a vertical free shaft which is fitted with a flat rectangular paddle above the magnetic bar, which effects the stirring. Neon light, which can pass through translucent windows in the fibre-glass case, provides good jar lighting. Samples of up to 2 litre volume may be used.

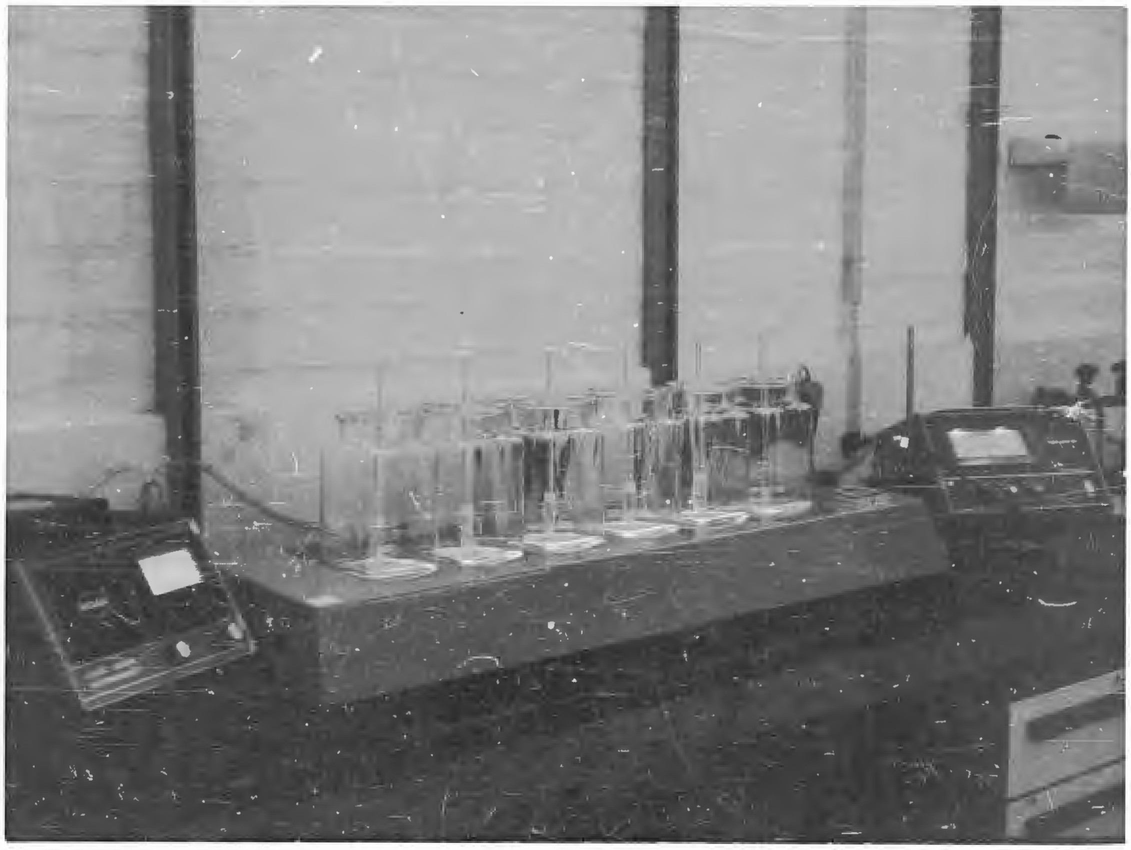


Figure 3.2 The jar test apparatus.

A major criticism of the jar tester is that it cannot be assumed to be a true hydraulic model of a large prototype basin. On the other hand, the size of the floc particles cannot be scaled down according to the principles of similitude for the jar tester. Since jar test devices are operated as batch reactors, they do not suffer from the problems of short-circuiting that are encountered in the flow-through units.

3.3 EXPERIMENTAL METHOD AND PROCEDURES

The first step of the laboratory scale experimental programme was the collection of initial bulk effluent samples from the municipal treatment plant. These were carried to the laboratory in 20 litre containers. A small representative sample was taken at a time, and analyses were done on it to determine their organic and inorganic solids load as well as its optical properties. These analyses usually included the following determinations: total solids, total dissolved solids, total suspended solids, total volatile solids, total and filtered COD, turbidity, pH, colour, and determinations of the concentration of certain inorganic anions in solution. The 20 litre containers were placed in the refrigerator and kept there under 3°C until further use.

To determine the effect of the period of storage under 3°C on the initial total COD level, the following procedure was followed:

Every day following that of collection of the bulk sample, a small sample was taken from a container and its total COD was determined. The relative COD decrease with time which occurred during the period of storage was thus determined. If plotted against time this would indicate the length of time an effluent sample could be stored in the refrigerator under 3°C and be usable for the coagulation tests before its pollutional strength, measured in terms of COD, deteriorated considerably. Usually, a limit of 5 per cent total COD decrease was accepted as tolerable. When this limit was exceeded, the bulk sample was discarded and a fresh one was collected.

In order to test the effect of changing a single variable on the final COD, material from the same bulk sample was always used so as not to change the initial characteristics of the effluent. Under such conditions, the final COD after coagulation was not affected by changes of the initial COD. If, in such a case, the prolonged storage of the bulk sample resulted in a decrease of the initial total COD higher than the previously-mentioned limit before the end of the tests of a series, the bulk sample was not discarded but the decreased COD level was determined and recorded. This COD decrease was taken into consideration during the compilation of the experimental results. When the limit was not exceeded, the initial COD level was assumed to be equal to that of the fresh sample.

For each jar test usually six 1 litre effluent samples were required. To perform a jar test the required quantity of the raw effluent was withdrawn from the containers and placed in a bucket which, in turn, was placed in a warm water bath and was allowed to stay there in order that its temperature reached that of the laboratory. Following this, one litre of effluent was poured into each of the jars. A small sample of the raw effluent was also placed in a beaker for determination of its initial COD, turbidity, and pH levels. The stirrer of the jar tester was switched on to maximum speed and the strong electrolyte for pH adjustment - when needed -, the coagulant aid - if used -, and, finally, the coagulant were added. Certain mixing and stirring conditions were applied. If a polyelectrolyte flocculant was to be added, this was done after a certain short period, - usually one minute -, from the moment of coagulant addition. At the end of the stirring period (flocculation period) the stirrer was switched off and the system was allowed to stand for a specified time period for the flocs, which had been formed, to settle.

At the end of the settling period,a portion of the supernatant was removed from each jar - by means of a 100 ml. pipette whose tip was inserted about 2 cms below the surface during sampling -, and a portion of this sample was immediately used for a turbidity determination while the remaining portion was placed in a small bottle for other determinations to be carried out - COD, colour, etc. Following this the jars were tipped to one side (they were not removed from the jar tester in order to avoid disturbance of the settled flocs), and another of the supernatant was poured into a beaker for pH measurement.

The coagulant stock solutions were prepared fresh whenever a series of tests was to be performed. Their concentrations were such that their addition to the jars to result in the smallest possible increase of sample volume while ensuring that the amount of coagulant added was accurately known. The addition of coagulant was done by quickly pipetting the required volume of the coagulant solution out of its stock solution and discharging the pipette contents into the jars. In the cases of ferric chloride and alum coagulations, the concentrations of these solutions were 1 or 2 per cent w/w.

A similar method was followed for the addition of organic polyelectrolytes. The concentrations of the stock solutions of the organic polyelectrolytes were 1 or 2 per cent w/w for the low molecular weight ones, while concentrations of 0,1 or 0,05 per cent w/w were used for those of high molecular weight.

When a polyelectrolyte was not employed, the mixing time always was taken to have started as soon as the inorganic coagulant had been added into the last jar. When a polyelectrolyte was used, the beginning of the mixing time was taken as being when the polyelectrolyte had been added into the last jar.

All the coagulation tests were performed at room temperature (about 20°C).

The tests were divided into preliminary and main.

3.3.1 Preliminary Tests

The purpose of conducting preliminary tests was to study the approximate effects of various inorganic coagulants and polymer flocculants, when used with or without coagulant aid, as well as to study the effect of combinations of all three of these groups, under different coagulation conditions of pH and chemical dosing, on the final effluent quality. Also, to screen those organic polyelectrolytes which were selected for use in order to choose the most effective of them, either when these were applied alone or in conjunction with the inorganic coagulants as flocculant aids. Polyelectrolytes of all the ionic characters were employed.

The procedure according to which the preliminary tests were performed was as follows :

(1) A 0,5 litre effluent sample was placed in each of the six jars. The stirrer was turned on to maximum speed.

(2) The coagulant was added at increasing amounts from left to right with the middle jar receiving an amount estimated as being correct. The approximate minimum dosage at which a floc was formed was determined. The samples were stirred at maximum speed - 100 rpm - for 5 minutes.

(3) The stirrer speed was reduced, usually to 25 rpm, and stirring was continued for 5 minutes.

(4) The stirrer was switched off and the system was allowed to stand for the flocs to settle for 15 to 60 minutes.

(5) Samples were then withdrawn by pipetting out portions of the supernatant - about 100 ml - and analyses were done on them (COD, pH, turbidity, etc.)

During the preliminary tests the pH was not controlled, except occasionally, when hydrolyzing metal coagulants were employed. In the latter case this was done by adding different amounts of caustic soda or sulphuric acid solutions into each sample prior to the coagulant addition. By applying the same coagulant dosage to each jar, a different final pH was created. In this way the effect of pH on the final COD was determined for the same coagulant dosage.

The preliminary tests were performed in order to produce qualitative rather than quantitative results. Optimum conditions of pH and coagulant dosage were not determined during the course of this preliminary investigation.

3.3.2 Main Tests

The main tests dealt in detail with the effects of the inorganic coagulants alum, ferric chloride, and lime on the COD removal and, to a lesser extent, with their effects on turbidity and colour removals. These inorganic coagulants were used because they have been most widely employed for wastewater treatment in the past.

All the main tests were performed under identical mixing and stirring conditions. This, combined with the approximately constant temperature conditions, which prevailed throughout the experimentation period, eliminated the effects of variable temperature, velocity gradients and floc shear forces upon the coagulation and flocculation phenomena to a large extent.

The method according to which the main tests were performed enabled quantitative conclusions to be drawn about the effect of each particular coagulant on the removal of the organic waste matter, under controlled conditions. The pH was always controlled when hydrolyzing metal coagulants were employed, in order to test the efficiency of these coagulants over a wide pH range. To do this the following procedure was employed:

(1) A one litre sample of the raw effluent was placed in a jar. A pH meter probed was inserted into the sample and the stirrer was turned on to maximum speed. A 50 or 100 mg/l coagulant dosage was applied and, by means of a burette, 1N solution of caustic soda was added dropwise. The quantities of this solution required to create different pH environments - about 0,5 pH unit apart from each other - between the pH created by the coagulant when added alone and pH 8 were recorded.

(2) The above procedure was repeated using a 1N sulphuric acid solution. The amounts of this solution required to create different pH environments between the pH created by the coagulant when added alone and pH 2 were recorded.

(3) In a series of one litre fresh effluent samples, the predetermined from steps (1) and (2) above amounts of caustic soda and sulphuric acid solutions were added with the stirrer at maximum speed. The same coagulant amount used in those steps was added into each jar. After the coagulant addition the stirrer was allowed to run for 5 more

minutes at 100 rpm.

(4) The stirrer speed was reduced down to 25 rpm and the stirrer was allowed to run for 5 minutes.

(5) The stirrer was switched off and the flocs were allowed to settle for a specified time period - usually 60 minutes.

(6) Samples were withdrawn from the clarified effluent, according to the procedure described previously in the beginning of Section 3.3, and analysed for COD, turbidity, etc.

(7) The above steps were repeated for coagulant dosages 100 mg/l higher each time up to about 600 or 800 mg/l.

When lime was employed as coagulant, the procedure followed was different from that for alum or ferric chloride. The lime dosage was merely varied from jar to jar and the final pH, turbidity, and COD were determined after the application of identical mixing, stirring and settling conditions.

The organic polyelectrolytes, which had been found to be most effective when used in conjunction with the inorganic coagulants from the preliminary tests, were used to test their effect on the COD removal. This was done by maintaining such identical inorganic coagulation concentration and pH in each jar as to achieve very high COD removal and by subsequently increasing the polymer concentration stepwise to see whether the COD removal would be further increased.

A Final Test was performed in the end of treatment of each particular effluent. The purpose of this test was, firstly, to check on the reproducibility of the experimental results which had been obtained using certain inorganic coagulant-organic polymer combinations at such concentrations and pH as to simultaneously achieve optimum COD removal and good floc settling characteristics; and, secondly, to compare the efficiency of the three inorganic coagulants in removing COD,turbidity and colour on the same raw effluent quality basis. Two litre samples were used. The floc settling rate determination was done immediately after the stirrer was turned off. This was done by measuring the period required for the flocs in the jars to fall a certain distance, where a clear interface was created or, alternatively, for a certain percentage of the flocs to settle. The latter was visually estimated.

3.4 PRESENTATION OF RESULTS

The experimental results of the preliminary and the main tests are presented in a tabulated form in Appendices F, H, J, and G, I, K, respectively. Results of statistical analyses are presented in

Appendix L, while cost estimation results are presented in Appendix M. Appendix N deals with the error analysis.

The results of representative preliminary tests and the results of most of the main tests are presented graphically in Chapters 4, 5 and 6.

The final COD test results were plotted against final pH and/or coagulant dosage in linear co-ordinates, while the final turbidity results were plotted against final pH and coagulant dosage in semi-log co-ordinates.

The results of the Final Tests are presented in Tables 4.2, 5.2 and 6.2.

3.5 COAGULATION WITH Al or Fe(III) SALTS - TECHNIQUE EMPLOYED FOR THE DETERMINATION OF THE OPTIMUM COAGULATION CONDITIONS FOR COD REMOVAL

The final COD test results obtained from a series of tests were plotted against final pH with coagulant dosage as the changing parameter. This was done separately for alum and ferric chloride coagulations. The plotted results were then elaborated as described below to determine the optimum coagulation conditions for COD removal.

By means of a Wang electronic calculator, System 2200 (VS.01-2200, 01A.-00FI-0-0, GLBR 22A TAPE 701-0120), second or third order regression analyses were done on the final COD test results. This would be done for the results of each coagulant dosage. However, results corresponding to more than one adjacent coagulant dosages at a time were often considered for the regression analysis. This incorporation depended on the degree of overlapping of the experimental points corresponding to adjacent coagulant dosages, and, also, on the availability of an adequate number of them. If the degree of overlapping - which was visually estimated - was high, the same population was assumed and regression analysis was done simultaneously on all the experimental points which corresponded to the coagulant dosages chosen to be considered together. Thus, the final COD values of the resulting regression curve corresponded to the coagulant dosage range considered and not to a specific coagulant dosage. The benefit of this incorporation was that it increased the number of experimental points available for the regression analysis, with the best fit having a higher statistical value which best corresponded to the mean coagulant dosage of the coagulant dosage range considered. Following this, the final COD was plotted as the changing parameter with the coagulant dosage as ordinate and the final pH as abscissa.

Joining the points corresponding to identical COD values, contours were obtained each corresponding to a particular final COD value. These contours covered a wide pH range and a wide coagulant dosage range. The optimum pH for COD removal was then determined to be the one at which the distance between any of these contours and the pH axis was minimum. The optimum coagulant dosage was the minimum dosage above which no further COD removed occurred.

3.6 METHODS OF ANALYSIS

The following eight parameters were employed in order to test the quality of the effluent:

(1) Chemical Oxygen Demand

During the course of the main tests, the initial total and filtered (through a GF/A filter disc) COD values as well as the final COD values were determined by refluxing the sample with acidic dichromate under controlled conditions, as described in Standard Methods, (28). Excess mercuric sulphate was always used to eliminate chloride interference. During the course of the preliminary tests, the initial filtered and final COD values were mostly determined by means of an autoanalyzer (Technicon, Model II). The method described by the manufacturer of the autoanalyzer for the COD determination could tolerate a maximum chloride level of 200 mg/l in the sample. The chloride concentration of the effluents, especially that of the MMP and MHT effluents, was higher than this level. Therefore a systematic error was introduced in those results. Efforts to correct this error by making a calibration curve in which the deviation of COD from the true value was plotted against known chloride concentrations proved unsuccessful, due to poor reproducibility of results. Therefore, the results of these COD determinations of the preliminary tests have only a qualitative value. However, the AMP effluent preliminary COD test results, which were obtained after alum or lime coagulations by means of the autoanalyzer, may be considered reliable and having a quantitative significance, since the chloride concentration in that effluent was about 200 mg/l.

(2) Turbidity

The turbidity was measured by means of a light scattering turbidimeter (Hach, Model 2100A). The results are expressed in Formazin Turbidity Units (FTU). The instrument was calibrated against standard suspensions before the performance of each set of tests.

(3) Colour

For colour determination, the sample was filtered through a GF/A filter disc under vacuum. Adequate material was filtered in order to minimize the effect of possible adsorption of colour onto the filter disc during filtration. The retention ability of the GF/A filter disc is not specified by its manufacturer (Whatman). The GF/A filter disc manages, however, to retain all the particulate matter and a clear solution is produced. Colour and invisible colloidal particles are not retained. Colour was measured by means of a colorimeter (Beckman, Model 1211), equipped with a 10 mm light path rectangular cell. A 420 nm violet filter showed maximum absorbance for the purpose and it was therefore used for the colour determinations. Colour is expressed in terms of absorbance.

(4) pH

For the preliminary tests a Metrohm Herisau, Model E520, electronic pH meter was used. During the course of the main tests the initial and final pH values were measured by means of a Corning-EEL, Model 12, electronic pH meter equipped with an expanded scale.

(5) Residual Metal Coagulant Concentration

The concentrations of Al^{3+}, Fe^{3+}, Ca^{2+}, Mg^{2+} were occasionally determined in the clarified effluent after coagulation. These determinations were carried out following filtration of the samples. The concentrations of Fe^{3+}, Ca^{2+} and Mg^{2+} were determined by means of an atomic absorption spectrophotometer (Varian Techtron, Model 1100), while that of Al^{3+} was determined by means of a similar spectrophotometer (Varian Techtron, Model 70).

(6) Residue

The residue determination includes the following determinations: TS, TSS, TVS, TDS. They were carried out as described in Standard Methods, (28).

(7) Floc Settling Rate

This was measured as the time period elapsed for the floc bed/ supernatant interface to fall a certain distance in the jar, when a clear interface was formed, or as the time period elapsed for a certain fraction of the flocs to settle, when an interface was not formed.

(8) Inorganic Cation or Anion Concentration

The concentrations of some anions, e.g. Cl^-, SO_4^{2-}, etc. were determined by means of the autoanalyzer. The Na^+ concentration was determined by means of the atomic absorption spectrophotometer.

The natural polymer Floccotan and the low molecular weight synthetic cationic polyelectrolytes were easily diluted in water for the preparation of the stock solutions (usually 1 per cent in concentration). All the high molecular weight polyelectrolytes required vigorous mixing to be applied for a considerale time period in order to become dissolved in water. These were slowly added into the vortex created by a magnetic stirrer vigorously stirring warm distilled water in a beaker. The concentration of their stock solutions was usually 0,1 per cent. The stock solutions of the high molecular weight organic polyelectrolytes were quite viscous - even at concentrations as low as 0,05 per cent. The stock solutions were prepared fresh before a series of tests was performed. A certain time period was allowed after preparation in order the stock solutions to equilibrate at room temperature.

3.7.3 Coagulant Aids

Bentonite was the only coagulant aid employed throughout this study. It was added as a 1 per cent suspension. This was freshly prepared before use. The method of addition was similar to that employed for lime.

CHAPTER 4

CHEMICAL COAGULATION APPLIED TO THE TREATMENT OF THE MILNERTON MATURATION POND EFFLUENT

4.1 CHARACTERIZATION OF THE EFFLUENT

The appearance of the effluent indicated that it was not highly polluted. It looked quite clear in small quantities and was slightly yellow in colour. It had no odour. Its organic content was low and did not vary appreciably from sample to sample. Its characteristic properties are shown in Table 4.1 below.

TABLE 4.1

CHARACTERISTIC PROPERTIES OF MMP EFFLUENT

Turbidity, FTU	: 1 - 2,5	Mg^{2+}, mg/l	: 55-70
pH	: 7 - 8,5	Ca^{2+}, mg/l	: 55-70
Total COD, mg/l	: 40-60	Na^{+}, mg/l	: appr. 300
Filtered COD, mg/l	: 40-55	K^{+}, mg/l	: appr. 20
Colour, absorbance	: appr. 0,025	Fe^{3+}, mg/l	: non-detectable
TS, mg/l	: 1500-1700	Al^{3+}, mg/l	: " "
TDS, mg/l	: 1500-1700	SO_4^{2-}, mg/l	: appr. 190
TSS, mg/l	: 10-30	HCO_3^{-}, mg/l	: appr. 170
TVS, mg/l	: appr. 300	NO_3^{-}, mg/l	: appr. 50
Cl^{-}, mg/l	: 500-600	Phosphates, mg/l	: appr. 10 (as P)

Note: These values are based on samples collected during the course of the experiments.

The total COD change of a representative sample of the effluent plotted as a function of the storage period under $3^{o}C$ is shown graphically in Figure 4.1. It may be observed that the COD of the raw sample decreased at a rate of less than 10 per cent in a week. The limit of 5 per cent COD decrease - see Section 3.3 - could be exceeded in two days and, therefore, a bulk sample of the effluent was normally discarded after 48 hours of storage.

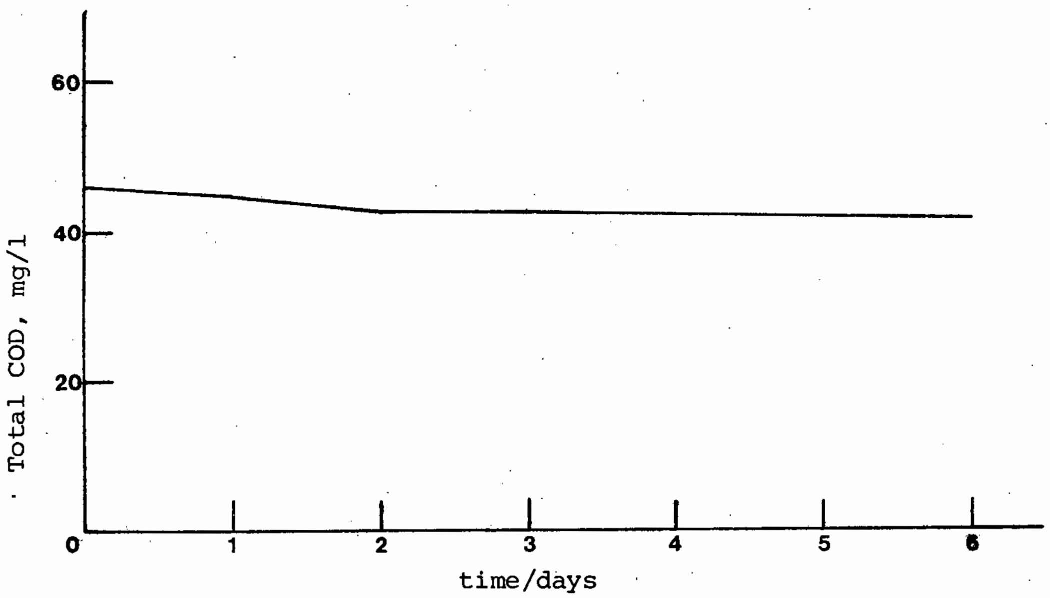


Figure 4.1 Total COD change with period of storage

4.2 PRELIMINARY TESTS

The preliminary tests were carried out according to the method described in Section 3.3.1. All three inorganic coagulants were employed. Most of the organic polyelectrolytes mentioned in Table 3.1 were tested.

4.2.1 Presentation and Discussion of the Experimental Results

The experimental results are presented in a tabulated form in Appendix F. Certain final turbidity and correct final COD results are presented graphically in Figures 4.2, 4.3, 4.4, 4.5, 4.6 and 4.7 as a function of pH and/or coagulant dosage for alum or ferric chloride coagulations. Figures 4.3 and 4.4 represent tests in which pH was controlled.

From the test results reported in Sections I.1, I.2 and I.3 of Appendix F - results of alum or ferric chloride coagulations - the following conclusions may be drawn:

For alum coagulation the critical coagulation concentration (CCC) was between 0 and 20 mg/l - as $Al_2(SO_4)_3$ - for both turbidity and COD removals.

The final turbidity values were sometimes much higher than the level of turbidity in the raw effluent - especially at low pH. This suggests that stable colloids were formed after the addition of alum.

The final COD, on the other hand, seemed to be independent of turbidity changes. The characteristic phenomenon of progressively

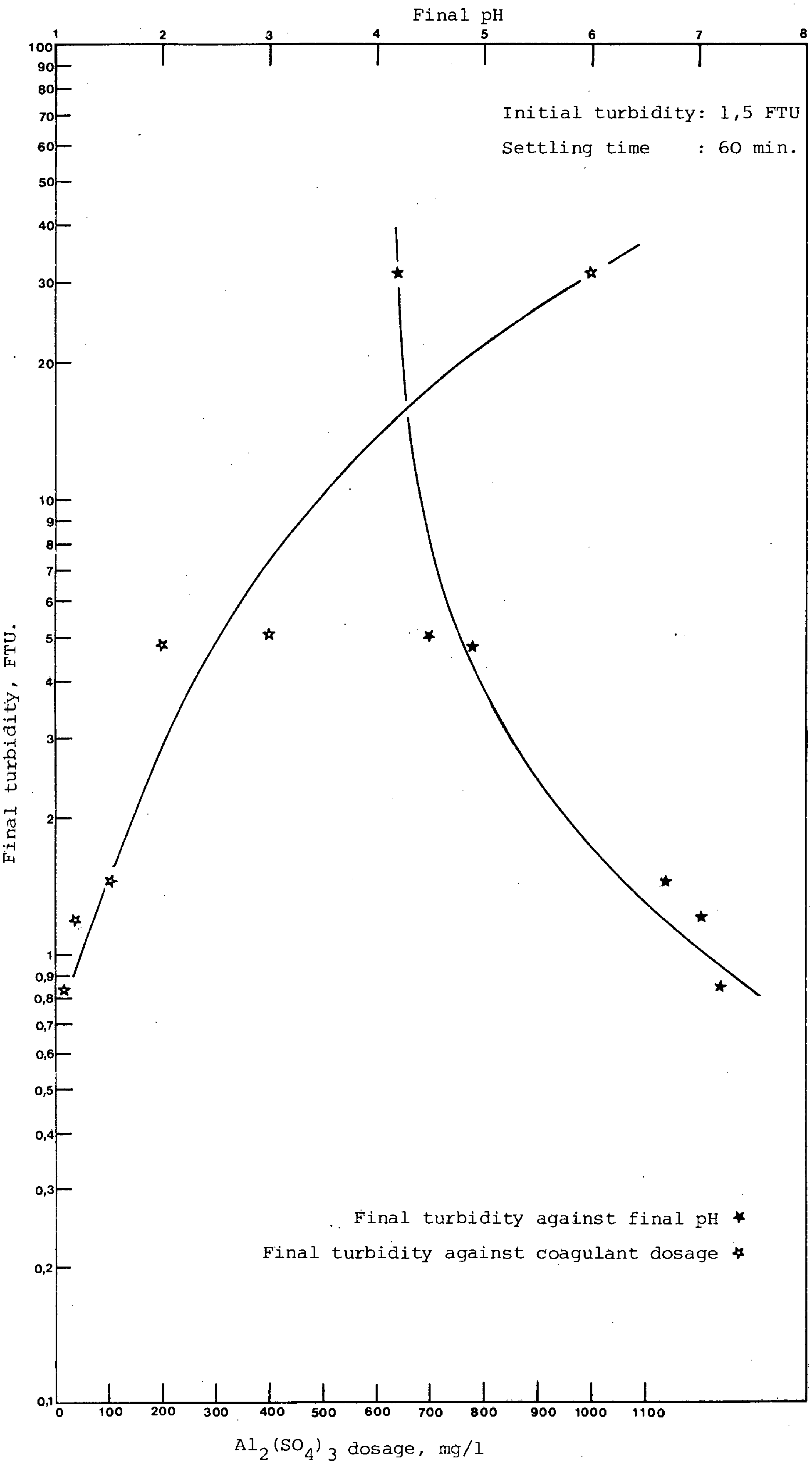


Figure 4.2 Alum coagulation. Final turbidity is plotted against final pH or coagulant dosage.

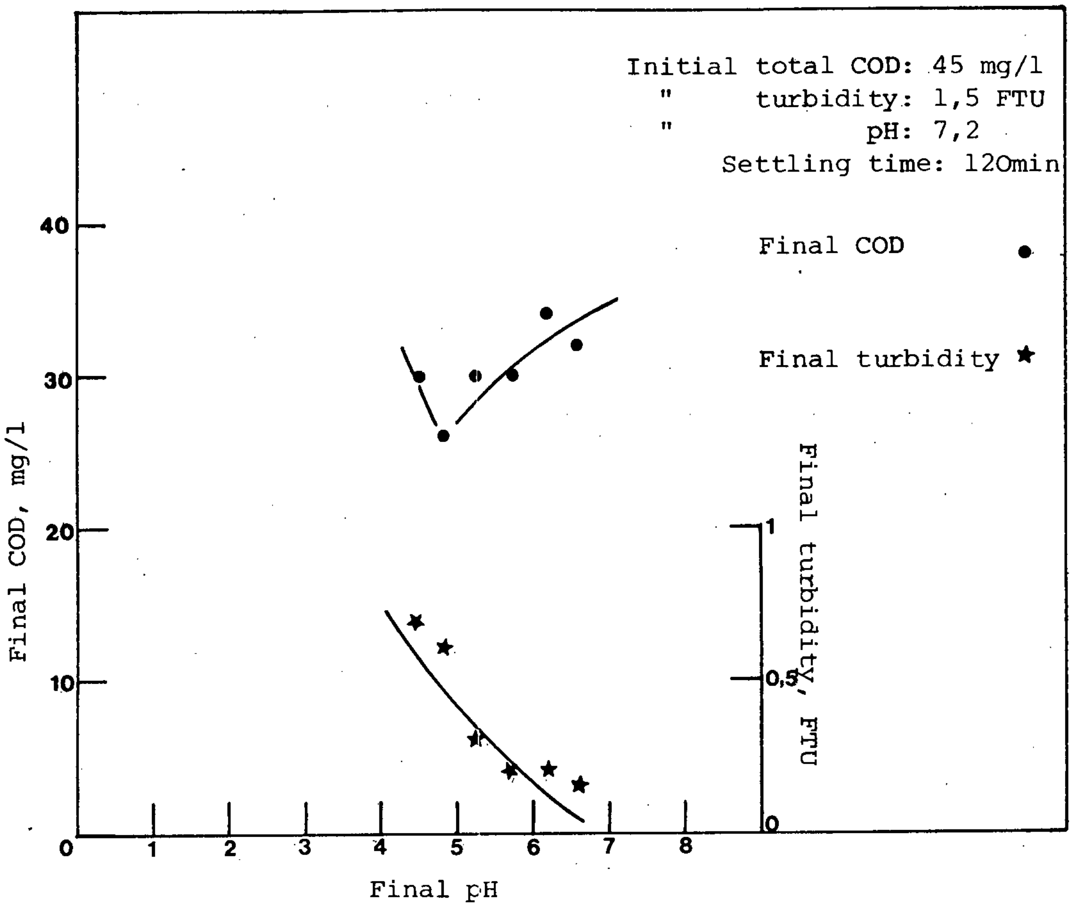


Figure 4.3 Coagulation with 100 mg/l $Al_2(SO_4)_3$. Final COD and final turbidity are plotted against final pH.

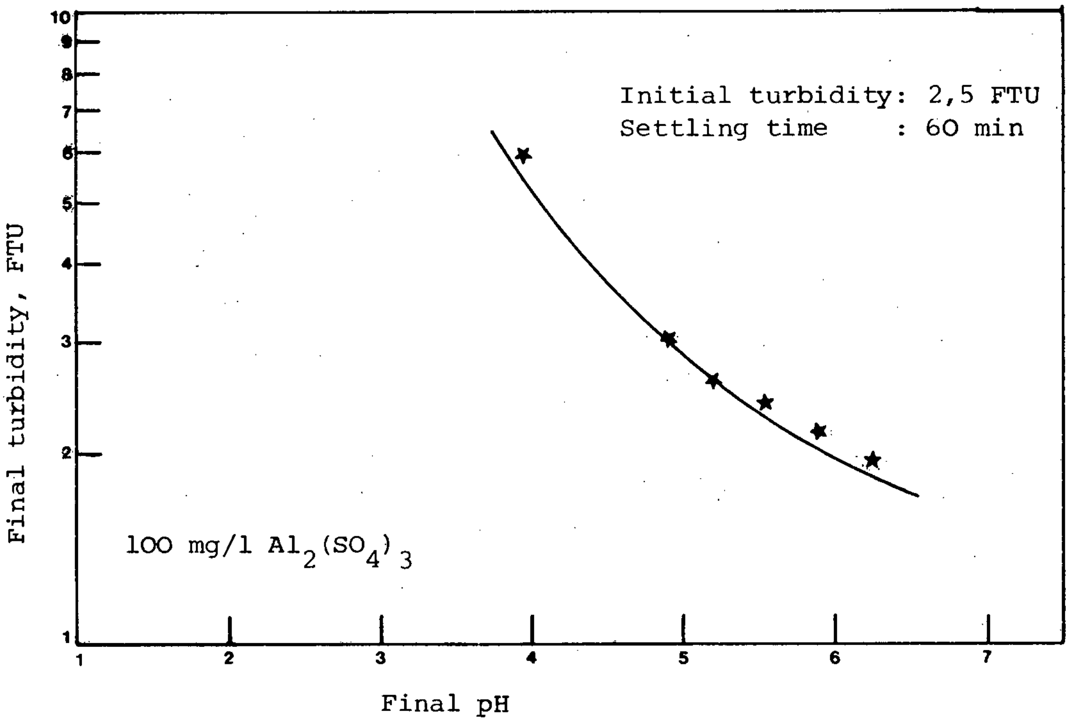


Figure 4.4 Alum coagulation. Final turbidity is plotted against final pH.

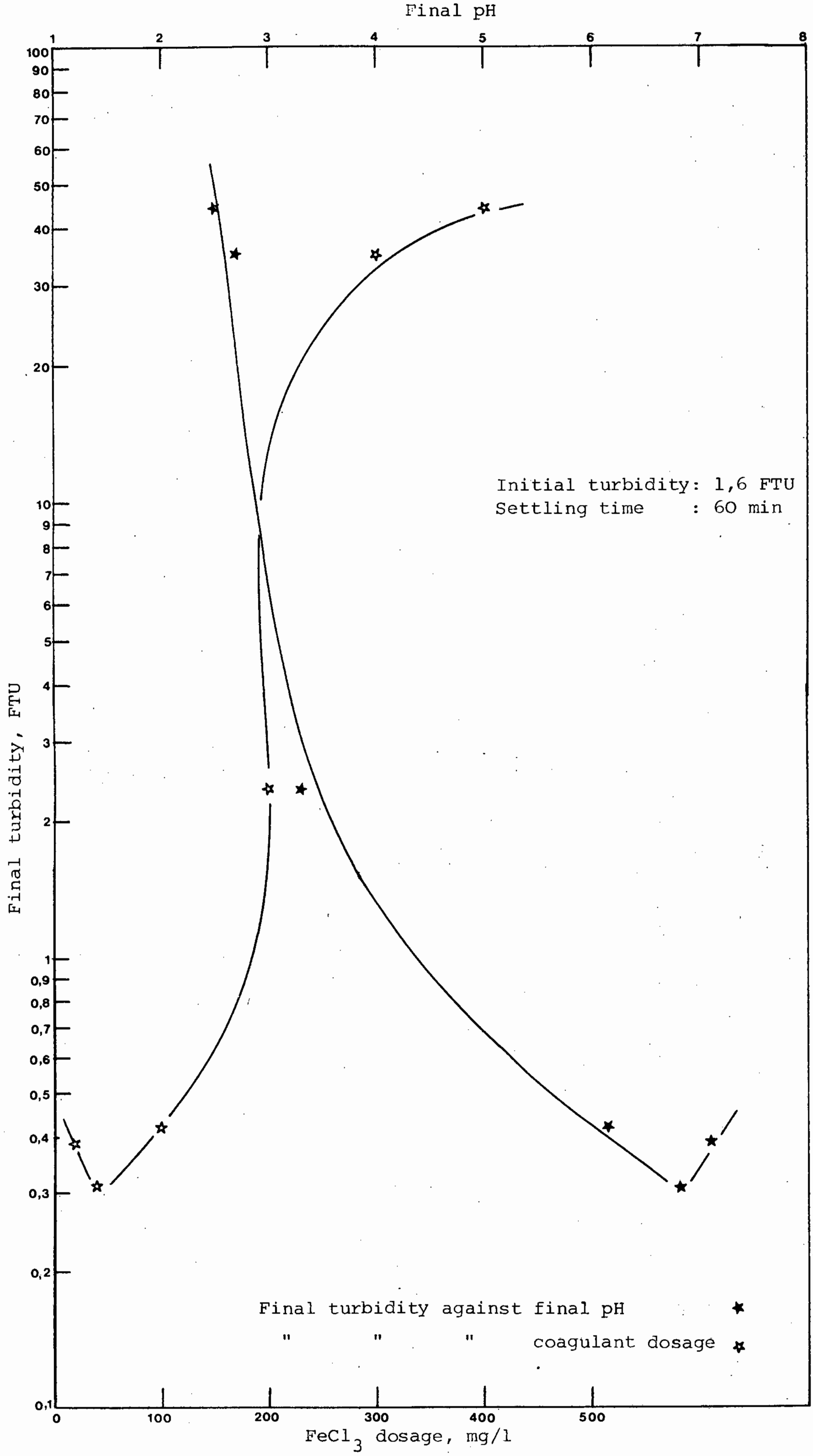


Figure 4.5 Ferric chloride coagulation. Final turbidity is plotted against final pH or coagulant dosage.

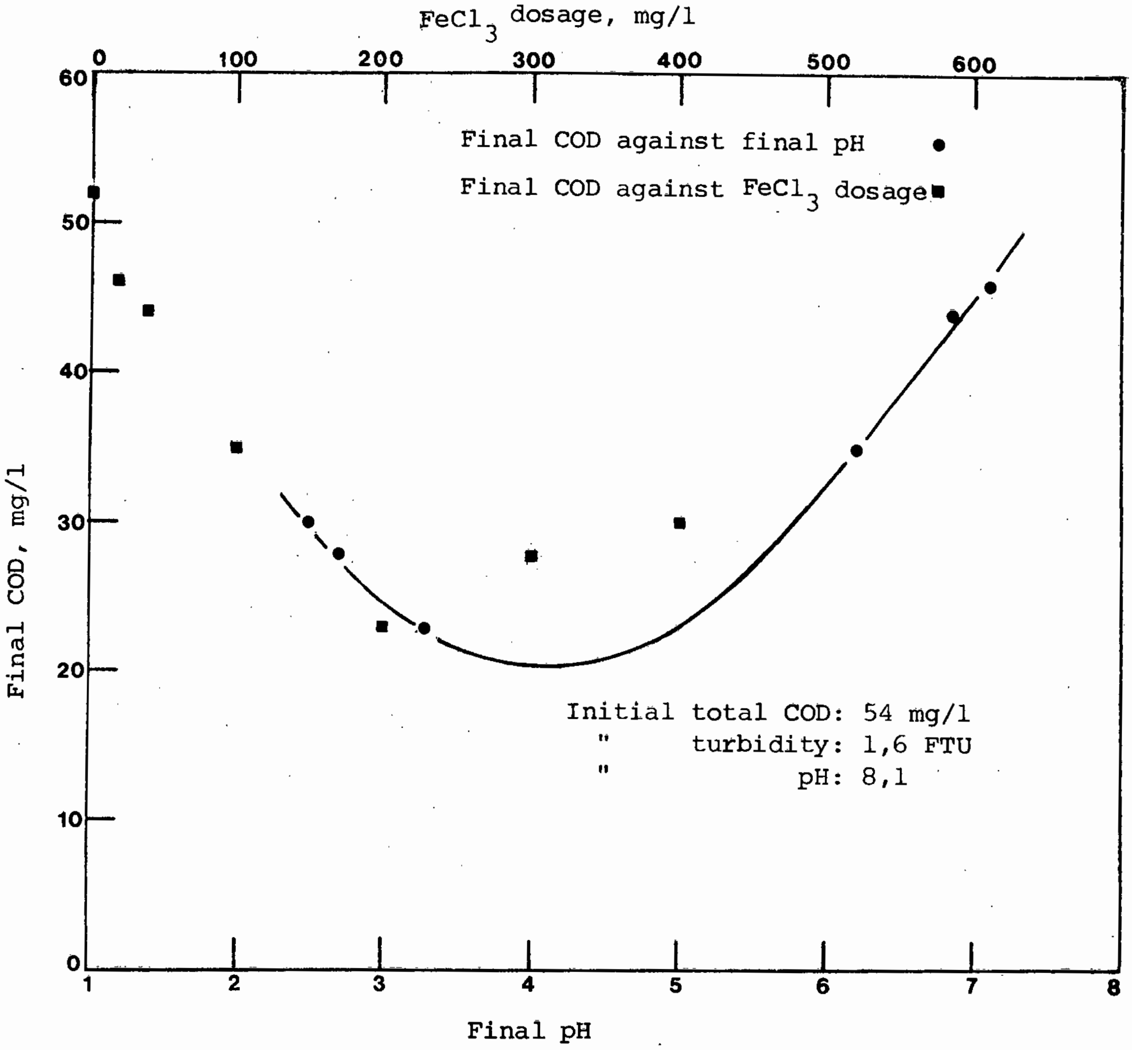


Figure 4.6 Ferric chloride coagulation. Final COD is separately plotted against final pH and coagulant dosage.

decreasing final COD values while the final turbidity values were simultaneously increasing - Test 1, Section I.1, Figure 4.2 - suggests that the additional turbidity was of inorganic character.

In Test 2, Section I.1 - Figure 4.3 -, the final COD was accurately determined. At pH 4,8 the COD removal was highest. The turbidity, however, was higher the lower the pH. Again, the final COD values seemed unrelated to final turbidity values. Since the coagulant concentration was identical in all samples of this test, pH was shown to play a significant role in the removal of the organic waste matter, because the coagulant was rendered more efficient at a certain pH region - approximately pH 5 in this case.

That the remaining turbidity was a function of the pH prevailing after coagulation is also shown by the results of Test 3, Section I.1, which are shown in Figure 4.4. The results of Test 1, Section I.1.1, show that the remaining turbidity was unrelated to the effluent's natural

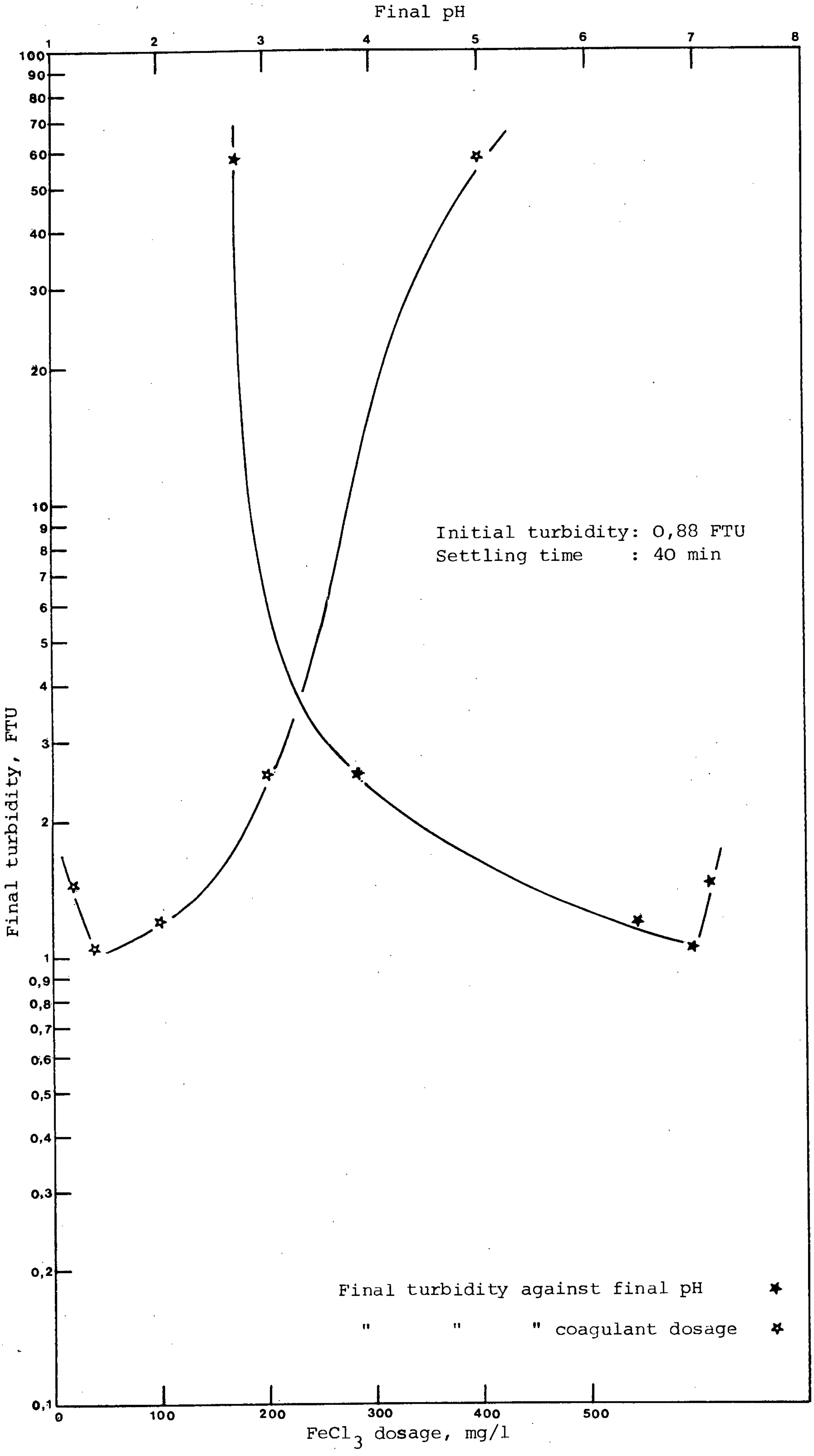


Figure 4.7 Ferric chloride coagulation. Final turbidity is plotted against final pH or coagulant dosage.

turbidity or, even more, to the increased turbidity caused by the addition of bentonite. It was rather related to other precipitates formed once the coagulant was added.

The results of Tests 1 and 2, Section I.2, suggest that the observed partial removal of organics was due to the precipitation of Ca^{2+} and Mg^{2+} ions from the solution at the high pH created by the caustic soda addition. Bentonite could be completely removed together with the calcium and magnesium precipitates, if added before the caustic soda addition.

The results of Test 1, Section I.3 - Figures 4.5 and 4.6 -, show that after coagulation with ferric chloride the CCC for both turbidity and COD removals was approximately between 0 and 20 mg/l. In this test the final COD was accurately determined and it was minimum at about pH 4.

The increase of final COD at dosages above 200 mg/l (and, consequently, at pH values below 4) was not an indication of restabilization of the destabilized organic waste matter, since that increase was not accompanied by a proportional increase in turbidity (besides the fact that the increased turbidity which appeared below pH 4 was much higher than the natural turbidity of the effluent). This suggests that the effect of ferric coagulant was similar to that of aluminum, and that stable inorganic colloids were formed. These colloids could have been the reaction products of a reaction between the metal hydrolysis species and anions in solution. Similar results to those previously mentioned - Test 1, Section I.3 - were obtained in Test 2, Section I.3 - Figure 4.7.

From the test results reported in Section I of Appendix F it may be concluded that, when alum or ferric chloride were added, highest COD removals were achieved at acidic pH values, while lower final turbidity values were achieved at neutral pH values. Lime proved to be an effective coagulant at dosages high enough to create a pH greater than 11, above which a voluminous precipitate appeared. The higher the lime dosage, the higher the COD removal in this case. Test 1, Section I.4, shows that a lime dosage of 450 mg/l resulted in the least carbonate hardness after coagulation (final pH 11,3).

Better floc settling characteristics were observed with lime coagulation than with alum or ferric chloride coagulations.

The results obtained when bentonite was used as coagulant aid did not seem worth the cost involved, because it did not aid either in the removal of the natural turbidity of the effluent to a large extent or in the removal of COD.

Test 1, Section II.6, shows that the colour removal was higher for ferric chloride than for alum coagulations, while lime showed a similar removal ability to alum.

The testing of the organic polyelectrolytes involved two steps. In the first step qualitative tests were performed in small beakers. The results are reported below:

Among the polymers tested alone, Floccotan was the only organic polymer which removed the effluent's particulate matter at dosages higher than 50 mg/l. It was the only polymer which formed big flocs immediately after its addition. These flocs, however, did not settle fast.

The flocs formed by Floccotan were well flocculated by very small amounts of Separan AP-273.

The precipitation of aluminum or ferric hydroxide resulted in formation of flocs which were easily flocculated with small amounts of Superfloc N-100 and Superfloc A-150.

Superfloc C-521 used in conjunction with inorganic coagulants proved to be effective as flocculant aid at dosages above 20 mg/l.

The flocs formed after lime addition were well flocculated with small dosages of Separan AP-273.

In the second step quantitative tests were performed. The results are reported below:

The results of Tests 1 amd 2, Section II.1, show that the synthetic organic polymers, with the exception of Praestol 444-K and Superfloc C-521, did not form flocs at all when added alone at dosages as high as 20 mg/l. Superfloc C-521 resulted in the formation of very small slow settling flocs which increased the turbidity of the effluent. Bentonite addition, prior to the polymer addition, resulted in the formation of flocs in those systems in which the polymer alone had no effect.

The results of Test 3, Section II.1, show that, among the polymers used, the non-ionic polyelectrolytes best removed the bentonite particles.

Tests 1, 2 and 3, Section II.2, show that the flocs formed after alum addition were well flocculated by small amounts of anionic and non-ionic high M.W. polymers, while the cationic low M.W. polymers had to be added at higher concentrations to become effective to a similar extent.

The results of Test 3, Section II.2, show that the use of non-ionic polymers as flocculant aids after alum coagulation, can result in slightly improved removals of turbidity and of the organic waste matter. It is believed that the improvement in COD removal was only incidental accompanying the better floc settling characteristics which were observed after the polymer addition.

The results of Test 4, Section II.2, show that the use of non-ionic polyelectrolytes as flocculant aids after alum coagulation, can significantly reduce the settling period which would otherwise be required with alum only added. These polyelectrolytes do not, however, remove the stable colloids formed after the alum addition at low pH to a good extent.

The results of Test 1, Section II.4, show that the flocs formed after lime addition were flocculated by both anionic and cationic polymers. However, the anionic ones required a smaller dosage to become effective. This indicated that the pH played an important role in this case, rendering the anionic polymers fully ionized and, consequently, more effective.

The results of Test 1, Section II.6 show that when Floccotan is added in excess, results in an increase of the COD level because a portion of it becomes dissolved in water. (solution becomes reddish).

The results of Section III show that if 1 mg/l of a high M.W. polymer of acrylamide is dissolved in the effluent, instead of binding to flocs, a negligible increase in the effluent's COD level should be expected. This suggests that high M.W. polyacrylamides can be safely used as flocculants, if added at small dosages.

The summarize, the polymers Separan AP-273, Superfloc N-100 and Superfloc A-150 worked well with lime, alum and ferric chloride, respectively, and reduced the floc settling period otherwise required.

4.3 MAIN TESTS

All the main tests were performed according to the experimental method described in Section 3.3.2. Here, the effect of polyelectrolyte flocculants, when used in conjunction with inorganic coagulants, on the final COD achieved solely by the action of the inorganic coagulants, was also studied. These flocculants were: Superfloc A-150 with ferric chloride, Superfloc N-100 with alum, and Separan AP-273 with lime.

4.3.1 Presentation of the Experimental Results

All the experimental results of the main tests are tabulated in Appendix G. The final COD and final turbidity test results are presented graphically in Figures 4.8, 4.9, 4.10 and 4.10, 4.11, 4.12 respectively.

The test results which show the effect of the organic polyelectrolyte flocculants used in conjunction with inorganic coagulants on the COD removal are tabulated in Section B of Appendix G.

The results of the Final Test are tabulated in Table 4.2.

4.3.2 Determination of the Optimum Coagulation Conditions for COD Removal for Al or Fe(III) Coagulations

The technique described in Section 3.5 was employed for the statistical evaluation of the final COD test results which are reported in Sections A.I, A.II and A.III of Appendix G.

The calculated final COD values are presented in Tables L.1 and L.2 of Appendix L. These are also presented graphically in Figures 4.13 and 4.14. From these Figures it may be readily observed that for alum coagulation the optimum pH for COD removal was between 5 amd 5,5, while for ferric chloride coagulation it was between 4 and 4.5.

4.3.3 Al and Fe(III) Coagulations - The Remaining Turbidity Studied as a Function of Coagulant Dosage and Final pH

Denoting the final residual turbidity measured after 60 minutes of settling as FRT and the final pH as FpH, a plot of the log (FRT) values against the log (FpH) values was made irrespective of coagulant dosage for the coagulants alum and ferric chloride. For alum coagulation the FRT values corresponding to pH greater than 3,5 were only considered, as no flocs - or, more correctly, no stable colloids - appeared below this pH. For ferric chloride coagulation the FRT values corresponding to pH greater than 2,5 were only considered. Below approximately pH 2,5 destabilization of the stable colloids formed after coagulation seemed to occur - See Figure 4.12.

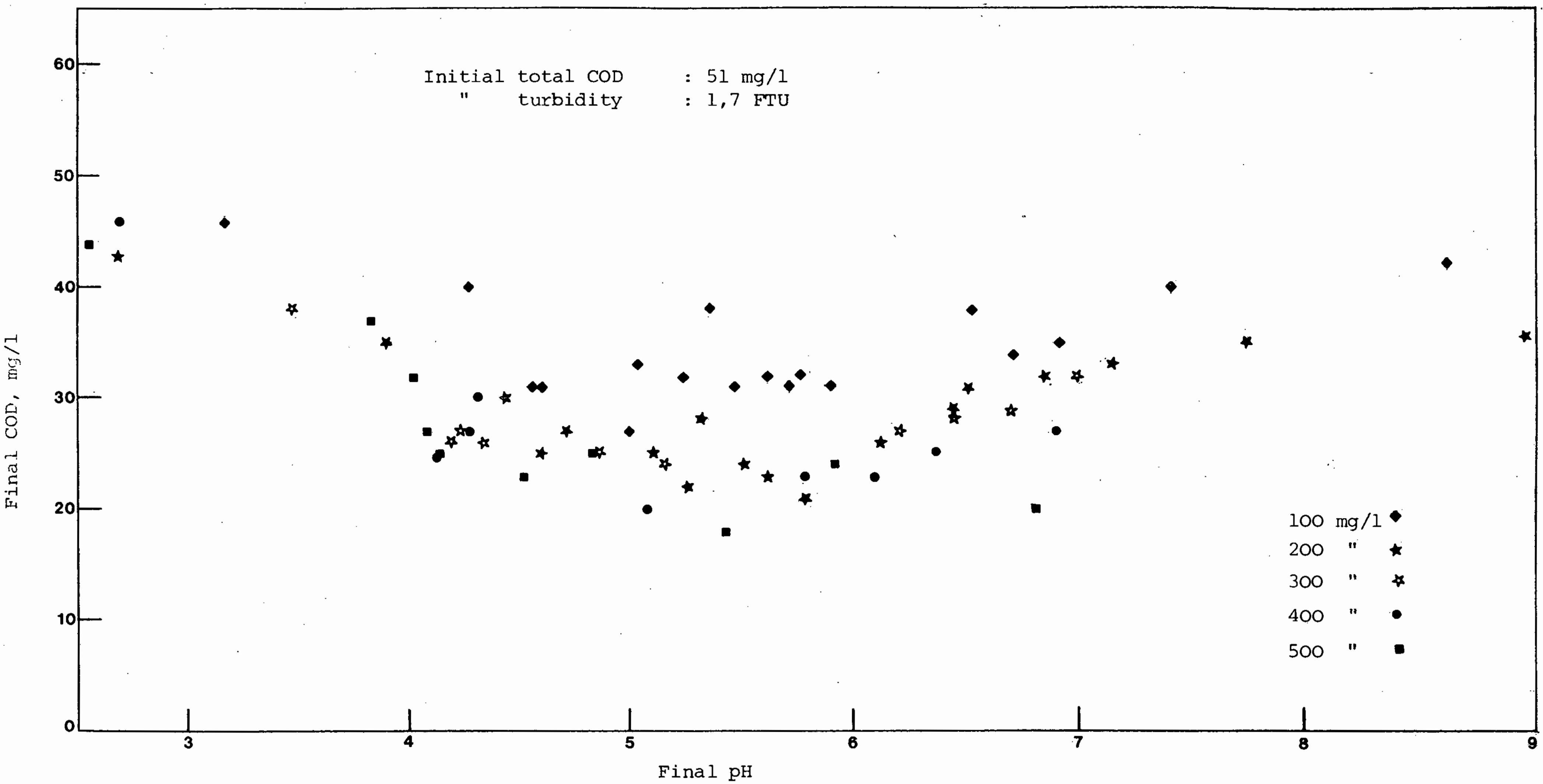


Figure 4.8 Alum coagulation. Final COD is plotted against final pH and coagulant dosage.

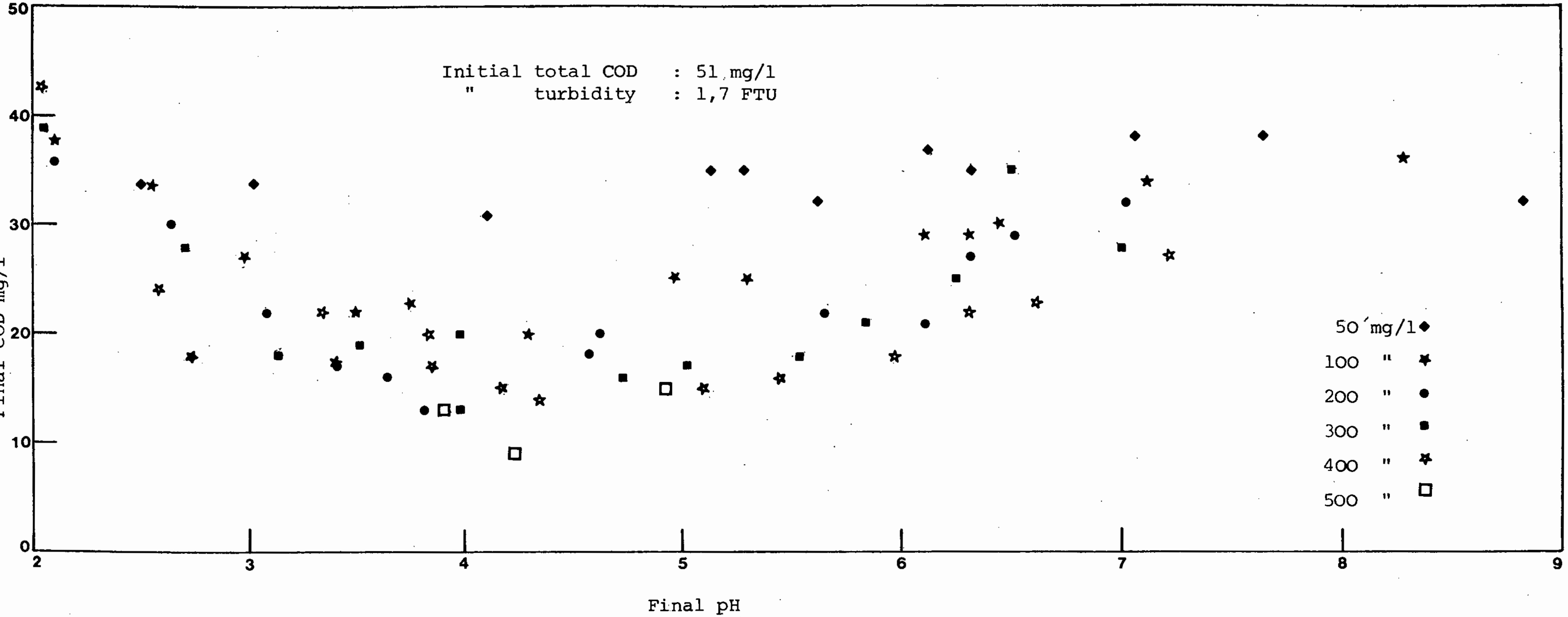


Figure 4.9 Ferric chloride coagulation. Final COD is plotted against final pH and coagulant dosage.

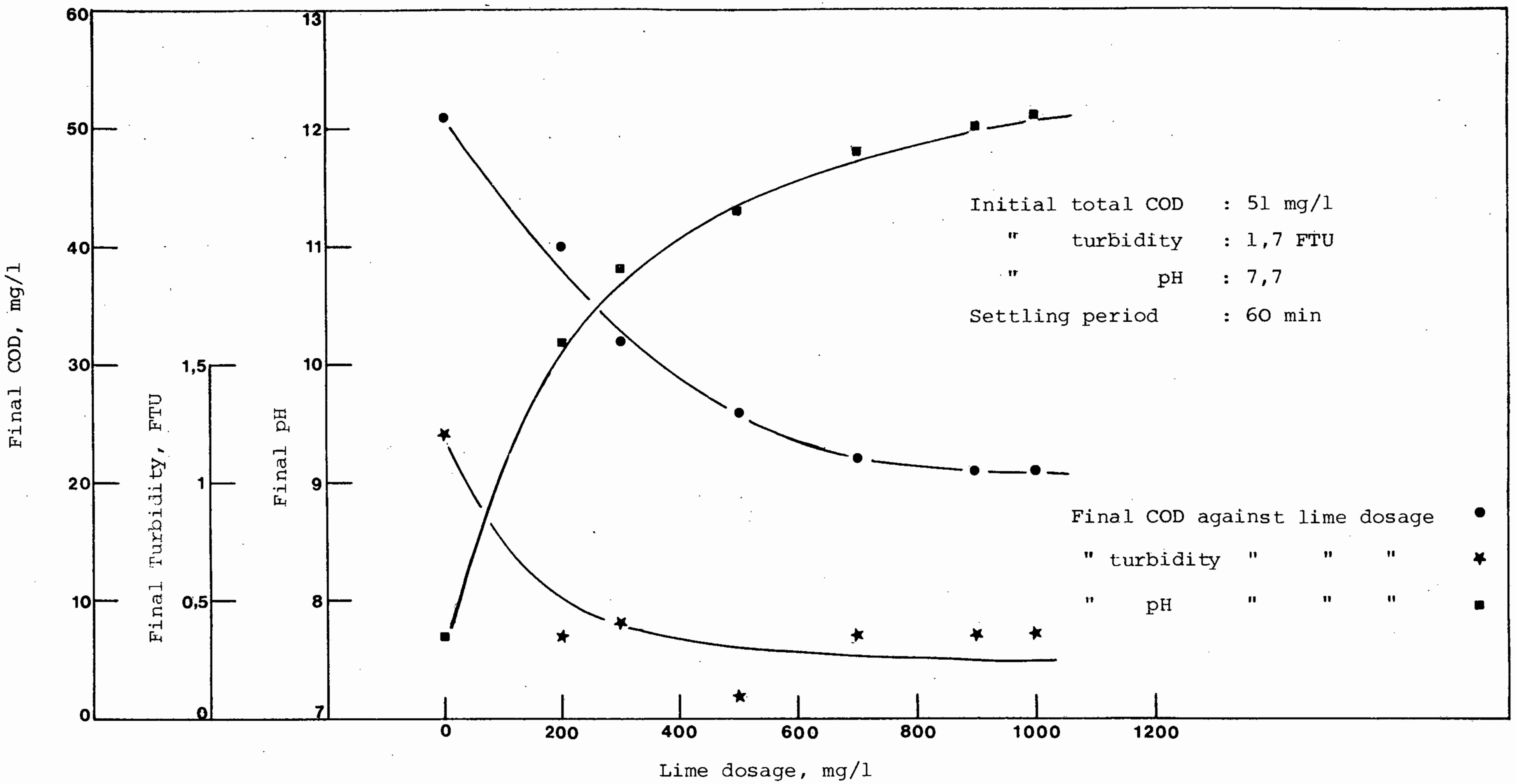


Figure 4.10 Lime coagulation. Final COD, final turbidity, and final pH are plotted against lime dosage.

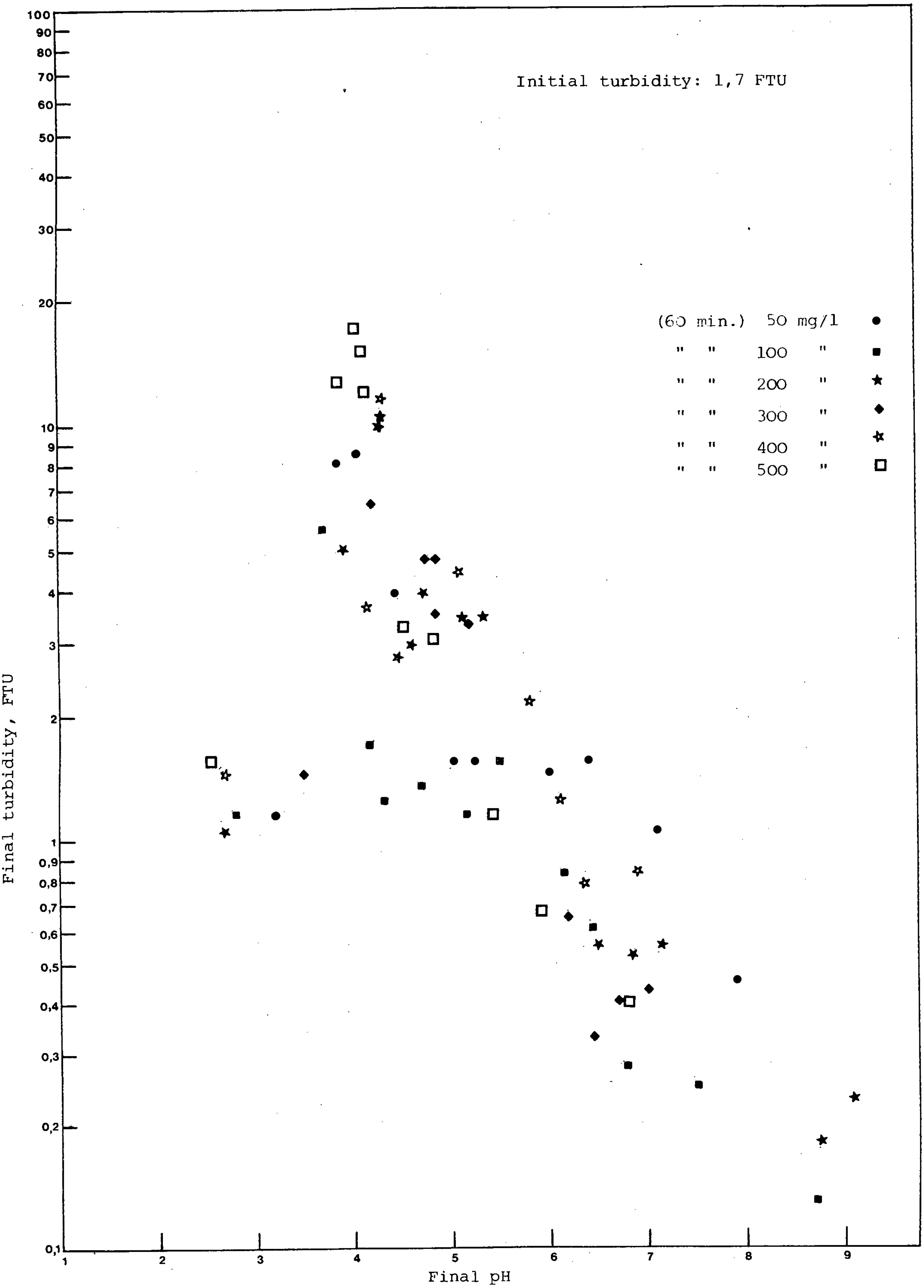


Figure 4.11 Alum coagulation. Final turbidity is plotted against final pH and coagulant dosage.

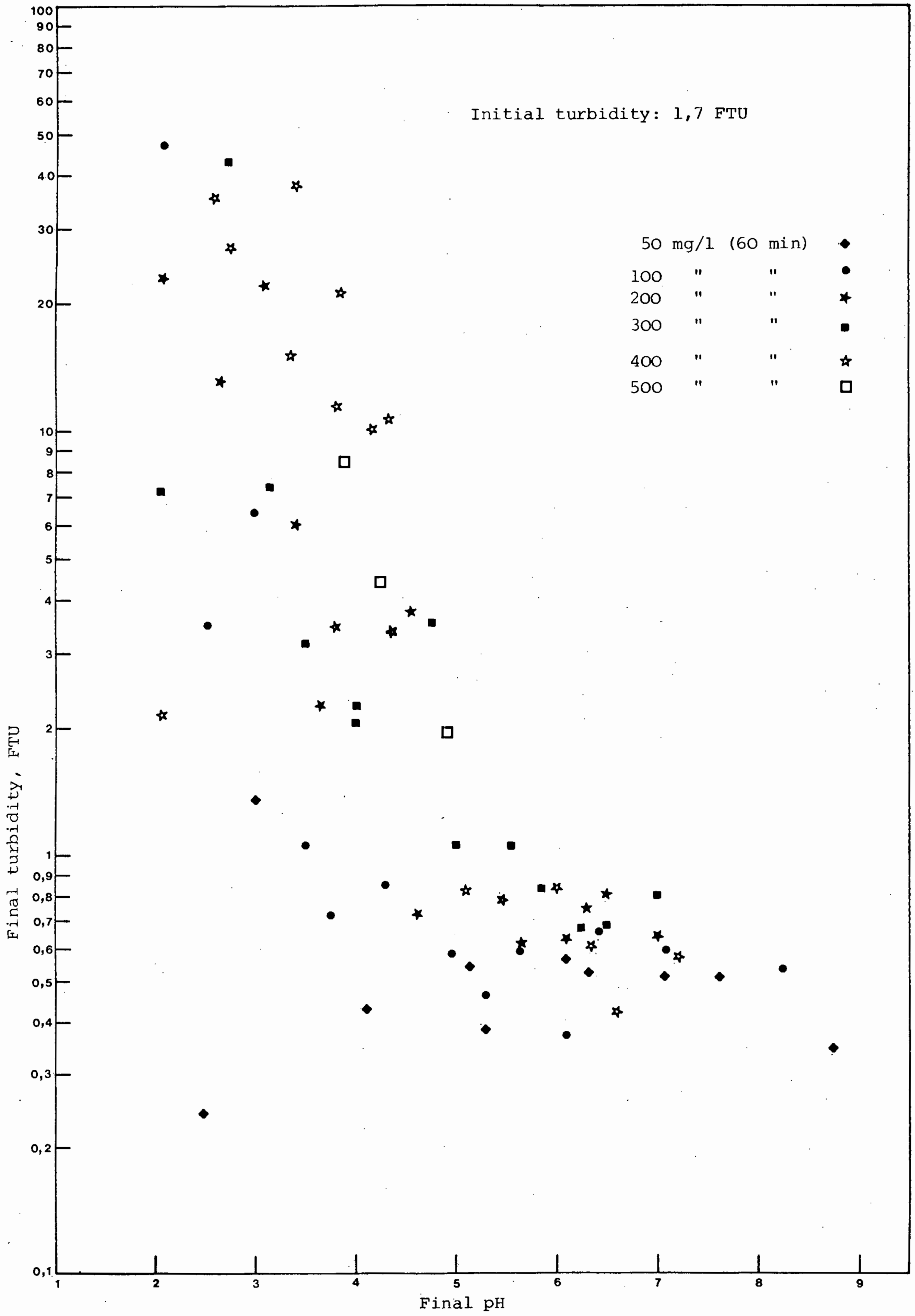


Figure 4.12 Ferric chloride coagulation. Final turbidity is plotted against final pH and coagulant dosage.

TABLE 4.2

Final-Test Results of the MMP Effluent Treatment

Characteristic properties of the raw effluent sample used:

Turbidity, FTU	2,15	TVS, mg/l	300
pH	7,7	Colour, absorbance	0,0315
Total COD, mg/l	54	Cl^-, mg/l	600
Filtered COD, mg/l	52	Ca^{2+}, mg/l	55
TS, mg/l	1530	Na^+, mg/l	320
TDS, mg/l	1520	Al^{3+}, mg/l	0,5 appr.
TSS, mg/l	5	Fe^{3+}, mg/l	negligible

ml 1 N H_2SO_4	0,8	0,8	0,8	0,8	-	-
Coagulant added :	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$FeCl_3$	$FeCl_3$	$Ca(OH)_2$	$Ca(OH)_2$
Coagulant dosage:	200	200	200	200	700	700
Polymer added :	-	N-100	-	N-100	-	AP-273
Polymer dosage :	-	1	-	1	-	1
Final pH :	5,26	5,38	3,87	3,82	11,73	11,75
Final Turbidity (60 min.) :	3,95	3,05	2,25	2,95	0,57	0,68
% Turbidity Removal :	-83	-42	-5	-37	73	68
Final COD :	27	28	20	21	29	30
% Total COD Removal :	50	50	63	63	46	46
% Filtered COD Removal* :	48	48	61	61	44	44
Final Colour :	0,008	0,007	0,0035	0,0045	0,008	0,0075
% Colour Removal:	75	78	89	86	75	76
Final Ca^{2+} :	-	-	-	-	150	150
Final Fe^{3+}, Al^{3+} :	negligible		negligible		-	-
Final TDS :	1530	1555	1560	1570	1830	1850
Settling Rate:	(cm of depth or % floc removal)					
1 min :	-	0,5	0,5	1	7	7
2 " :	0,3	1	2	7	99%	99%
3 " :	1	-	7	99%	-	-
4 " :	1	5			99,9%	99,9%
5 " :	2	90%				
10 " :		99%				

*The filtered COD removal represents the relative difference between the filtered initial COD and the final COD values achieved, and is expressed as a percentage of the initial filtered COD.

MILNERTON MATURATION POND EFFLUENT

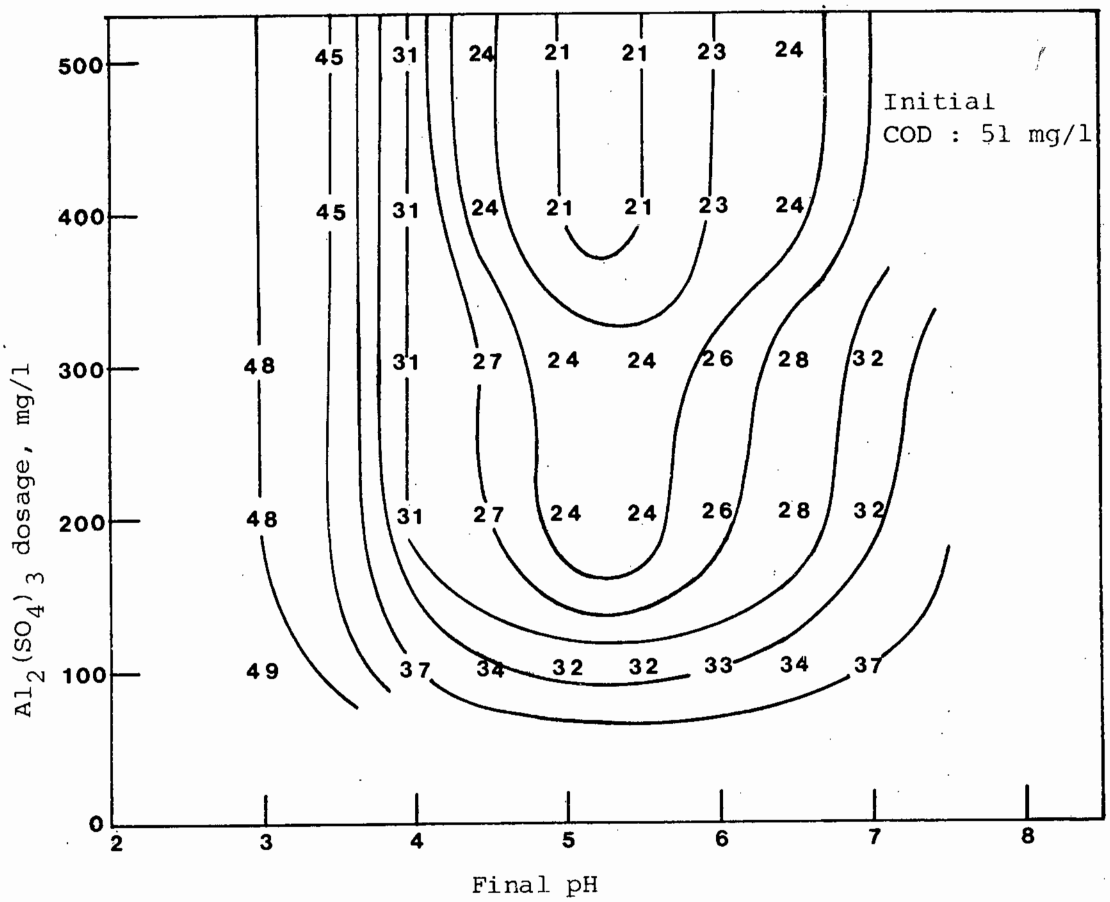


Figure 4.13 Alum coagulation. Variation of final COD with coagulant dosage and final pH.

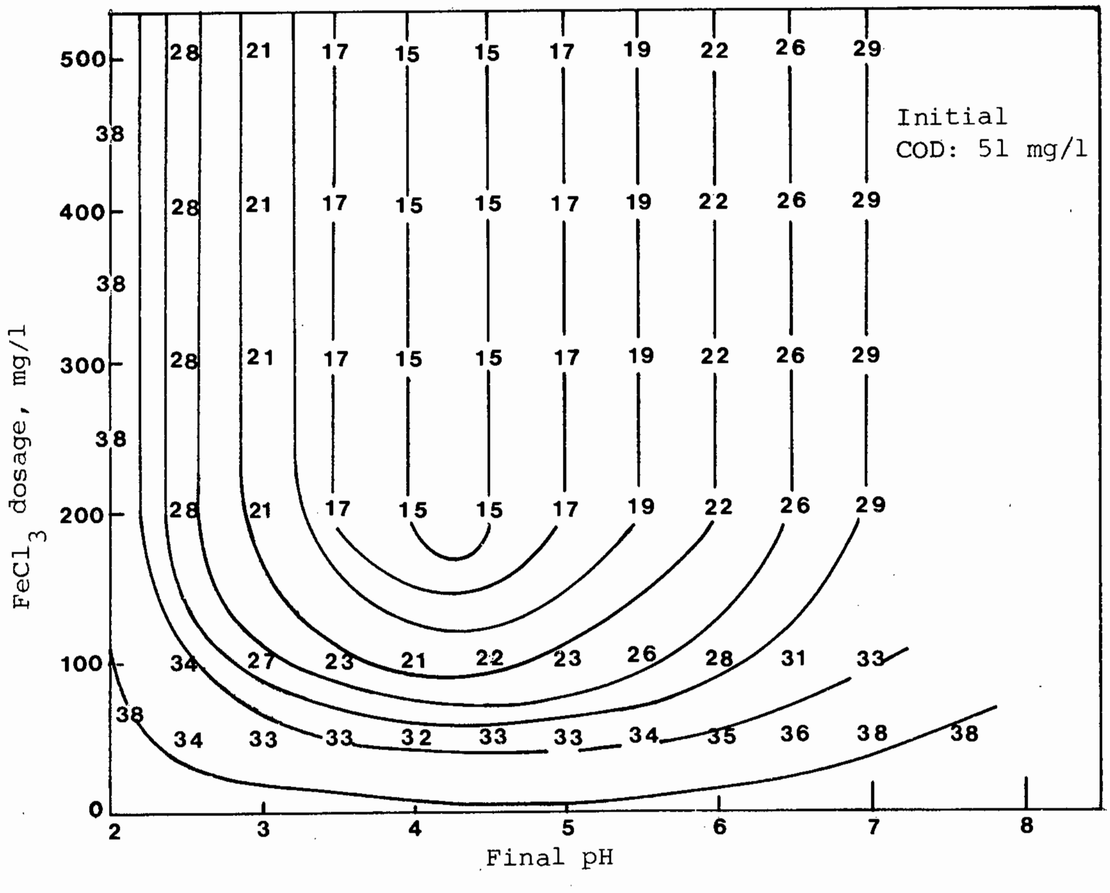


Figure 4.14 Ferric chloride coagulation. Variation of final COD with coagulant dosage and final pH.

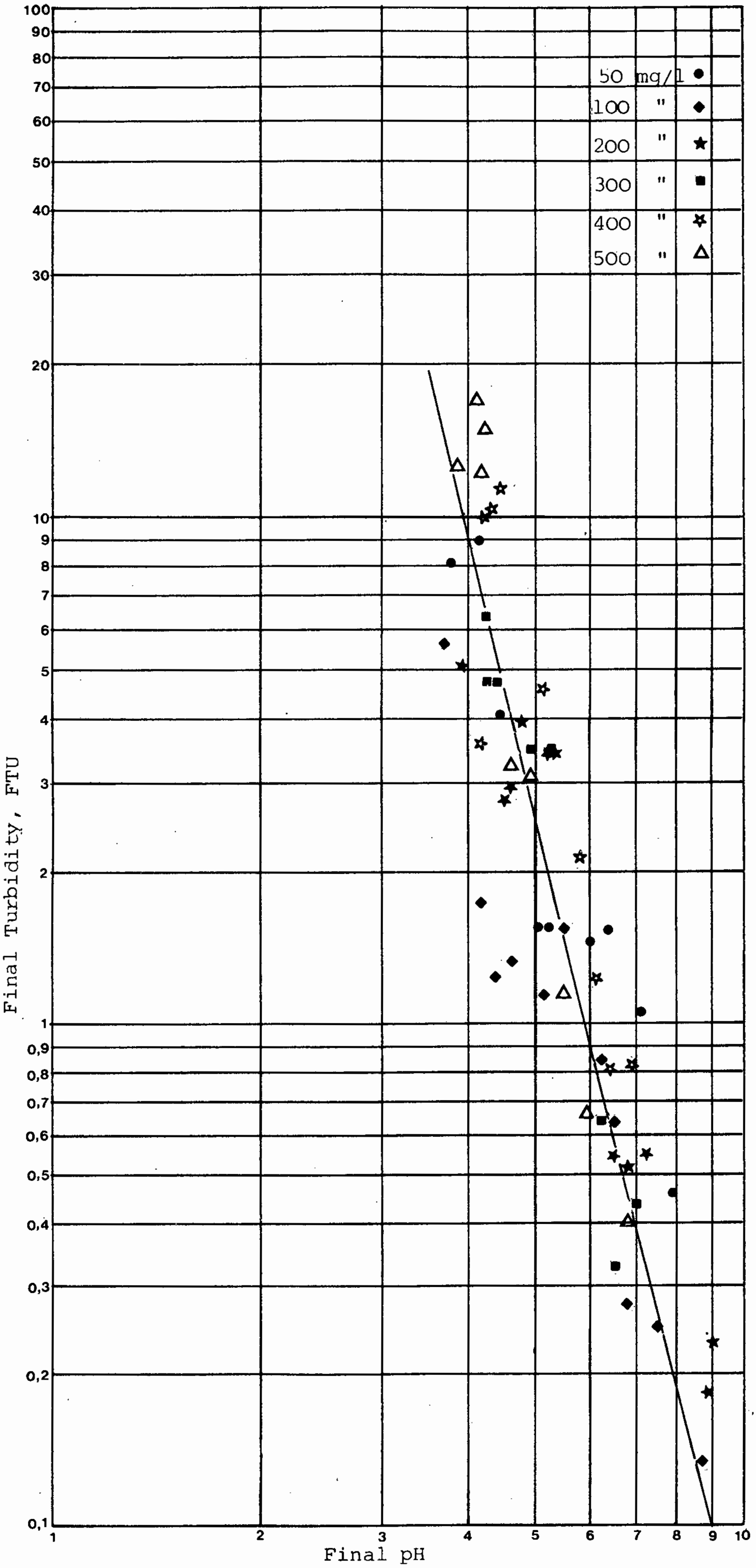


Figure 4.15. Alum coagulation. The final turbidity measured after 60 minutes settling is plotted against final pH and coagulant dosage.

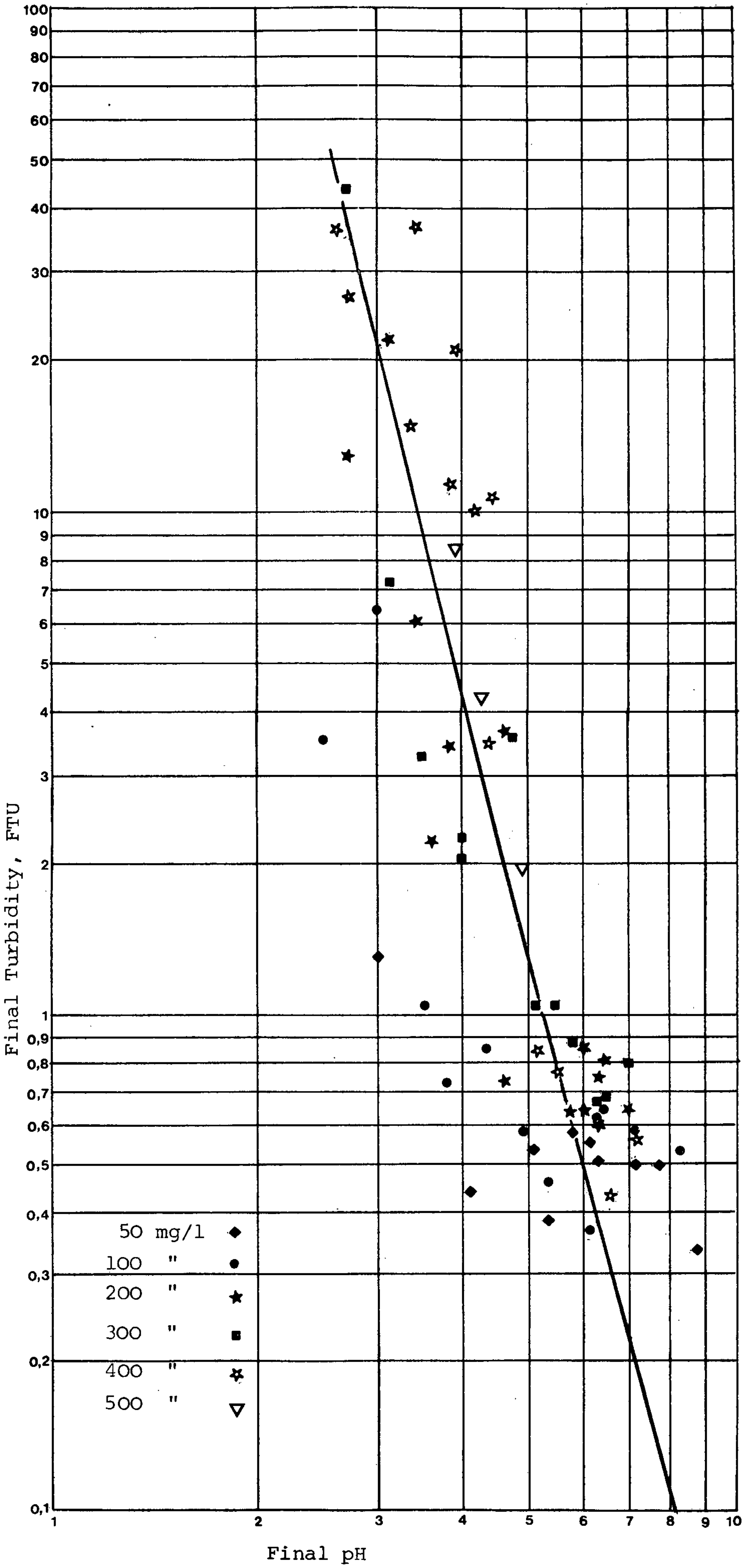


Figure 4.16. Ferric chloride coagulation. The final turbidity measured after 60 minutes settling is plotted against final pH and coagulant dosage.

These plots are shown in Figures 4.15 and 4.16. It is readily observed that the resulting points lie in a straight line. In addition to this, the FRT values seem to be independent of the coagulant dosage, being dependent only on the final pH. pH seemed to be the parameter which primarily controlled the formation of the stable colloids.

If the values of log (FRT) are elaborated,according to the method described in Section L.2 of Appendix L, the results reported in Tables L.3 and L.4 of Appendix L may be obtained. The regression lines obtained are shown in Figures 4.15 and 4.16.

4.3.4 Discussion of the Results of the Main Tests

A. COD Removal

Considering the effects of alum and ferric chloride, the following conclusions may be drawn:

From Figures 4.13 and 4.14 it became apparent that both pH and coagulant dosage played an important role in the removal of the organic waste matter. Always, no matter how high the coagulant concentration, the COD removal was highest at a certain pH - the optimum pH. A pseudostoichrometric relationship - in the sense defined by Stumm and O'Melia, (15) - between the amount of organic waste matter removed as COD and the applied coagulant dosage was observed at constant pH. At the optimum pH this was more pronounced. This relationship was observed to occur between certain limits of coagulant dosage. The lower limit was not determined because of its low practical significance. The higher limit was approximately determined. It was between 200 and 400 mg/l for alum and between 100 and 200 mg/l for ferric chloride coagulations, depending on the pH. Above this limit no further COD removal occurred.

The above discussion suggests that the pH and not stoichiometric considerations was primarily responsible for the oontrol of the destabilization reactions. Stoichiometric considerations were important but of minor consequence. A conclusion similar to this has been drawn by McLellon *et al.*, (30).

The significance of the effect of pH on destabilization of the organic waste matter strongly suggests that, although both specific chemical interactions - responsible for the prominent effect of pH - and adsorption - responsible for the pronounced stoichiometry - took place between the organic colloids and the metal hydroxo-polymers formed, the effect of specific chemical interactions was primarily responsible for the destabilization of the organic colloid waste matter - see Appendix A.

Figures 4.13 and 4.14 show that for constant pH, restabilization of the organic colloids did not occur within the coagulant dosage range applied. At constant pH, any excess coagulant added immediately formed a precipitate which settled rapidly. A similar effect has been observed by McLellon *et al.*, (30) when the pH of coagulation was controlled.

Figures 4.8 and 4.9 show that good COD removal occurred between pH 4 and 7 for alum and between 2 and 7 for ferric chloride coagulations.

At the optimum coagulation pH,the minimum coagulant dosage above which no further COD removal occurred was approximately 400 mg/l for alum and 200 mg/l for ferric chloride coagulations.

The higher the lime dosage used, the more efficient the COD removal in the pH range between about 10,5 and 12.

Although on lime coagulation the removal of the organic waste matter is believed to occur primarily via the agency of the magnesium hydroxide precipitate, the high concentration of the calcium ions at high pH (> 11) seemed to have played an important role, too. Their possible effect should not be ignored, because the precipitation of only magnesium hydroxide cannot normally result in the high COD removal which has been observed. This was indicated by the results of Test 2, Section I.2 of Appendix F, where the high pH created by the caustic soda addition resulted in the precipitation of only magnesium hydroxide from the solution which did not remove the organic waste matter to an appreciable extent.

Lime was as effective as alum on COD removal at dosages as high as 900 mg/l.

The lowest final COD values achieved after coagulation were 21 mg/l, 15 mg/l and 21 mg/l with alum, ferric chloride and lime coagulations, respectively (total COD removal 59, 70 and 59 per cent, respectively), where the effluent's initial total COD was 51 mg/l. These results show clearly that ferric chloride was the most effective coagulant on COD removal.

The results of the Final Test - Table 4.2 - show that the relative colour removal was always about 30 per cent higher than the relative filtered COD removal. This occurred with all alum, ferric chloride and lime coagulants, and indicated that the efficiency of these coagulants in removing colour was higher than that in removing filtered COD. This was due to the predominantly acidic character of the colour substances - see Chapter 7.

Under conditions in the Final Test, which favoured good COD removal, the relative colour removal was 78, 89 and 76 per cent with alum, ferric chloride and lime, respectively. Again, ferric chloride proved to be the most effective coagulant, while lime was as effective as alum in removing colour.

B. Turbidity Removal

As was mentioned in Section 4.3.3 and shown in Figures 4.11 and 4.12, the remaining turbidities after 60 minutes settling were more or less independent of the coagulant dosage, being merely dependent on the pH prevailing on coagulation.

The remaining turbidity values obtained from the main tests were similar to those obtained from the preliminary tests for the same coagulant and the same final pH. This was irrelevant to whether the pH was controlled and suggests that the remaining turbidity did not depend on the levels of pH and alkalinity which prevailed before the coagulant addition, but only on the final pH.

In the discussion developed in Section 4.2.1 it was mentioned that the character of the remaining turbidity was unrelated to the character of the effluent's natural turbidity, which was mainly organic and, in fact, had already been removed requiring much smaller coagulant dosages than those applied for COD removal. The character of the remaining turbidity was inorganic. This was formed after the addition of the coagulant and was the product of a reaction between the metal ion hydrolysis species and inorganic anions in solution.

If the studies of McLellon *et al.*, (30) and Stumm and Morgan, (10) are considered, and, specifically, what they have stated about the behaviour of phosphates in solution after the addition of hydrolyzing metal coagulants, it is reasonable to suggest that the colloids formed were the product of interaction between the coagulant metal ion hydrolysis species and phosphates in solution. The stability of these colloids was not due to interaction with water, but to electrostatic repulsion among particles of similar charge. According to these investigators, when the ratio $\frac{[Me^{3+}]}{[PO_4^{3-}]}$ is less than unity, a negatively charged stable colloid is formed, while when it is greater than unity, mixed - metal-hydroxophosphate complexes also precipitate as stable colloids.

In the MMP effluent the phosphate concentration was once determined and found to be about 7 mg/l as phosphorous. This is equivalent to 0,22 M as PO_4^{3-}. From Figures 2.3 (a) and (b) it may be observed that in the pH range between 4 and 8 for alum coagulation, and between 2 and 8 for ferric chloride coagulation the concentrations of Al^{3+} and Fe^{3+} are well below 0,22 M, and this means that the ratio $\frac{[Me^{3+}]}{[PO_4^{3-}]}$ is always less than unity. Consequently, if the stable colloids formation were attributed to interaction with phosphates, the stable colloids formed would have been negatively charged. Under this assumption, their higher concentration at lower pH values suggested that their negative zeta potential increased as the pH decreased. On the other hand, the lower the pH, the higher the concentration of Al^{3+} and Fe^{3+} in solution - Figure 2.3. Eventually, as the pH decreased a moment should have come at which destabilization of the negatively charged stable colloids by the positively charged Al^{3+} and Fe^{3+} ions should have occurred. This, in fact became established by the fact that at low pH values - lower than about pH 2,5 for ferric chloride and lower than about pH 4 for alum - destabilization of these negatively charged colloids did take place (see Figures 4.11 and 4.12). At approximately these pH ranges the concentration of Al^{3+} and Fe^{3+} species became higher than 0,22 M (Figure 2.3).

The straight lines shown in Figures 4.15 and 4.16 have similar slopes. This means that the formation of the stable inorganic colloids was affected by pH in a similar manner on both alum and ferric chloride coagulations. This, however, was to be expected since the prevailing concentrations of the Al^{3+} and Fe^{3+} species are affected in an exactly similar manner by pH; the slopes of the lines of the Al^{3+} and Fe^{3+} species shown in Figure 2.3 are identical.

The independence of the remaining turbidity after coagulation of the effluent's natural turbidity level as well as of the coagulant concentration applied may be explained by the above model.

The best pH for achieving lowest remaining turbidity after coagulation with alum or ferric chloride is at around neutral pH. In this region the concentrations of aluminum and ferric species in solution are quite low - Figure 2.3.

Lime removed the effluent's natural turbidity completely. The addition of high lime dosages - in order to create a high pH and result in magnesium hydroxide precipitation - caused supersaturation of the solution by C_a^{2+} ions. These reacted with atmospheric carbon dioxide to form a thick calcium carbonate film on the surface, which could interfere with the turbidity determination, if adequate care was not taken.

The flocs formed after coagulation with ferric chloride were slower in settling than those formed after coagulation with alum. Lime coagulation, however, produced the fastest settling flocs.

The results of the Final Test - Table 4.2 - show that the concentrations of aluminum or iron, remaining in solution after coagulation at near the optimum pH for COD removal, were negligible.

C. Effect of Organic Polyelectrolytes when Used in Conjunction with Inorganic Coagulants for COD Removal

In all the tests reported in Section B of Appendix G it was assumed that 0,1 mg/l polymer concentration had no effect on the final COD results. This concentration should have hardly affected the COD level achieved by solely the action of the inorganic coagulant - see Section III of Appendix F.

The test results reported in Section B.I of Appendix G indicate that for an identical alum dosage and almost identical final pH, an increasing polymer dosage resulted in increasing final COD. However, the remaining turbidity did not decrease. These results also show that the higher the alum dosage, the lower the polymer dosage above which the addition of polymer can result in increased final COD values. This occurs because a higher alum dosage results in a lower final COD level (at approximately, the optimum coagulation pH), which is more sensitive to dilution of small amounts of polymer.

Similarly, the results of Tests 1 and 2 reported in Section B.II of Appendix G show that the addition of increasing amounts of polymer, following the inorganic coagulant addition, resulted in increasing final COD values while the remaining turbidity was not decreased. The results of Tests 3 and 4, however, in which the final turbidity was measured after 60 minutes settling, show that the remaining turbidity was increasingly removed at increasing polymer dosages. This finding indicates that polymer addition could, under certain conditions, remove the remaining turbidity. These conditions, however, have not been defined here.

According to the above discussion, to achieve good removal of stable coilloids, the application of a relatively high polymer dosage might be required. This, however, could result in the polymer going into solution with a subsequent increase in the final COD. Consequently, a compromise should be found between the required polymer dosage to efficiently improve the floc settling characteristics and that required to remove the stable colloids without increasing the COD level achieved by the action of the inorganic coagulant. In the case of the above-mentioned Tests 3 and 4, this "optimum" polymer dosage lay between 1 and 2 mg/l.

The test results reported in Section B.III of Appendix G show that when the addition of lime is followed by addition of an anionic polyelectrolyte, a significiantly clearer supernatant may result. The effective polymer dosage was found to be between 0 and 5 mg/l. Polymer dosages higher than 2 mg/l did not result in final COD levels higher than that achieved by solely the action of lime. This indicates that all the excess polymer had been firmly bound onto the flocs formed after the lime addition, and was removed with them during settling. In this case, the increased polymer concentration simply resulted in increased floc magnitude. In such a case the choice of the polymer dosage would be dictated by the required floc settling characteristics and by cost data.

From the above discussion it may be concluded that, in general, it is not necessary to use organic polyelectrolytes in conjunction with inorganic coagulants for COD removal. Their use may be justified when improvements of the clarity of the supernatant or the floc settling characteristics are envisaged. This conclusion is established by the results of the Final Test - Table 4.2 - which show that the use of organic polyelectrolytes did not improve the COD removal appreciably, but did improve the floc settling characteristics. (The estimated floc settling period required for 99 per cent of the flocs to settle in the jars was 10, 3 and 2 minutes for (alum + Superfloc N-100), (ferric chloride + Superfloc N-100), and (lime + Separan AP-273) coagulations, respectively).

CHAPTER 5

CHEMICAL COAGULATION APPLIED TO THE TREATMENT OF THE MILNERTON HUMUS TANK EFFLUENT

5.1 CHARACTERIZATION OF THE EFFLUENT

The origins of the MHT and MMP effluents were identical. The MHT effluent was more turbid than the MMP effluent, because it contained, among other contaminants, those bacterial aggregates which had not settled in the secondary clarifiers. These aggregates were settleable. Their settling pattern was similar to that shown in Figure 5.1.

The characteristic properties of the MHT effluent are given in Table 5.1 below:

TABLE 5.1

Characteristic Properties of the MHT Effluent

Turbidity, FTU	: 5-20	TVS, mg/l	: appr. 350
pH	: 7-8	Cl^-, mg/l	: 500-600
Total COD, mg/l	: 80-135	Ca^{2+}, mg/l	: appr. 55
Filtered COD, mg/l	: 65-80	Mg^{2+}, mg/l	: appr. 55
Colour, absorbance	: appr. 0,05	Na^+ , mg/l	: appr. 300
TS, mg/l	: appr. 1500	Fe^{3+}, mg/l	: non-detectable
TDS, mg/l	: appr. 1500	Al^{3+}, mg/l	: non-detectable
TSS, mg/l	: appr. 30		

Note: these values are based on samples collected throughout the experimentation period.

The total COD change of a representative sample of the effluent is shown graphically as a function of the storage period under 3^oC in Figure 5.2. In this Figure it is shown that the total COD decrease was higher than 5 per cent when the storage period exceeded two days.

5.2 PRELIMINARY TESTS - PRESENTATION AND DISCUSSION OF THE EXPERIMENTAL RESULTS

The results of small scale qualitative tests (using small beakers) suggested that the same inorganic coagulants and organic polyelectrolyte flocculants which produced good results in the case of treatment of the MMP effluent would also produce good results if applied to the treatment

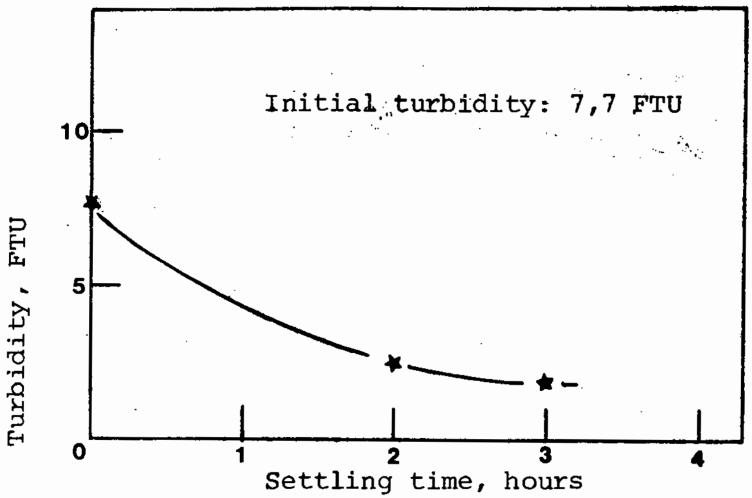


Figure 5.1 The turbidity of the effluent is plotted against settling time.

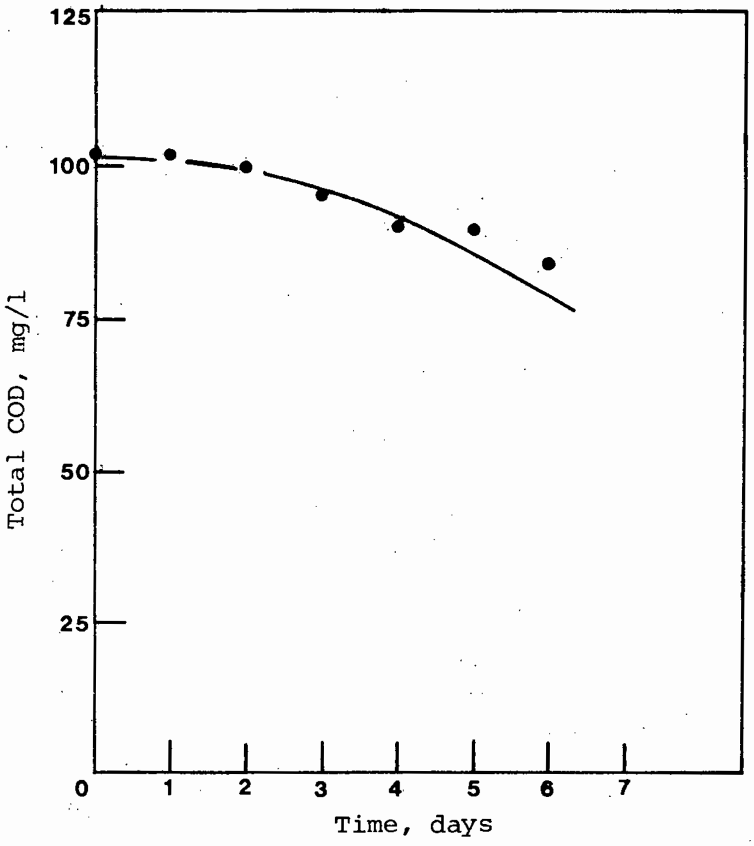


Figure 5.2 The total COD is plotted against storage time under 3°C.

of the MHT effluent. To verify this they were tested on the MHT effluent under conditions which would presumably lead to effective COD removal. The results are presented in Appendix H and suggest that, among the three inorganic coagulants tested, ferric chloride was most effective for COD and colour removals. Lime was as effective as alum in removing colour or COD.

5.3 MAIN TESTS

All the main tests were performed according to the procedure described in Section 3.3.2.

5.3.1 Presentation of the Experimental Results

The experimental results of the main tests are tabulated in Appendix I. The final COD and final turbidity test results are presented graphically in Figures 5.3, 5.4, 5.5, 5.6 and 5.7, 5.8, 5.9 respectively.

The results of the Final Test are given in Table 5.2.

5.3.2 Al and Fe(III) Coagulations - Determination of the Optimum Coagulation Conditions for COD Removal

The technique described in Section 3.5 was employed for the statistical evaluation of the final COD test results which are presented in Sections A.I, A.II and A.III of Appendix I.

The calculated final COD values are presented as described in Section 3.5, in Tables L.5 and L.6 of Appendix L. These are also presented graphically in Figures 5.10 and 5.11, from which it is readily observable that the optimum pH for COD removal was at around pH 5 for alum coagulation, and at around pH 4,5 for ferric chloride coagulation.

5.3.3 Al and Fe(III) Coagulations - The Remaining Turbidity Studied as a Function of Coagulant Dosage and Final pH

A similar plot to that shown in Figure 4.15 was made only for alum coagulation and not for ferric chloride coagulation due to lack of experimental final turbidity values obtained after 60 minutes settling in the latter case. For this plot the FRT values reported in Tests 2, 3, 4 and 5 of Section A.I and in Test 1, Section B, of Appendix I were considered. The reason the results of Test 1, Section B, were considered for the plot was that the final turbidity values reported in that test corresponded to a similar initial turbidity with that of the raw material used for Tests 2, 3, 4 and 5 and, also, to a 60 minutes settling period. The plot is shown in Figure 5.12. The experimental points shown in Figure 5.12 lie in a straight line. This suggests

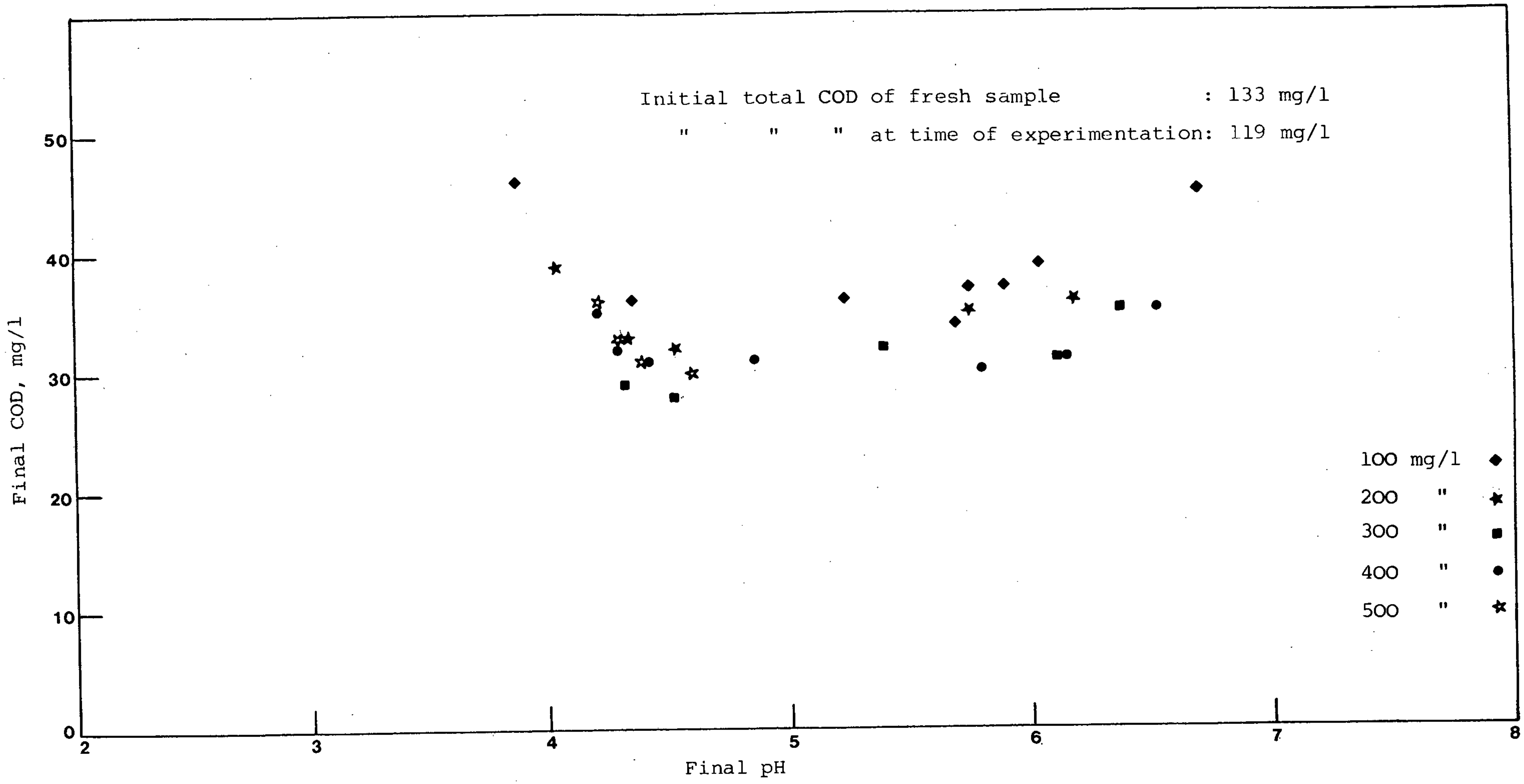


Figure 5.3 Alum coagulation. Final COD is plotted against final pH and coagulant dosage.

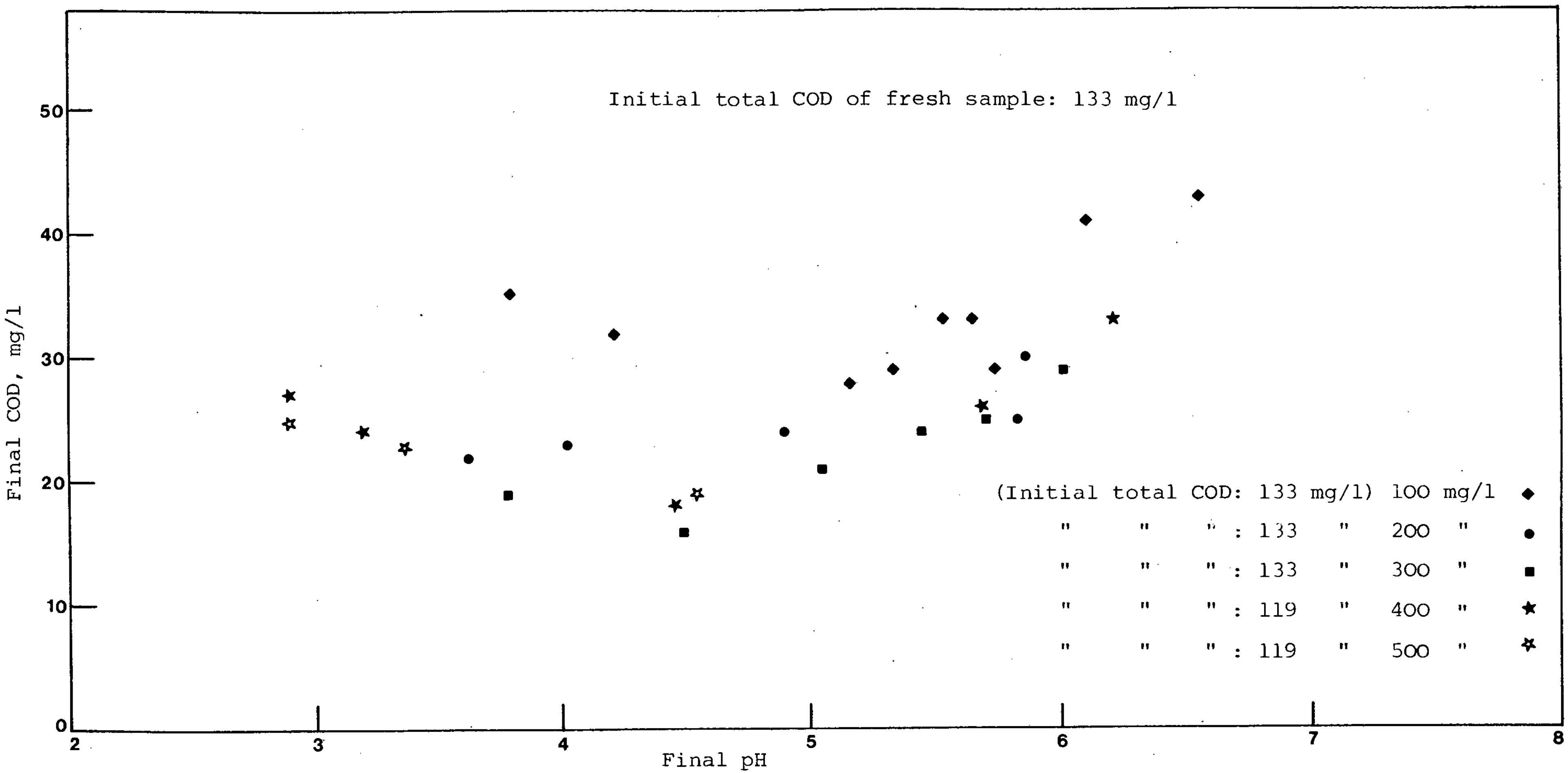


Figure 5.4 Ferric chloride coagulation. Final COD is plotted against final pH and coagulant dosage.

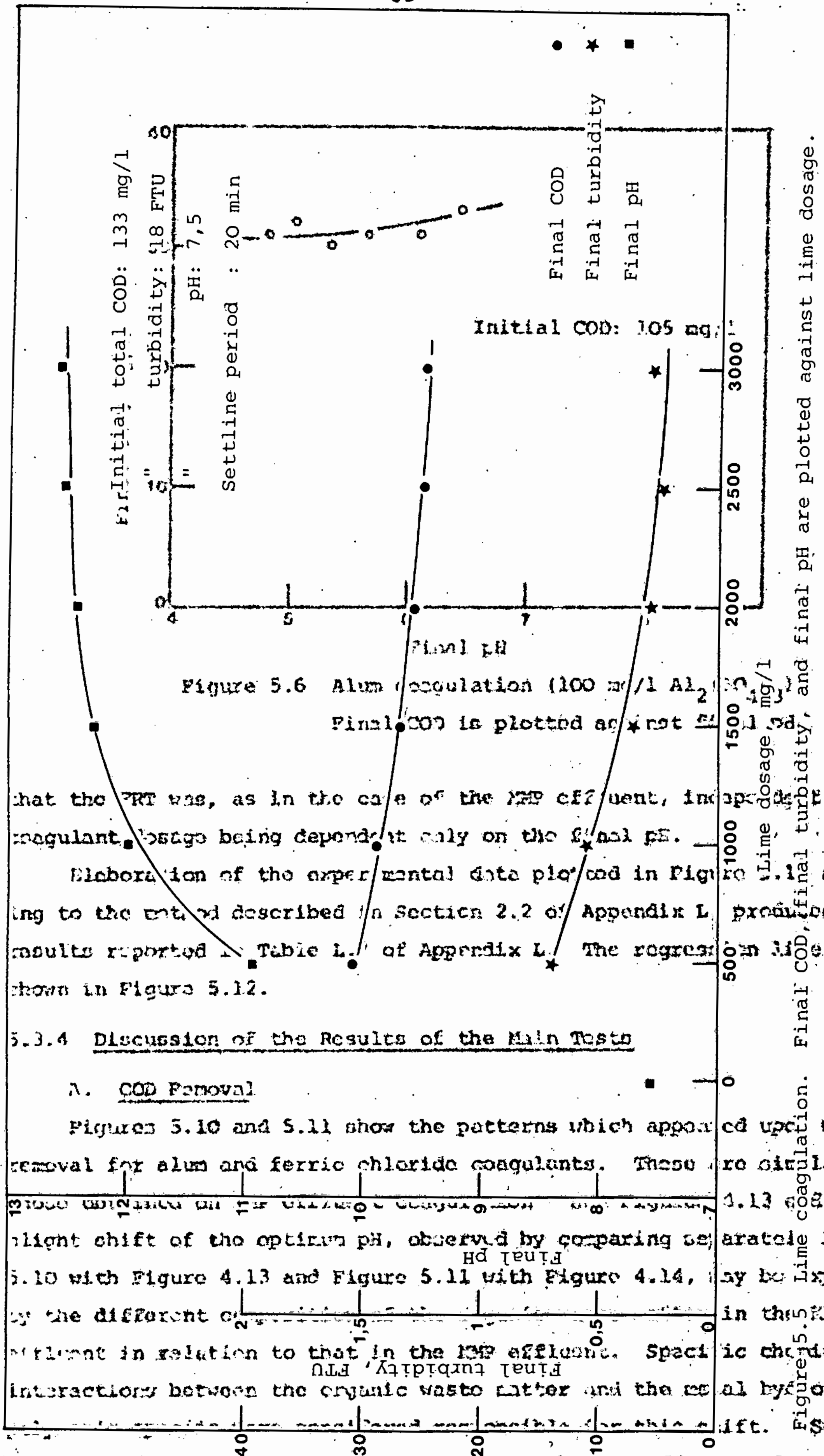


Figure 5.6 Alum coagulation (100 mg/l $Al_2(SO_4)_3$). Final COD is plotted against final pH.

Figure 5.5 Lime coagulation. Final COD, final turbidity, and final pH are plotted against lime dosage.

that the PRT was, as in the case of the MMP effluent, independent of the coagulant dosage being dependent only on the final pH.

Elaboration of the experimental data plotted in Figure 5.1[illegible] according to the method described in Section 2.2 of Appendix L produced the results reported in Table L.[illegible] of Appendix L. The regression line is shown in Figure 5.12.

5.3.4 Discussion of the Results of the Main Tests

A. COD Removal

Figures 5.10 and 5.11 show the patterns which appeared upon COD removal for alum and ferric chloride coagulants. These are similar to [illegible] 4.13 and 4.14. The slight shift of the optimum pH, observed by comparing separately Figure 5.10 with Figure 4.13 and Figure 5.11 with Figure 4.14, may be explained by the different c[illegible] in the MHT effluent in relation to that in the MMP effluent. Specific chemical interactions between the organic waste matter and the metal hydroxo- [illegible] shift. See Chapter 7 for a detailed explanation. For the MHT effluent, 300 mg/l of alum or ferric chloride was the approximate minimum coagulant dosage

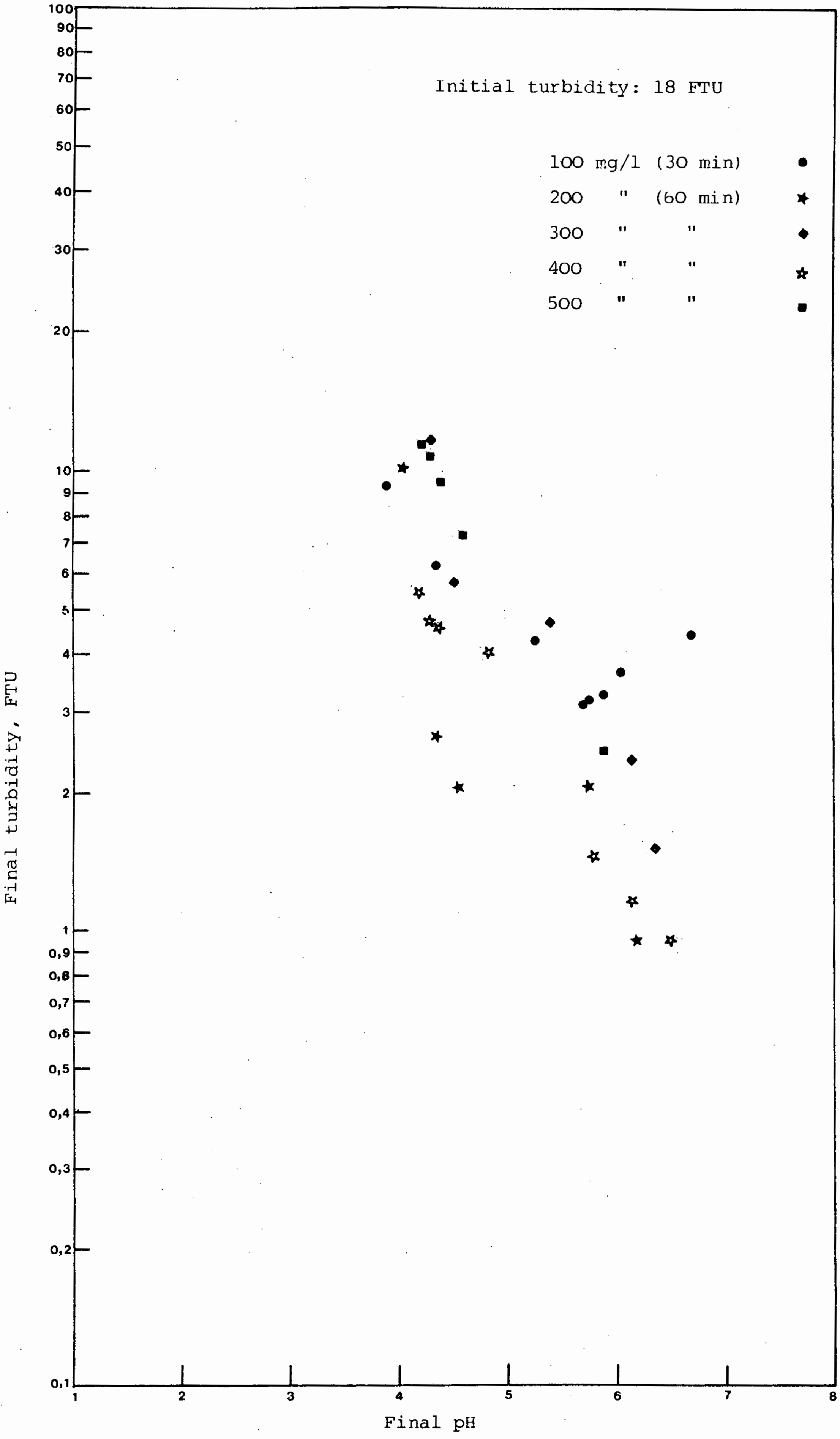


Figure 5.7 Alum coagulation. Final turbidity is plotted against final pH and coagulant dosage.

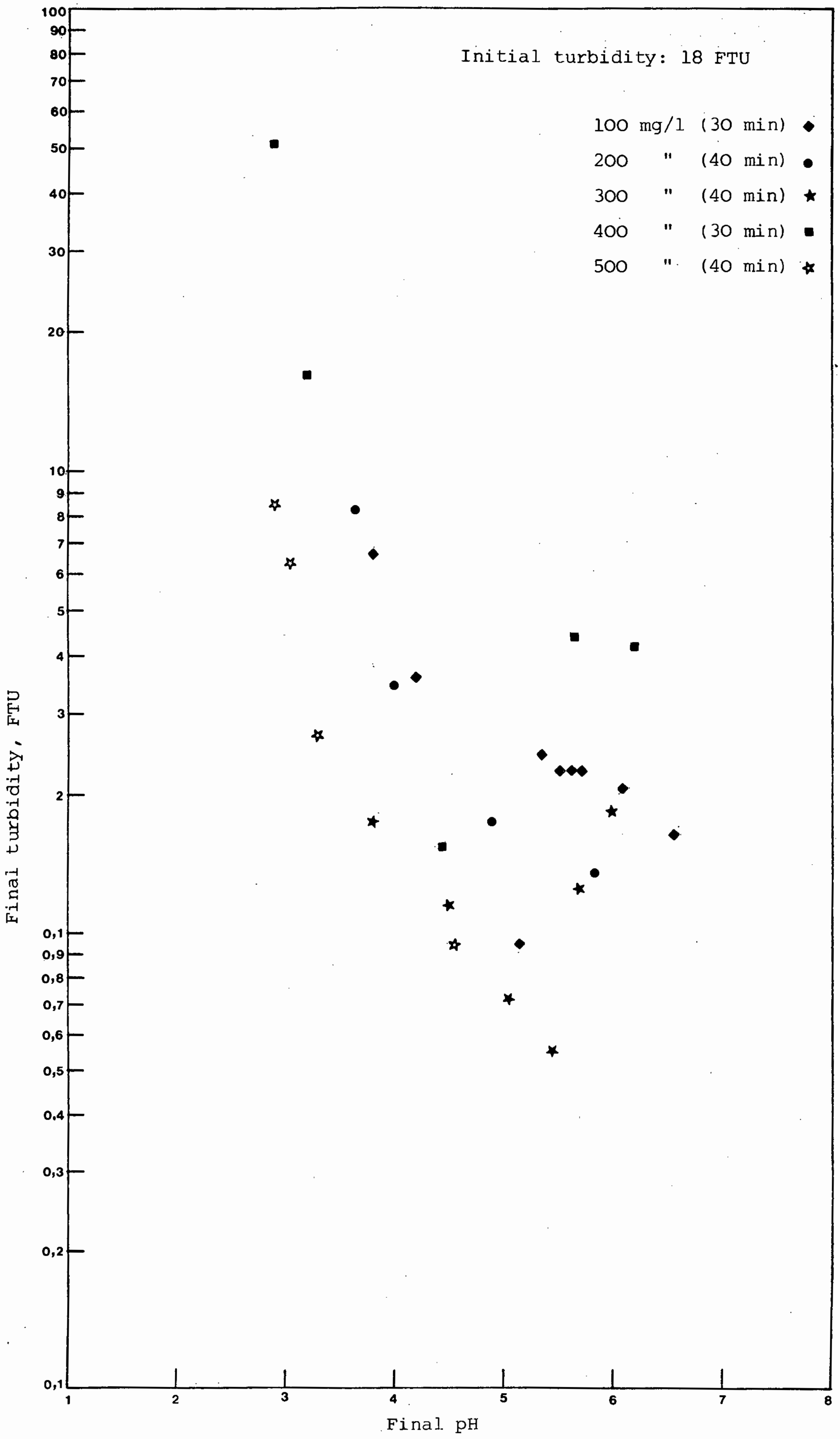


Figure 5.8 Ferric chloride coagulation. Final turbidity is plotted against final pH and coagulant dosage.

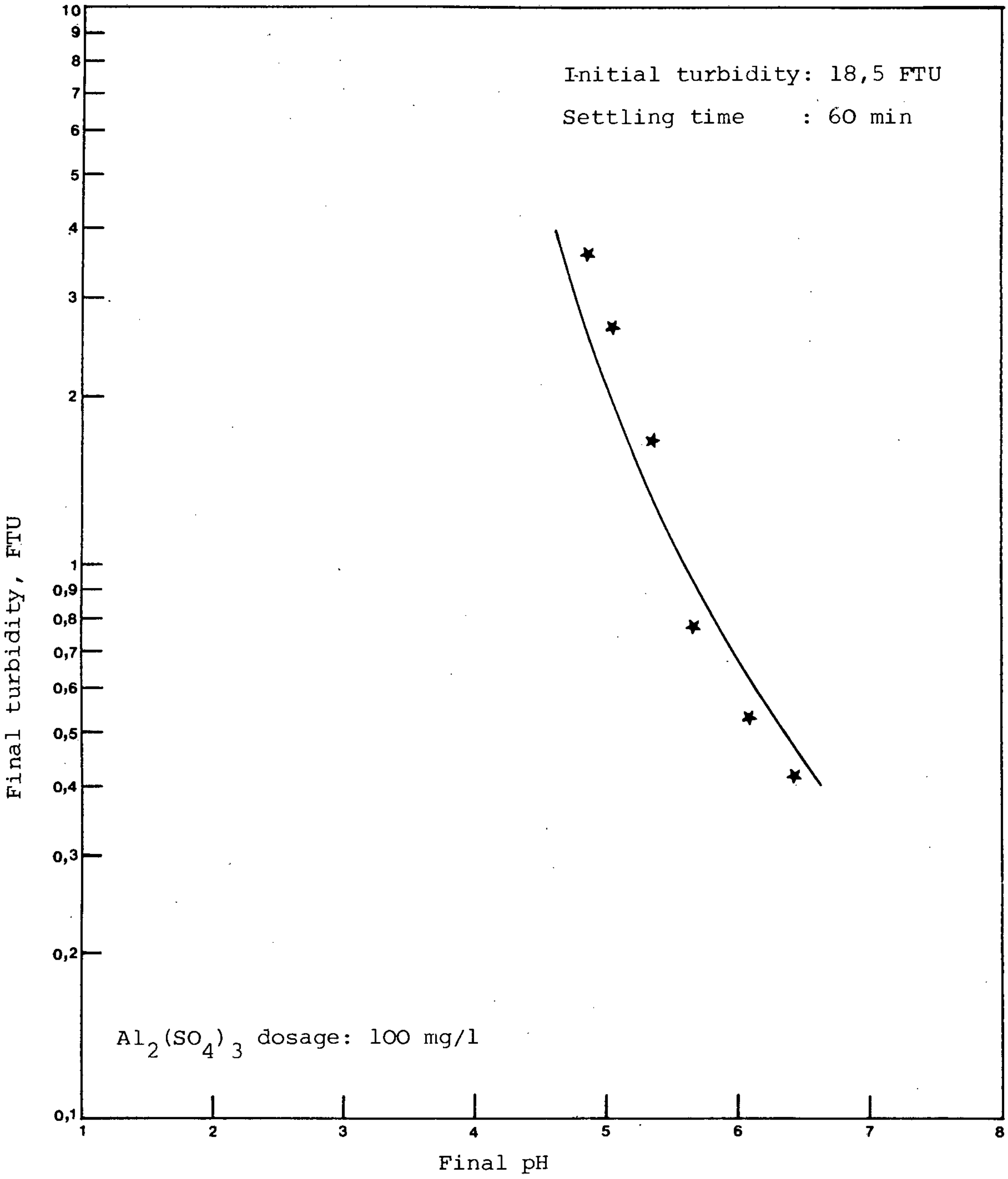


Figure 5.9 Alum coagulation. Final turbidity is plotted against final pH.

above which no further COD removal occurred (at the optimum coagulation pH in each case). In the case of the MMP effluent, this minimum dosage was 400 mg/l for alum coagulation. This, however, should not have been higher than 300 mg/l, because the organic load in the MMP effluent was always lower than that in the MHT effluent. This seeming discrepancy was due to the way the statistical evaluation of the experimental results

TABLE 5.2

Final-Test Results of the MHT Effluent Treatment

Characteristic properties of the raw effluent sample used:

Turbidity, FTU	11,5	TVS, mg/l	340
pH	7,7	Colour, absorbance	0,052
Total COD, mg/l	120	Cl^-, mg/l	600
Filtered COD, mg/l	79	Ca^{2+}, mg/l	55
TS, mg/l	1590	Na^+, mg/l	320
TDS, mg/l	1570	Fe^{3+}, mg/l	Non-detectable
TSS, mg/l	30	Al^{3+}, mg/l	Non-detectable

ml 1 N NaOH :	1,2	1,2	2	2	-	-
Coagulant added :	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$FeCl_3$	$FeCl_3$	$Ca(OH)_2$	$Ca(OH)_2$
Coagulant dosage:	400	400	400	400	1500	1500
Polymer added :	-	N-100	-	N-100	-	AP-273
Polymer dosage :	-	2	-	2	-	2
Final pH :	4,88	4,81	4,25	4,12	12,33	12,31
Final Turbidity (30 min) :	4,05	1,25	2,95	3,15	0,35	0,34
% Turbidity Removal :	65	89	74	72	97	97
Final COD :	30	29	20	23	27	29
% Total COD Removal :	75	75	83	82	77	77
% Filtered COD Removal :	62	62	75	74	66	66
Final Colour :	0,011	0,01	0,004	0,005	0,01	0,01
% Colour Removal :	79	81	92	90	81	81
Final TDS :	1630	1640	1725	1745	2240	2260
Final Ca^{2+} :	-	-	-	-	400	400
Final Fe^{3+} :	-	-	Non-detectable		-	-
Final Al^{3+} :	0,5	0,5	-	-	-	-

Table 5.2 contd. overleaf . . .

Table 5.2 (continued)

Settling Rate : (cm of depth or % floc removal)

1 min	-	2	-	2	-	7
2 min	-	-	-	7	7	-
3 min	0,5	7	7	-	-	99%
4 min	-	-	-	-	-	-
5 min	-	-	-	99%	99%	
10 min	95%	99%	99%			
30 min	99%					

was carried out i.e. to the incorporation of results corresponding to adjacent coagulant dosages.

Lime was effective at dosages higher than about 500 mg/l, above which the COD removal was proportional to the coagulant dosage.

The lowest final COD values achieved after coagulation using a sample whose initial total COD was 133 mg/l, were 29 mg/l, 18 mg/l and 25 mg/l for alum, ferric chloride and lime coagulations, respectively (total COD removal 78, 86 and 81 per cent, respectively). These results show that ferric chloride was the most effective coagulant for COD removal and that lime was as effective or even more effective than alum.

The results of the Final Test - Table 5.2 - show that the relative colour removal was always higher than the relative filtered COD removal for all three inorganic coagulants tested. At approximately the optimum pH for COD removal the relative colour removal after alum, ferric chloride and lime coagulations was 80, 91 and 81 per cent, respectively. Ferric chloride was the most effective coagulant, while lime was as effective as alum in removing colour.

(B) Turbidity Removal

For 60 minutes floc settling period similar results to those reported in the case of the MMP effluent were obtained - see Figures 5.7 and 5.9. Simlilar conclusions may be drawn in this case, too. Different residual turbidities were, however, obtained when the remaining turbidity was measured after the lapse of less than 60 minutes - see Figures 5.7 (100 mg/l alum) and 5.8. The remaining turbidity in those cases showed a tendency to increase at around neutral or slight acidic pH. This seemed to occur independently of the coagulant dosage applied and was only pH dependent. The shorter the floc settling period, the higher the remaining

MILNERTON HUMUS TANK EFFLUENT

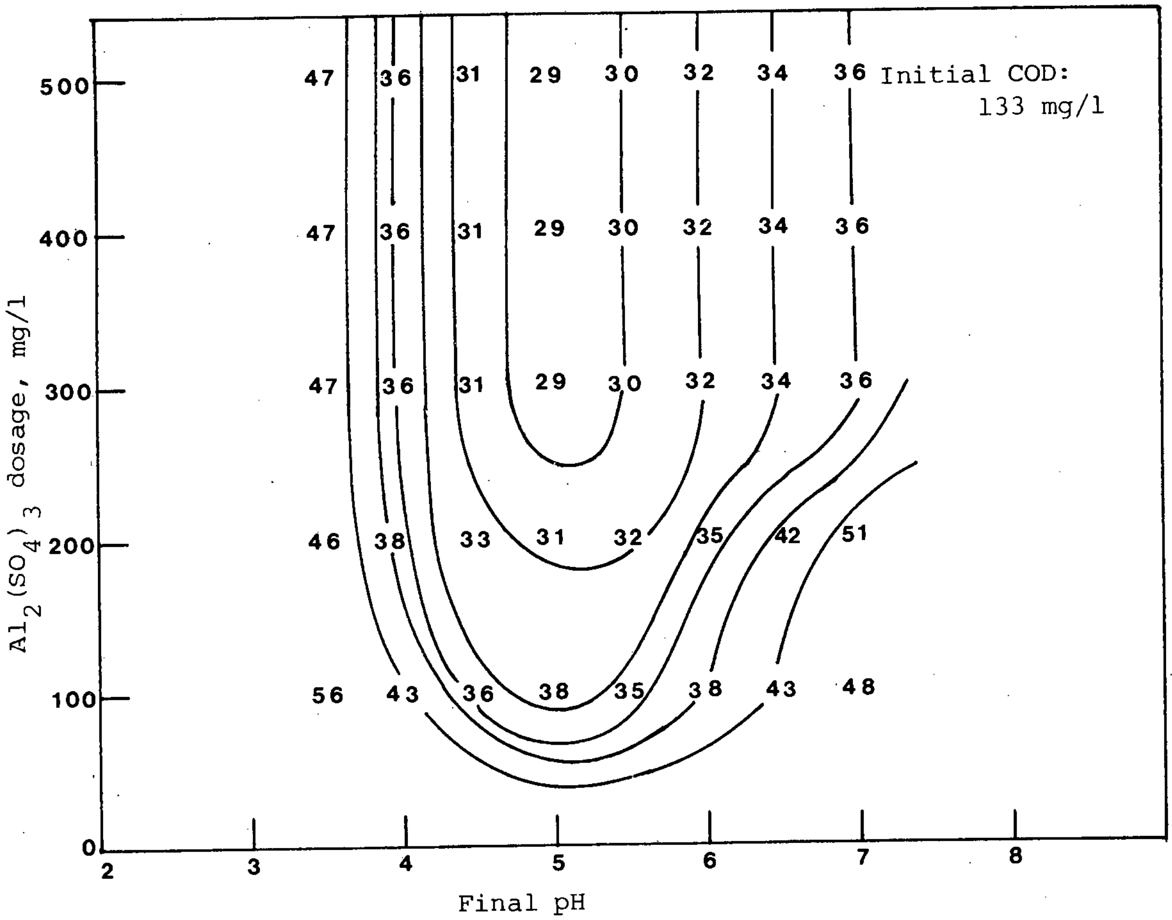


Figure 5.10 Alum coagulation. Variation of final COD with final pH and coagulant dosage.

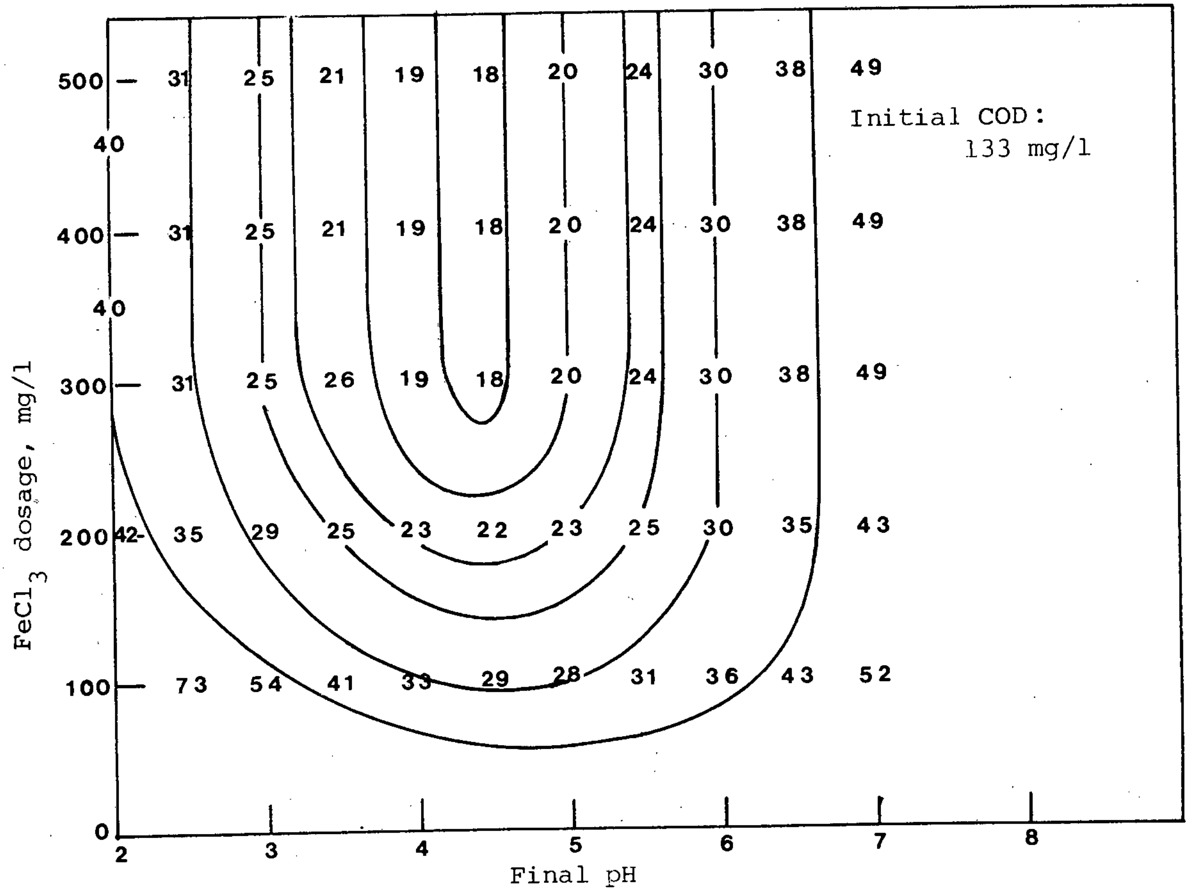


Figure 5.11 Ferric chloride coagulation. Variation of final COD with final pH and coagulant dosage.

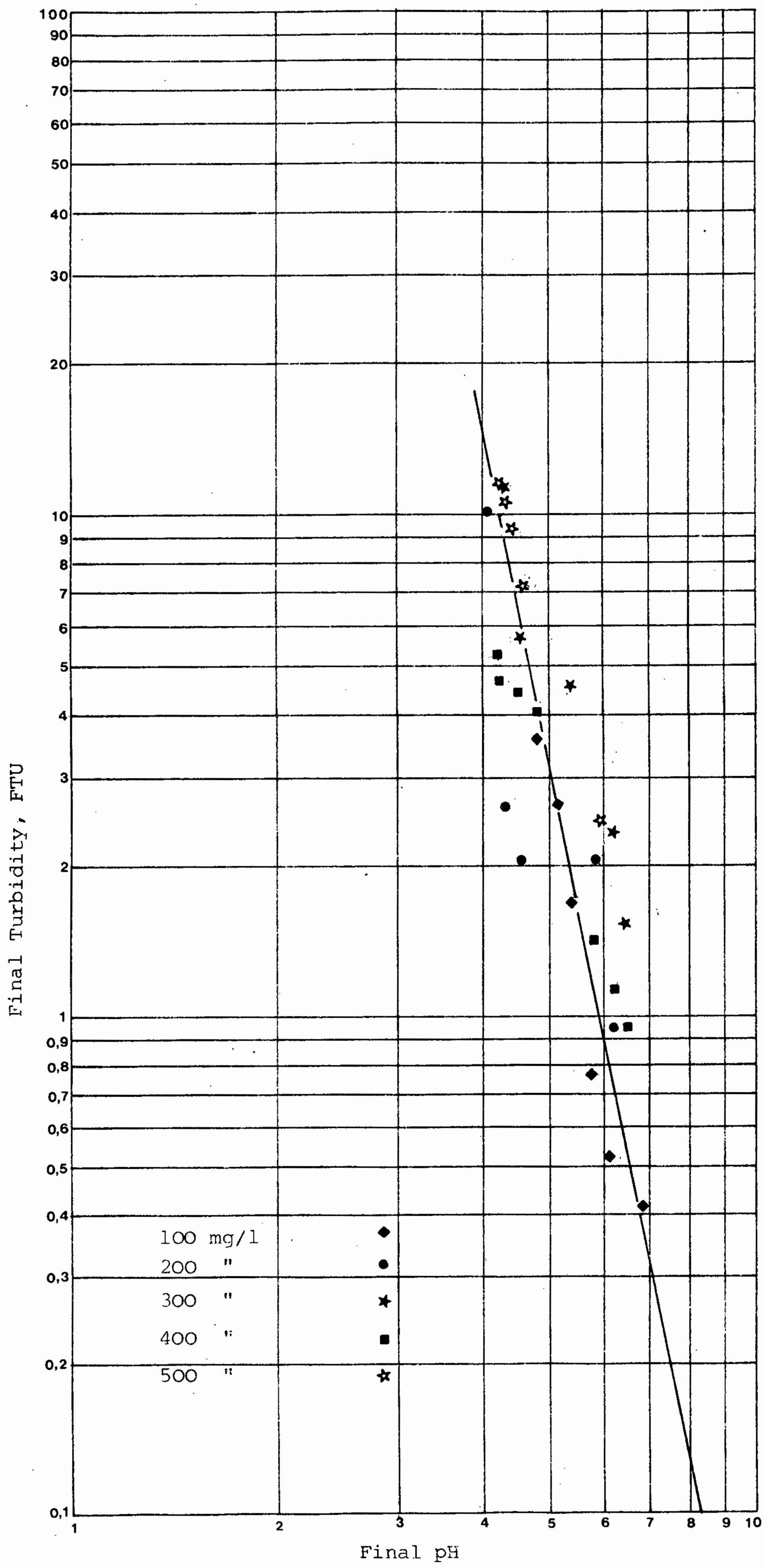


Figure 5.12 Alum coagulation. The final turbidity measured after 60 minutes settling is plotted against final pH and coagulant dosage.

turbidity at around neutral pH. Similar results were obtained in the case of the AMP effluent for shorter than 60 minutes settling periods (Section 6.3.4). A detailed explanation of this phenomenon will be presented in Section 6.3.4. It may only be mentioned here that the higher turbidity which was observed at around neutral pH values was related to the higher rate of precipitation of aluminum of ferric hydroxide in this pH region.

It may be observed that the regression line shown in Figure 5.12 has a similar slope to that of Figure 4.15. This suggests that the mechanism responsible for the appearance of the remaining turbidity was similar in both cases (see Section 4.3.4 - (B)).

Lime removed the effluent's particulate matter completely. The flocs formed after lime coagulation were the fastest in settling. Those formed after ferric chloride coagulation were faster in settling than those formed after alum coagulation - Table 5.2.

The test results reported in Table 5.2 show that when organic polyelectrolytes were used in conjunction with inorganic coagulants, the floc settling period required for 99 per cent of the flocs to settle in the jars was reduced to 10,5 and 3 minutes for (alum + Superfloc N-100), (ferric chloride + Superfloc N-100) and (lime + Separant AP-273) coagulations, respectively.

The concentrations of soluble aluminum or iron remaining after coagulation were negligible (Table 5.2).

CHAPTER 6

CHEMICAL COAGULATION APPLIED TO THE TREATMENT OF THE ATHLONE MATURATION POND EFFLUENT

6.1 CHARACTERIZATION OF THE EFFLUENT

The appearance of the effluent was yellowish-brown and its odour unpleasant. The turbidity was relatively high for a maturation pond effluent. Due to the higher organic load of this effluent, when compared to that of the MMP effluent, the values of characteristic properties of the AMP effluent showed a wider variation. These values are shown in Table 6.1.

TABLE 6.1

Characteristic Properties of the AMP Effluent

Turbidity, FTU	: 6-20	TVS, mg/l	: 50-200
pH	: 7-7,5	Cl^-, mg/l	: appr. 200
Total COD, mg/l	: 115-300	Ca^{2+}, mg/l	: appr. 30
Filtered COD, mg/l	: 100-150	Mg^{2+}, mg/l	: appr. 20
Colour, absorbance	: 0,1-0,2	SO_4^{2-}, mg/l	: appr. 100
TS, mg/l	: appr. 800	Na^+, mg/l	: appr. 200
TDS, mg/l	: 700-800	Al^{3+}, mg/l	: Non-detectable
TSS, mg/l	: 30-100	Fe^{3+}, mg/l	: Non-detectable

Note: These values are based on samples collected throughout the experimentation period.

The total COD change of a representative sample of the effluent is shown as a function of the storage period under 3°C in Figure 6.1-(a). It is observed that the COD decrease was higher than 5 per cent when the storage period exceeded one day.

A two-litre sample of this effluent was placed in a conical flask and was aerated by means of an air distributor. Every day the COD change of the sample was determined and recorded. The results are shown in Figure 6.1-(b). As it is observed, evaporation effects predominated over biological oxidation after a certain moment, and the slope of the line representing the phenomenon changed sharply. The COD values were corrected for evaporation losses and the corrected values are also shown in Figure 6.1-(b). It may be observed that at least 50 per cent of the

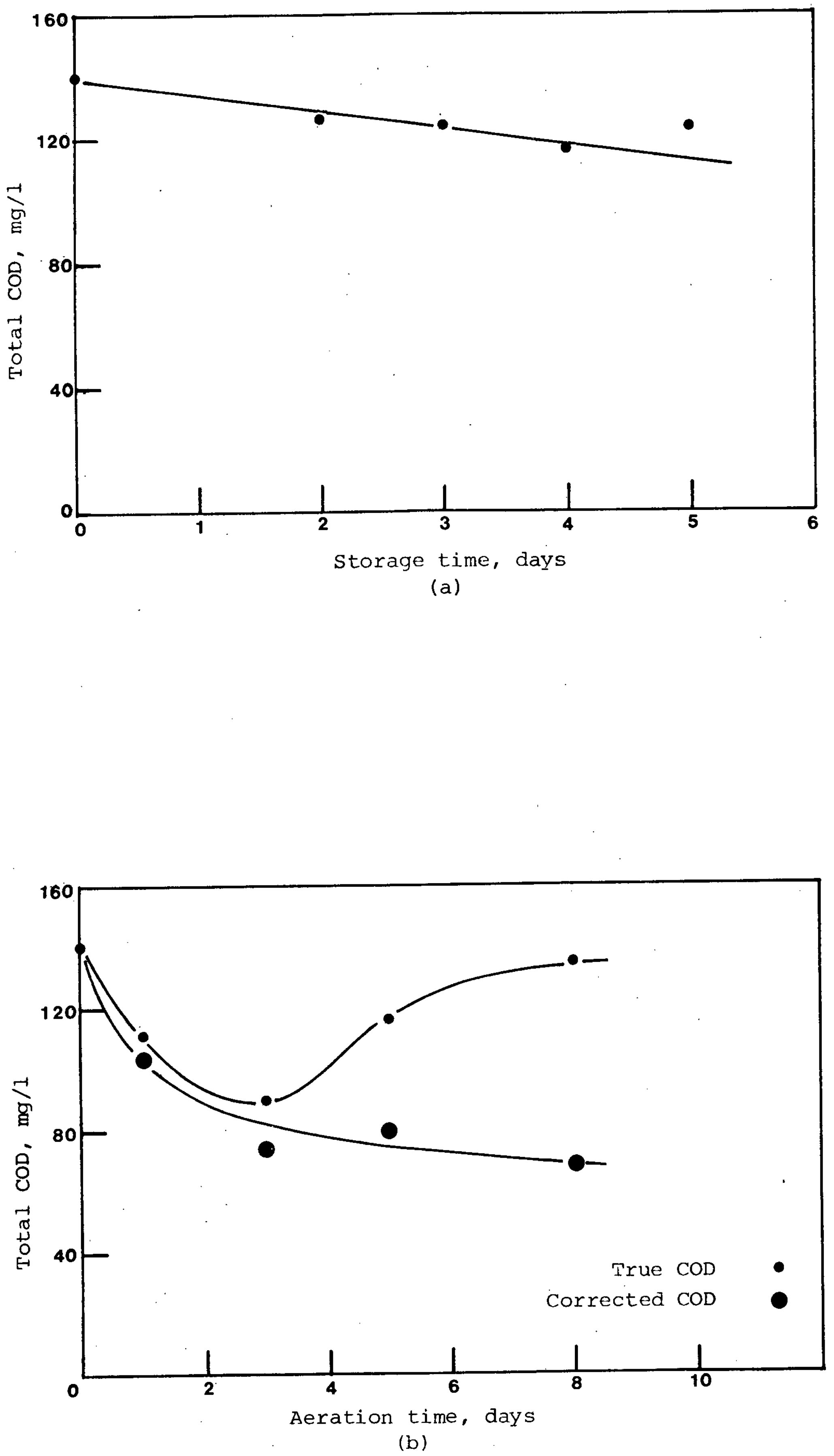


Figure 6.1 Total COD is plotted separately against storage and aeration times.

oxidizable waste matter in this sample of the effluent was biodegradable.

6.2 PRELIMINARY TESTS

Most of the preliminary tests were carried out according to the method described in Section 3.3.1. All three inorganic coagulants were employed. Most of the organic polyelectrolytes mentioned in Table 3.1 were tested.

6.2.1 Presentation and Discussion of the Experimental Results

The preliminary tests were performed in two steps:

In the first step preliminary qualitative tests were performed using small beakers. Similar quantitative results to those reported in Section 4.2.1 were obtained.

The second step involved tests from which quantitative conclusions could be drawn. The results of these tests are presented in a tabulated form in Appendix J. The final turbidity results obtained after alum, ferric chloride and lime coagulations are shown in Figures 6.2, 6.4 and 6.5. The final COD values obtained after coagulation with alum and lime are shown in Figures 6.3. and 6.5.

The results of Test 1, reported in Section I.1 of Appendix J - Figures 6.2 and 6.3 -, show that the final COD was considerably reduced by the addition of 100 mg/l alum. 295 mg/l initial total COD was reduced to 75 mg/l. The CCC was lower than 100 mg/l for both COD and turbidity removals.

Alum dosages higher than 300 mg/l did not seem to result in further COD removal, because the prevailed pH did not favour COD removal (pH was not controlled). The further addition of alum resulted in the formation of excessive turbidity which eventually became higher than the initial turbidity before coagulation. As in the case of the MMP effluent, the final COD values remained unaffected by changes in final turbidity.

Figures 6.2. and 6.4 show that at acidic pH the pattern of increased turbidity appeared - similar to that dealt with in Chapter 4.
The discussion developed in Chapter 4 concerning the probable cause of the appearance and disappearance of the remaining turbidity after coagulation at acidic pH applies here, as well. The increased turbidity observed near neutral pH values was due to the higher rate of precipitation of the metal hydroxides at this pH. This occurred only when the settling period was shorter than 60 minutes when the flocs were not given enough time to settle. This phenomenon will be discussed in

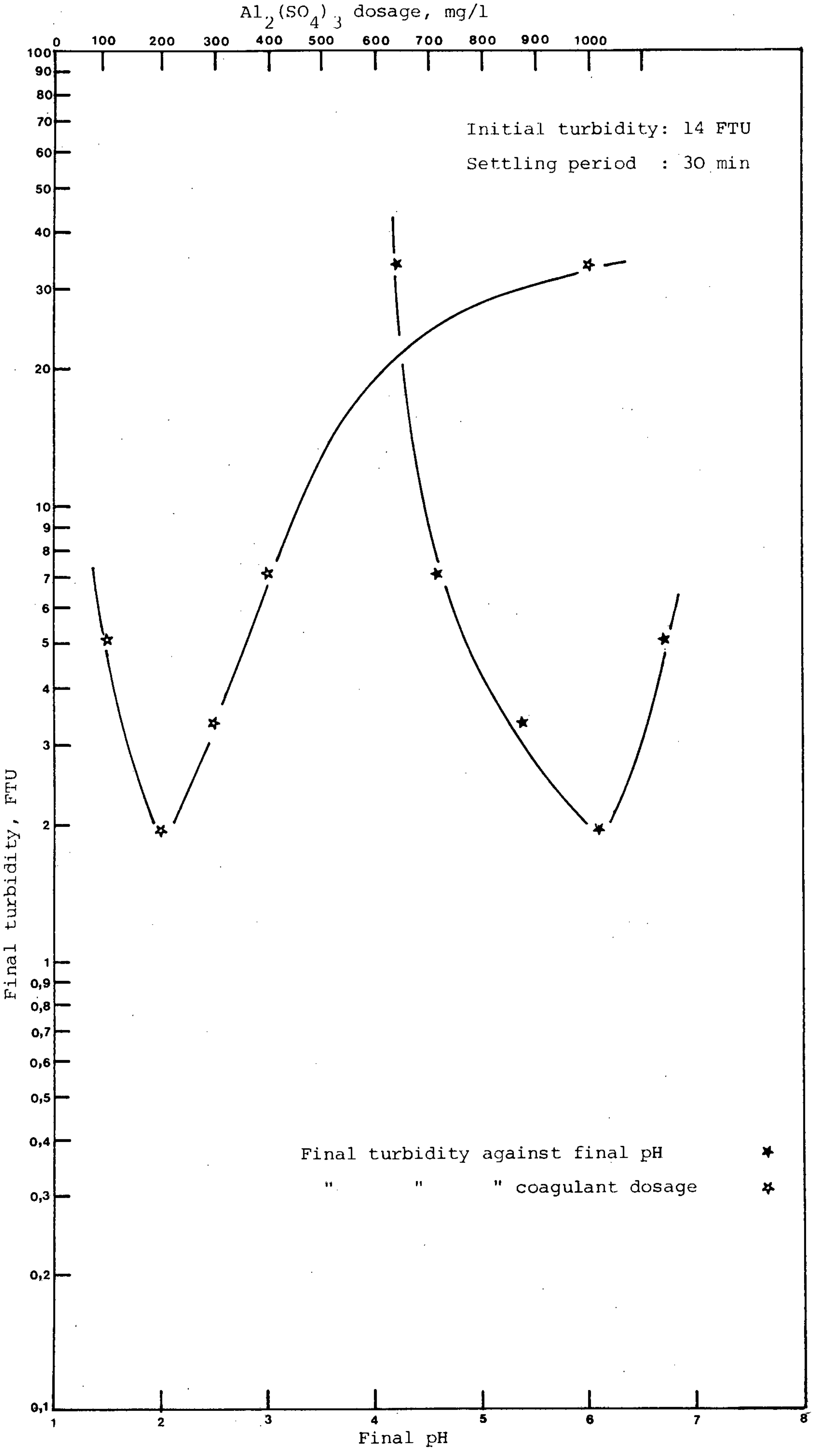


Figure 6.2 Alum coagulation. Final turbidity is separately plotted against final pH and coagulant dosage.

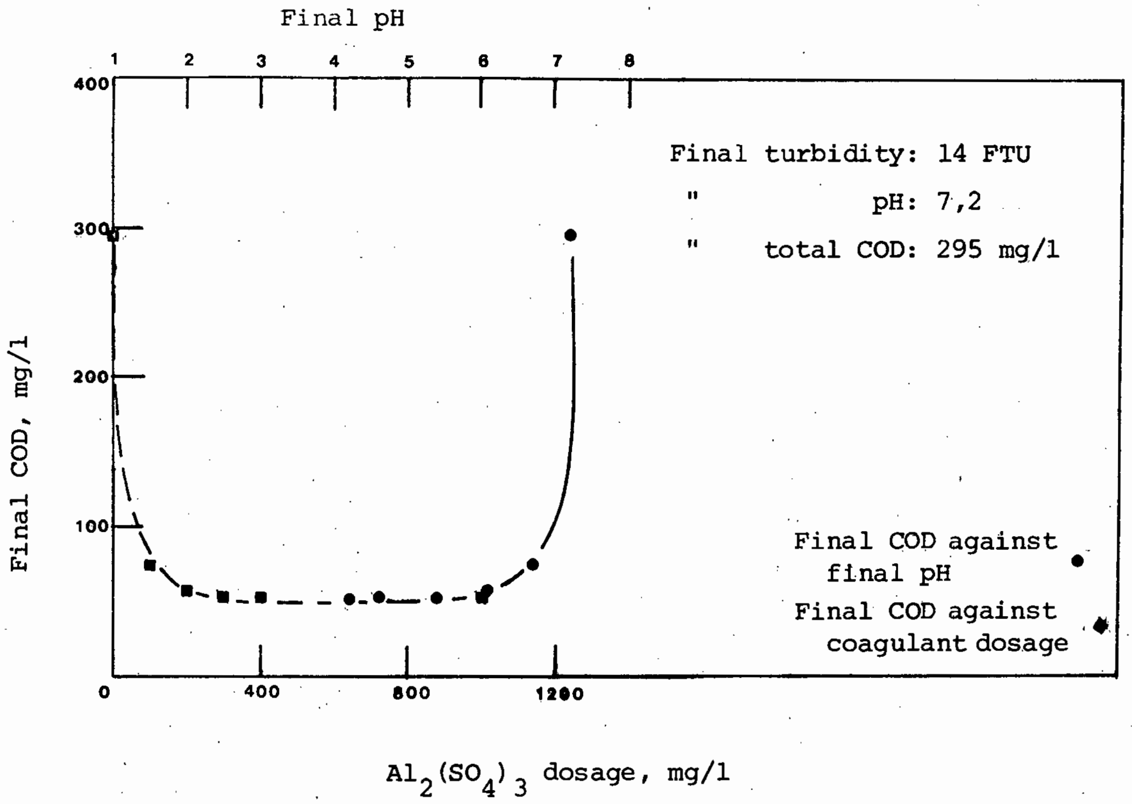


Figure 6.3 Alum coagulation. Final COD is separately plotted against final pH and coagulant dosage.

detail in Section 6.3.4.

The results of Test 1, Section I.1.1 of Appendix J indicate that the addition of bentonite had no appreciable effect either on COD or turbidity removals.

The final turbidity results of Test 1, Section I.2 are similar to those obtained after ferric chloride coagulation of the MMP effluent (Figure 6.4). The decrease in turbidity below about pH 3 was indicative of destabilization of the stable colloids by the Fe^{3+} ions, whose concentration was high below that pH. A similar phenomenon of destabilization of the stable colloids at low pH did not occur in the case of aluminum coagulation (Figure 6.2), because the relevant test was not carried out at adequately low pH (below 3,5 - see Figure 4.11) below which the colloids become destabilized.

The appearance of yellow colour in solution - Test 1, Section I.2 - after addition of amounts higher than 600 mg/l ferric chloride (pH lower than 2,6) was due to the effect of $Fe(OH)^{2+}$ species, which predominate below pH 3 - see Figure 2.3.

The CCC for turbidity removal was below 100 mg/l for ferric chloride coagulation - Test 1, Section I.2.

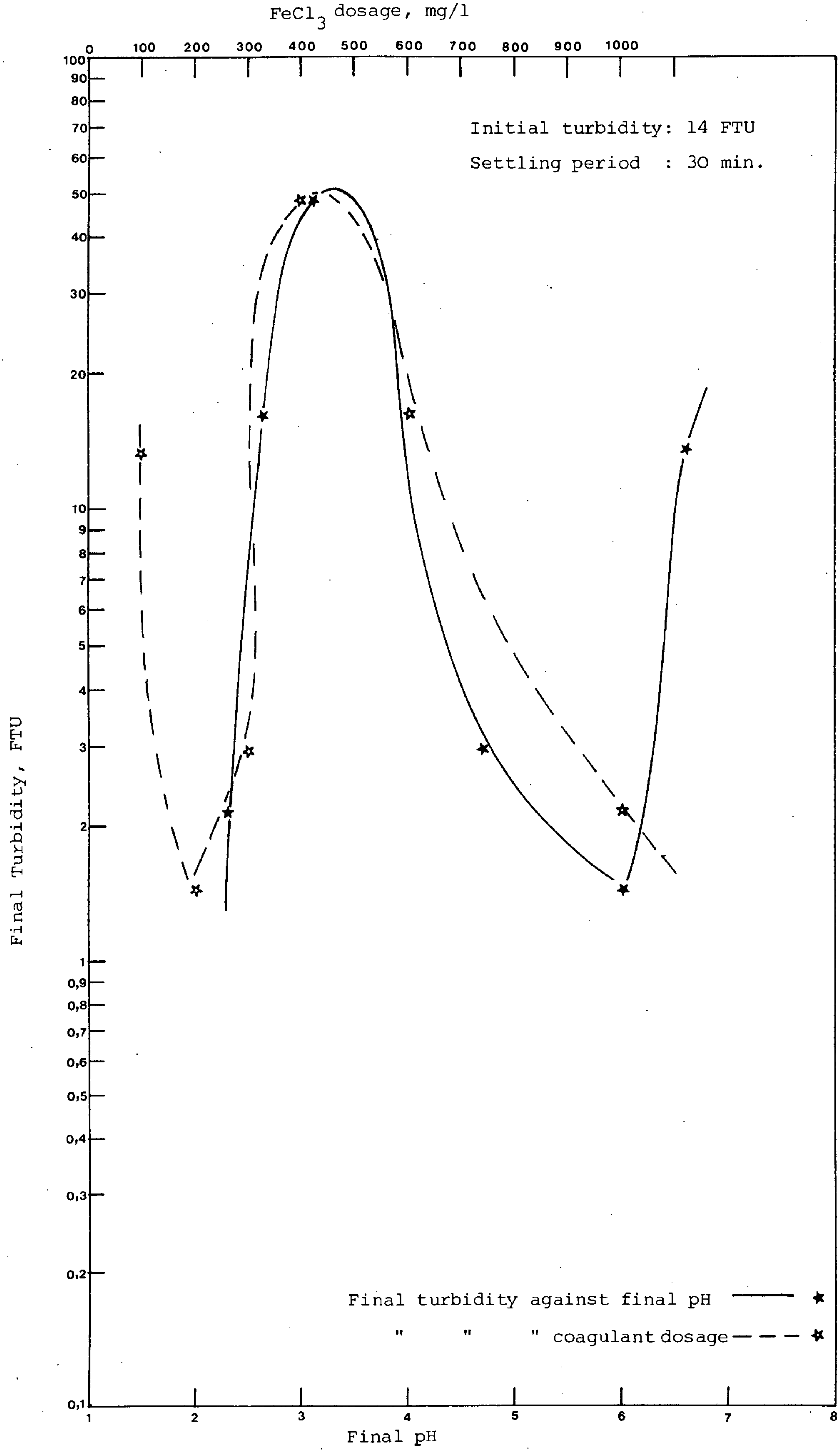


Figure 6.4. Ferric chloride coagulation. Final turbidity is plotted against final pH or coagulant dosage.

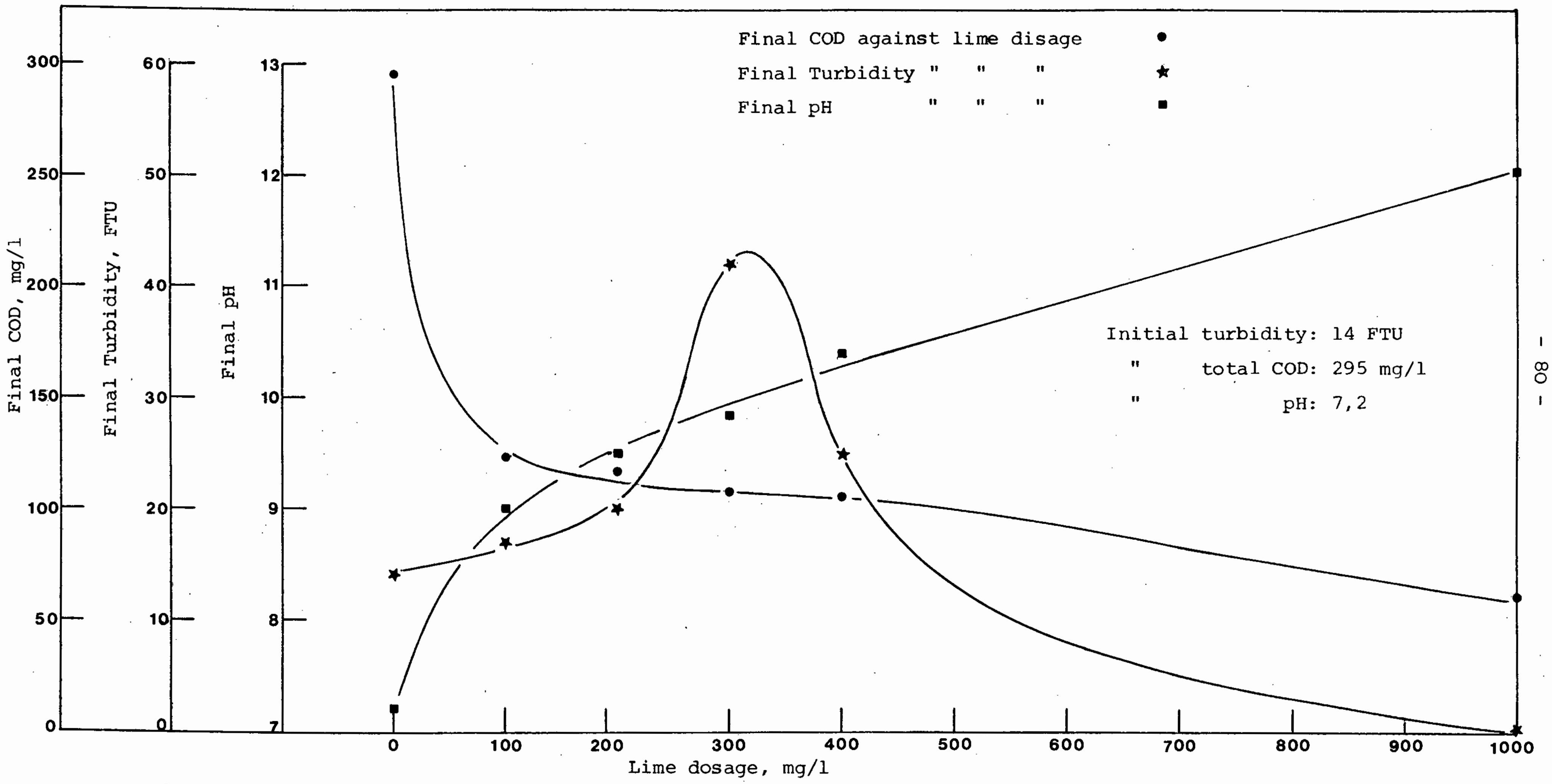


Figure 6.5 Lime coagulation. Final COD, final turbidity and final pH are plotted against lime dosage.

Bentonite had no appreciable effect on ferric chloride coagulation for either turbidity or COD removals - Test 1, Section I.2.1.

The results of Test 1, Section I.3 - Figure 6.5 -, show the extent of the effect of calcium carbonate and magnesium hydroxide precipitations on COD removal. At dosages as high as 400 mg/l lime (max. pH 10,4) the COD of the effluent was removed to approximately the same extent as that achieved by filtration of a raw sample of the effluent through a GF/A filter disc. This suggested that the calcium salts which precipitated up to pH 10,4 managed to remove the effluent's particulate matter. Lime dosages higher than 400 mg/l were considered responsible for the removal of the colloidal organic waste matter. Magnesium hydroxide as well as the destabilizing effect of Ca^{2+} ions were considered responsible for this removal (see Chapter 7). The final COD achieved after lime coagulation was 62 mg/l.

The results of Test 2, Section I.3, show that if the magnesium ions contained in the effluent sample used for Test 1, Section I.3, were precipitated by means of caustic soda addition, the final COD achieved would not be as low as it was in the case of lime coagulation. This suggests that, besides the portion of the organic colloids removed by the precipitation of magnesium hydroxide, some was removed by the action of the Ca^{2+} ions.

The results of Test 3, Section I.3, show that the colour removal was as high as 77 per cent after lime coagulation.

The results of Test 4, Section I.3, show that the colour removal was as high as 86 per cent when excessive lime dosages were applied. In this case the final COD achieved was as low as 43 mg/l (82 per cent COD removal).

The results of Test 1, Section II.1, indicate that the applied synthetic organic polyelectrolytes did not result in the removal of the raw effluent's turbidity when used alone. The addition of cationic polyelectrolytes - especially of Praestol 444-K - was followed by a turbidity increase to the extent that the final turbidity became higher than the initial turbidity before coagulation. A decrease in colour intensity was simultaneously observed. A similar phenomenon had been observed in the case of the MMP effluent, too.

The results of Test 2, Section II.1, show that Floccotan was effective when used alone and, also, when used in conjunction with Superfloc C-521. In the latter case, the colour removal was as high as 85 per cent and the COD removal as high as 62 per cent.

The results of Test 4, Section II.1, show that the flocs formed after the Floccotan addition were flocculated by polymers of any ionic character, but best results were obtained with Separan AP-273. Small amounts of Separan AP-273 resulted in very low final turbidity after flocculation as well as very good floc settling characteristics.

The results of Test 1, Section II.2, show that the amount of cationic polyelectrolytes,especially of those of low M.W., required to remove the turbidity of the effluent in the presence of bentonite was much higher than that of anionic or non-ionic polyelectrolytes. Even higher cationic polymer dosages were required to remove COD. This indicated that, as in the case of the MMP effluent, a reaction occurred between the polymer molecules and anions in solution. This is supported by the fact that a parallel decrease in colour intensity occurred. The overall COD removal, however, was not satisfactory. No polymer managed to remove the turbidity to a large extent. Best floc settling characteristics were observed when non-ionic polyelectrolytes were employed.

The results of Test 2, Section II.2, show that although Superfloc C-521 did not remove the effluent's natural turbidity when added alone, this turbidity was decreased to a certain extent when the polymer addition was preceded by bentonite addition. In the latter case, the COD removal was as high as 62 per cent and the colour removal as high as 61 per cent.

The results of the Tests reported in Sections II.1 and II.2 of Appendix J show that, although the addition of cationic polyelectrolytes can result in floc formation, the flocs do not settle unless bentonite is added. This suggests that the bentonite particles might act as nuclei for adsorption of the reaction products of reactions between the cationic polyelectrolytes and anions in solution. Similar effects have been observed by Rebhum *et al.*, (31) after adding cationic polyelectrolytes in sewage effluents in the presence of bentonite.

The results of Tests 1 and 2, Section II.3, show that the flocs which were formed after alum addition were removed by polyelectrolytes of any ionic character. The demand for cationic polyelectrolytes was much higher than that for non-ionic or anionic polyelectrolytes. At about neutral pH Superfloc N-100 was effective at a dosage as low as 0,5 mg/l. Superfloc A-150 resulted in highest turbidity removal. The results of Test 1, Section II,3, show that this polymer worked more efficiently with alum than the rest of the polymers used in this test did.

The results of Test 1, Section II.4, show that the results obtained after ferric chloride coagulation followed by polymer flocculation were similar to those obtained after alum coagulation followed by polymer flocculation. In both cases, Superfloc A-150 and N-100 were found to be very good flocculants when applied at very small dosages. The remaining turbidity was quite low. Results similar to these were obtained in Test 2, Section II.4, too.

The results of Test 1, Section II.5, clearly indicate that Superfloc C-521 was as effective as Superfloc N-100 when both were applied as flocculant aids in conjunction with ferric chloride, but the dosage of the former was one hundred times greater than that of the latter.

The results of Test 1, Section II.7, show that Separan AP-273 was a good flocculant when used in conjunction with lime. In another qualitative test the way of additions was reversed. AP-273 was added first followed by lime. In this case the polymer was not at all as effective as a flocculant. The floc magnitude after the addition of lime was similar to that observed when lime alone was added. A high pH was then necessary in order AP-273 to become effective. The results of Test 2, Section II.7, show that Separan AP-273 was not effective in removing the turbidity formed after the addition of lime in such amounts as to create a final pH not higher than 11. The above facts suggest that in order Separan AP-273 to become effective as flocculant, when used in conjunction with lime, it must be added after the lime addition and the prevailing pH must be higher than 11.

The purpose of performing Test 1, Section II.9, was to compare the effects of various combinations of inorganic coagulants and organic polyelectrolytes. The results of these tests show that low remaining turbidities were obtained, firstly, when lime was used in conjunction with Separan AP-273, secondly, when ferric chloride was used in conjunction with Superfloc A-150 and, thirdly, when Floccotan was used in conjunction with Separan AP-273. The highest colour removal was achieved with ferric chloride plus Superfloc A-150.

6.3 MAIN TESTS

All the main tests were performed according to the method described in Section 3.3.2.

6.3.1 Presentation of the Experimental Results

All the experimental results of the main tests are tabulated in Appendix N. The final COD and final turbidity test results are presented graphically in Figures 6.6, 6.7, 6.8, 6.11, 6.12, 6.13, 6.14 and 6.9, 6.10, 6.15, 6.16, 6.17, respectively.

The results of the Final Test are tabulated in Table 6.2.

6.3.2 Al and Fe(III) Coagulations - Determination of the Optimum Coagulation Conditions for COD Removal

The technique described in Section 3.5 was employed for the statistical evaluation of the final COD results reported in Sections A, B, C and D.I of Appendix K.

The calculated final COD values are presented in Tables L.8, L.9, L.10 and L.11 of Appendix L. These are presented graphically in Figures 6.18, 6.19, 6.20 and 6.21. From these Figures it may be readily observed that the optimum pH for COD removal was between 5 and 5,5 fo alum coagulation, while this was between 4,5 and 5 for ferric chloride coagulation with most probable value pH 4,5.

6.3.3 Al and Fe(III) Coagulations - The Remaining Turbidity Studied as a Function of Coagulant Dosage and Final pH

Similar plots to those made in Section 4.3.3 were made here for alum and ferric chloride coagulations. For alum coagulation the results of Tests 2, 3, 4, 5, 6, 7 and 8 reported in Section A.I of Appendix K were considered, while for ferric chloride coagulation the results of Tests 3, 4, 5, 6, 7 and 8 reported in Section A.II of Appendix K were considered. Experimental points corresponding to final pH lower than 3,5 for alum coagulation, and lower than 2,5 for ferric chloride coagulation were not considered for similar reasons to those given in Chapter 4.

These plots are shown in Figures 6.22 and 6.23. The resulting points lie in a straight line in each case.

The experimental data plotted in Figures 6.22 and 6.23 were elaborated as described in Section L.2 of Appendix L. This produced the results reported in Tables L.12 and L.13 of Appendix L. The regression lines are shown in Figures 6.22 and 6.23.

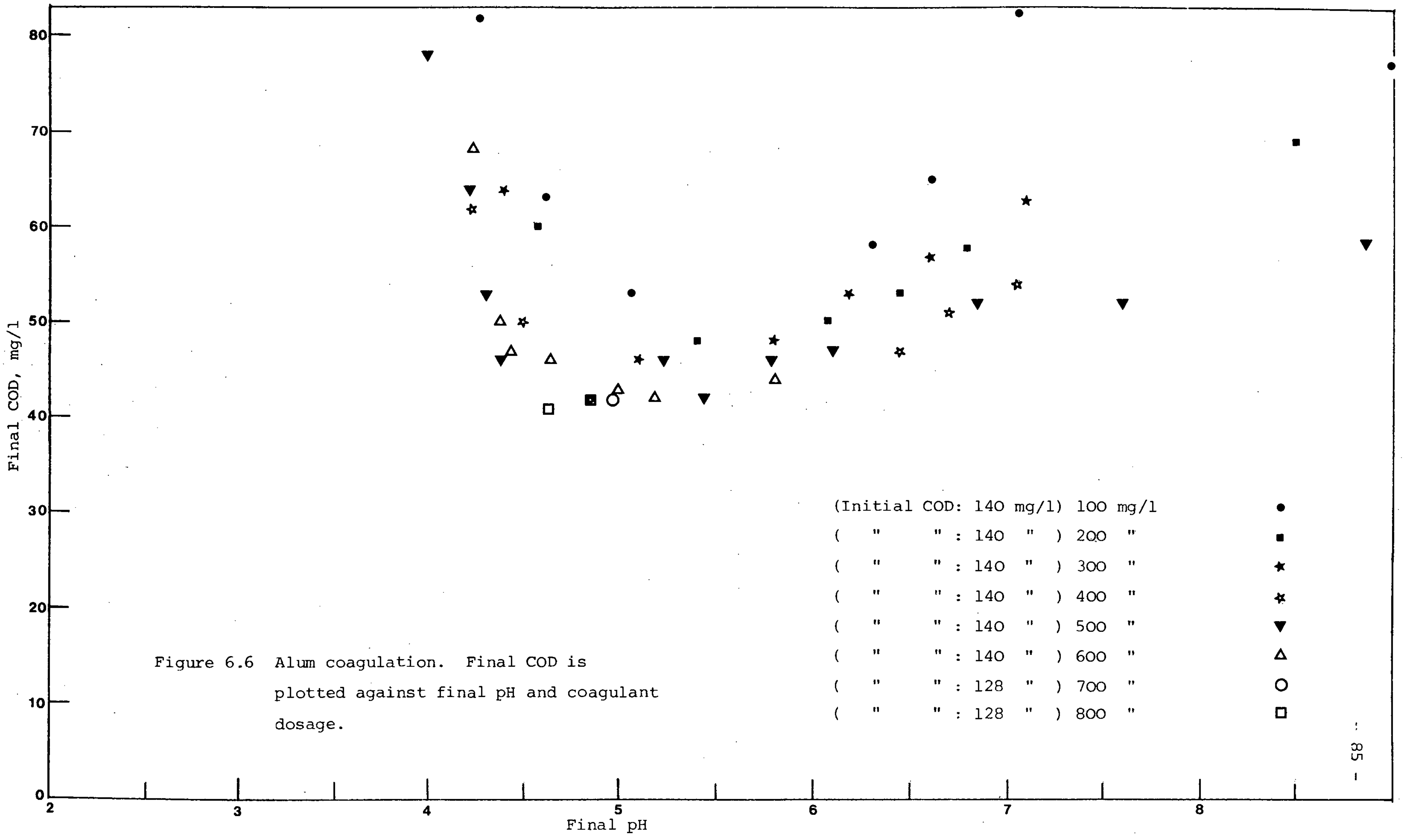


Figure 6.6 Alum coagulation. Final COD is plotted against final pH and coagulant dosage.

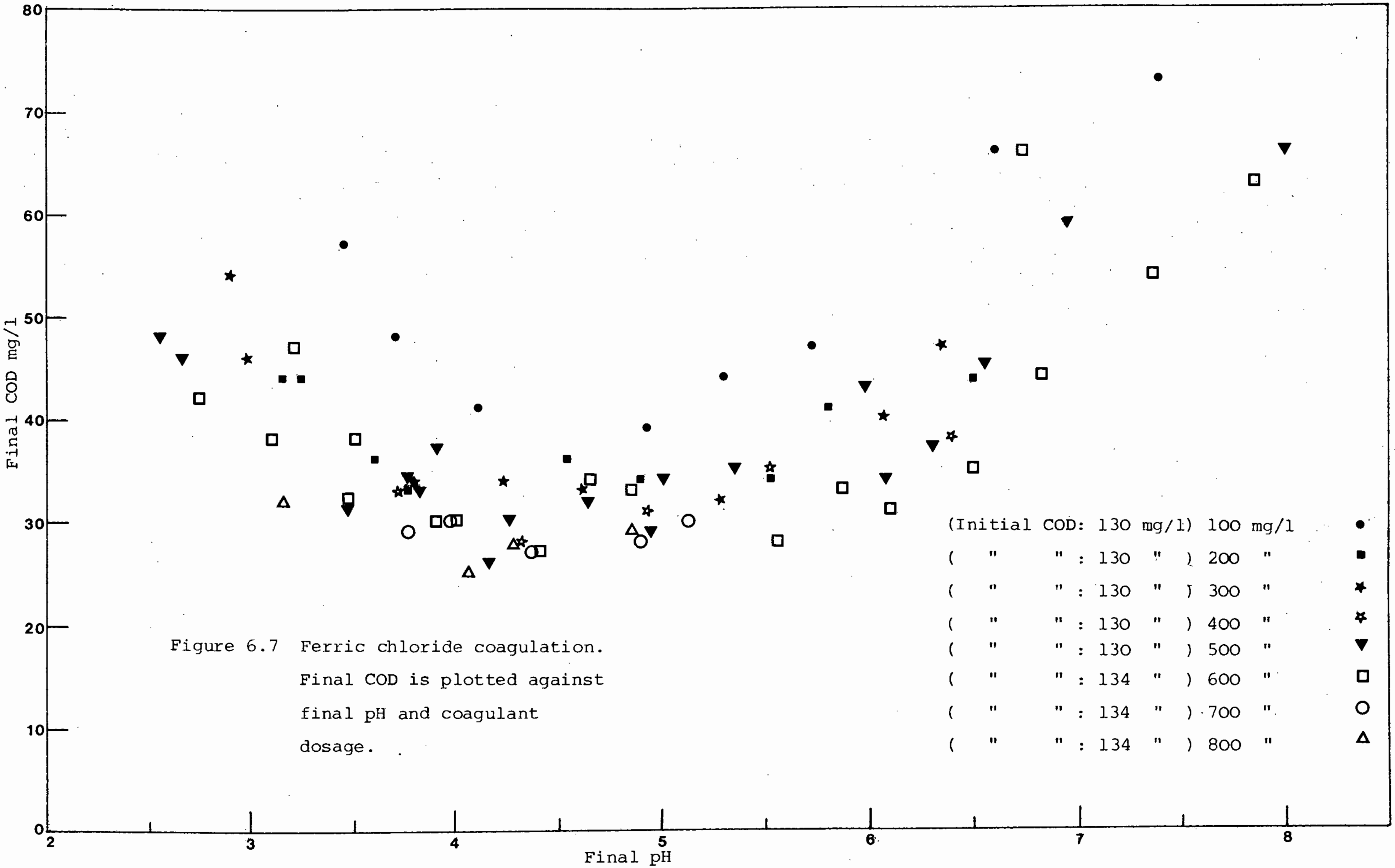
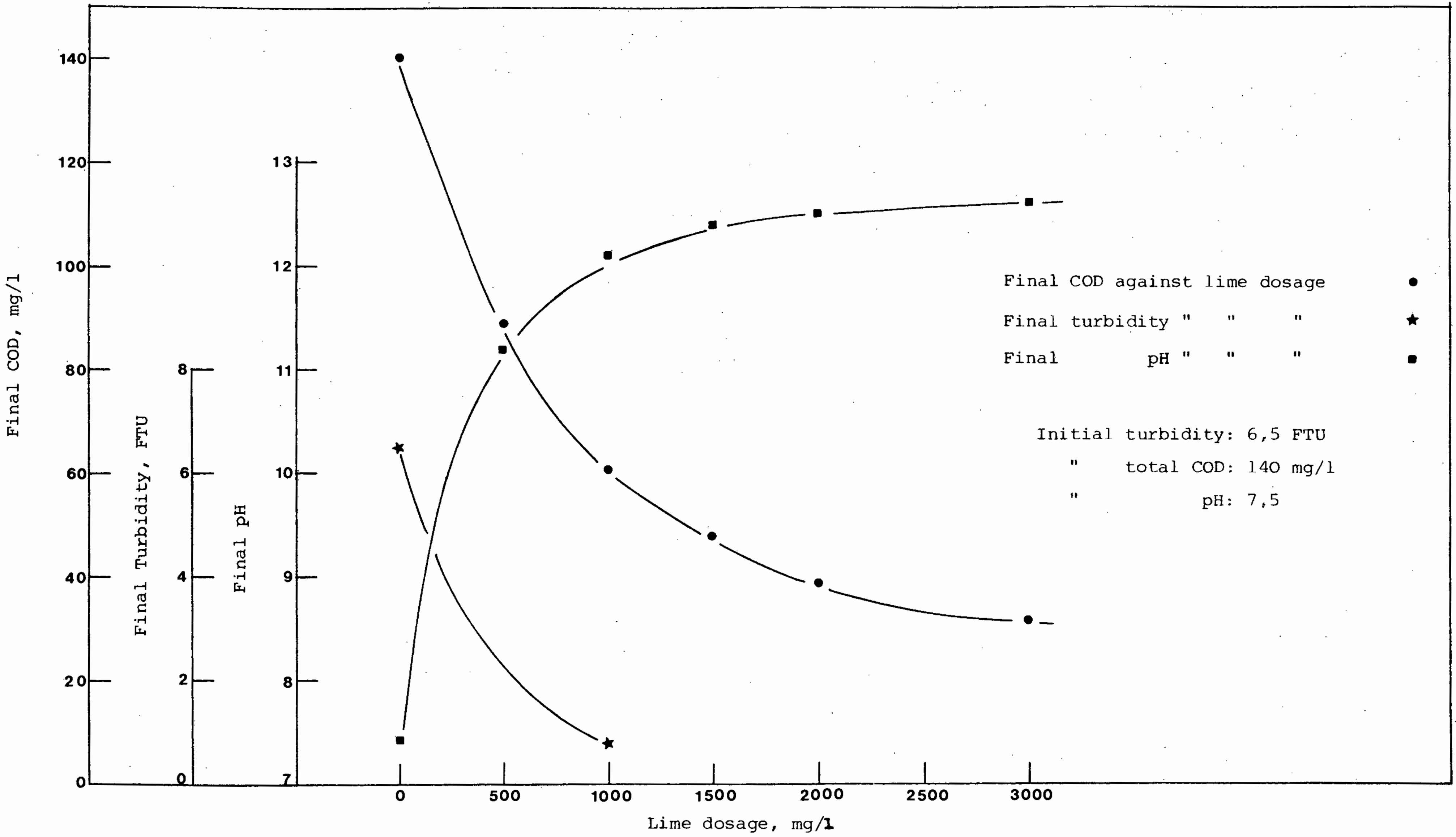


Figure 6.7 Ferric chloride coagulation. Final COD is plotted against final pH and coagulant dosage.

Figure 6.8. Lime coagulation. Final COD, final turbidity and final pH are separately plotted against lime dosage.



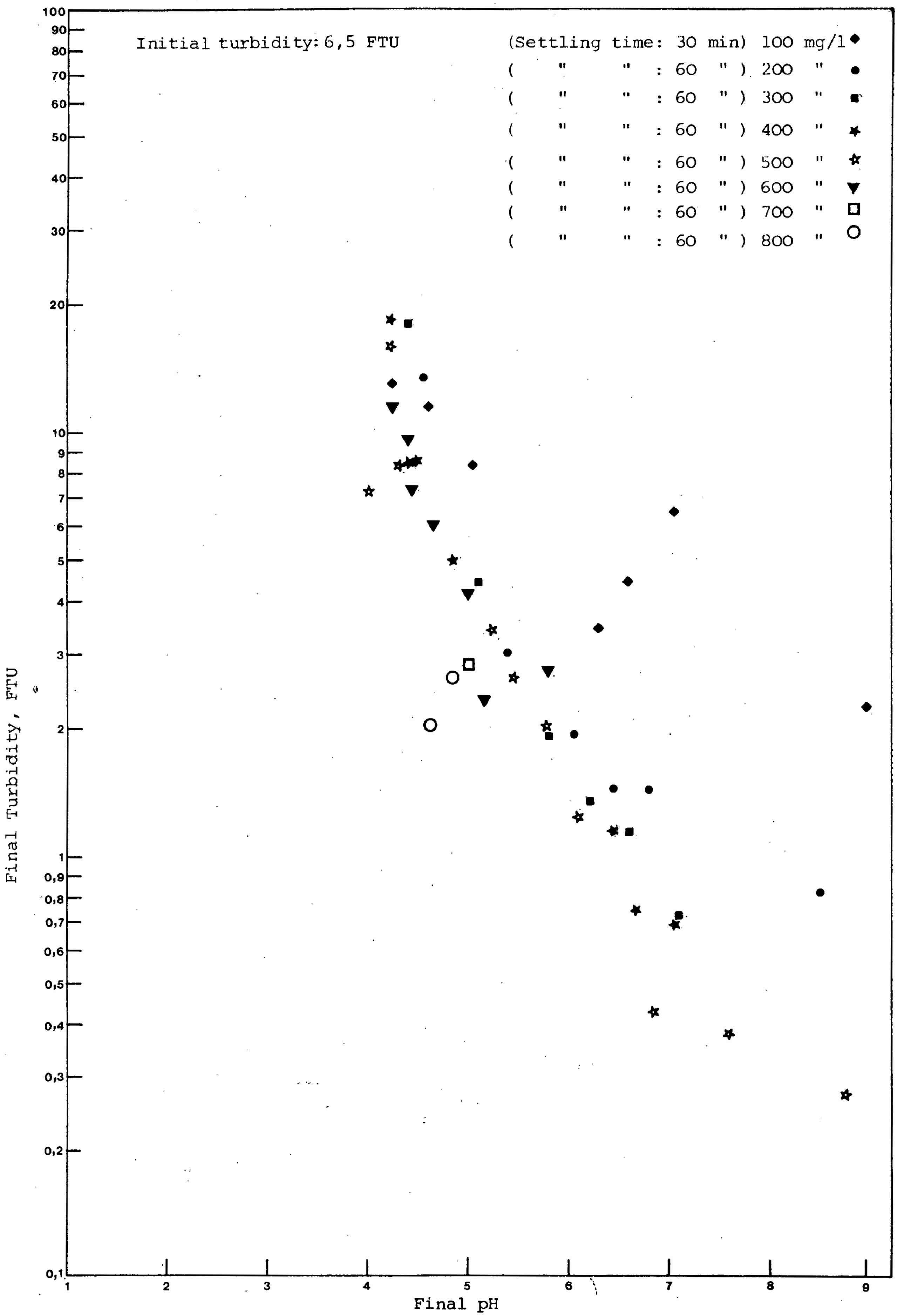


Figure 6.9 Alum coagulation. Final turbidity is plotted against final pH and coagulant dosage.

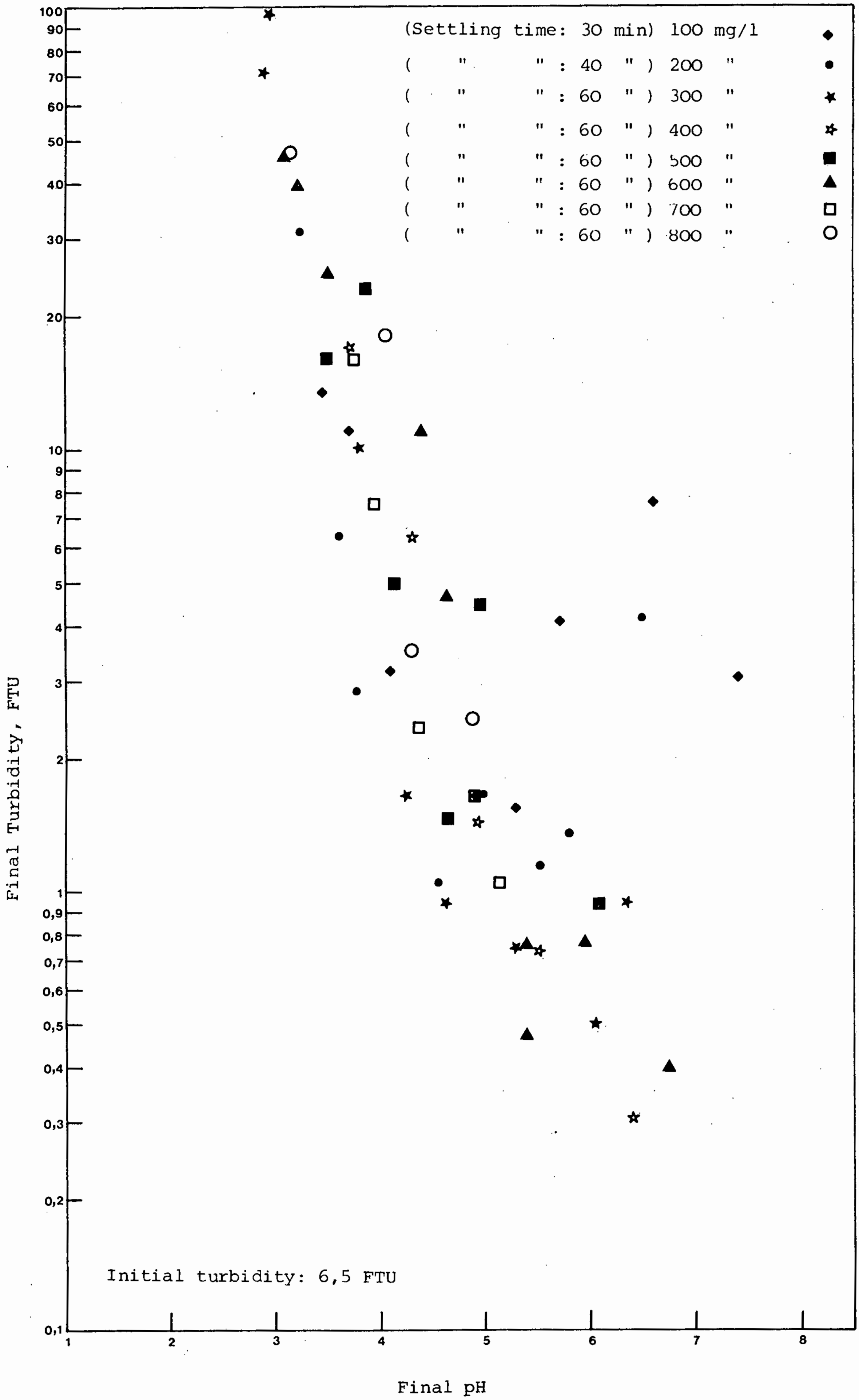
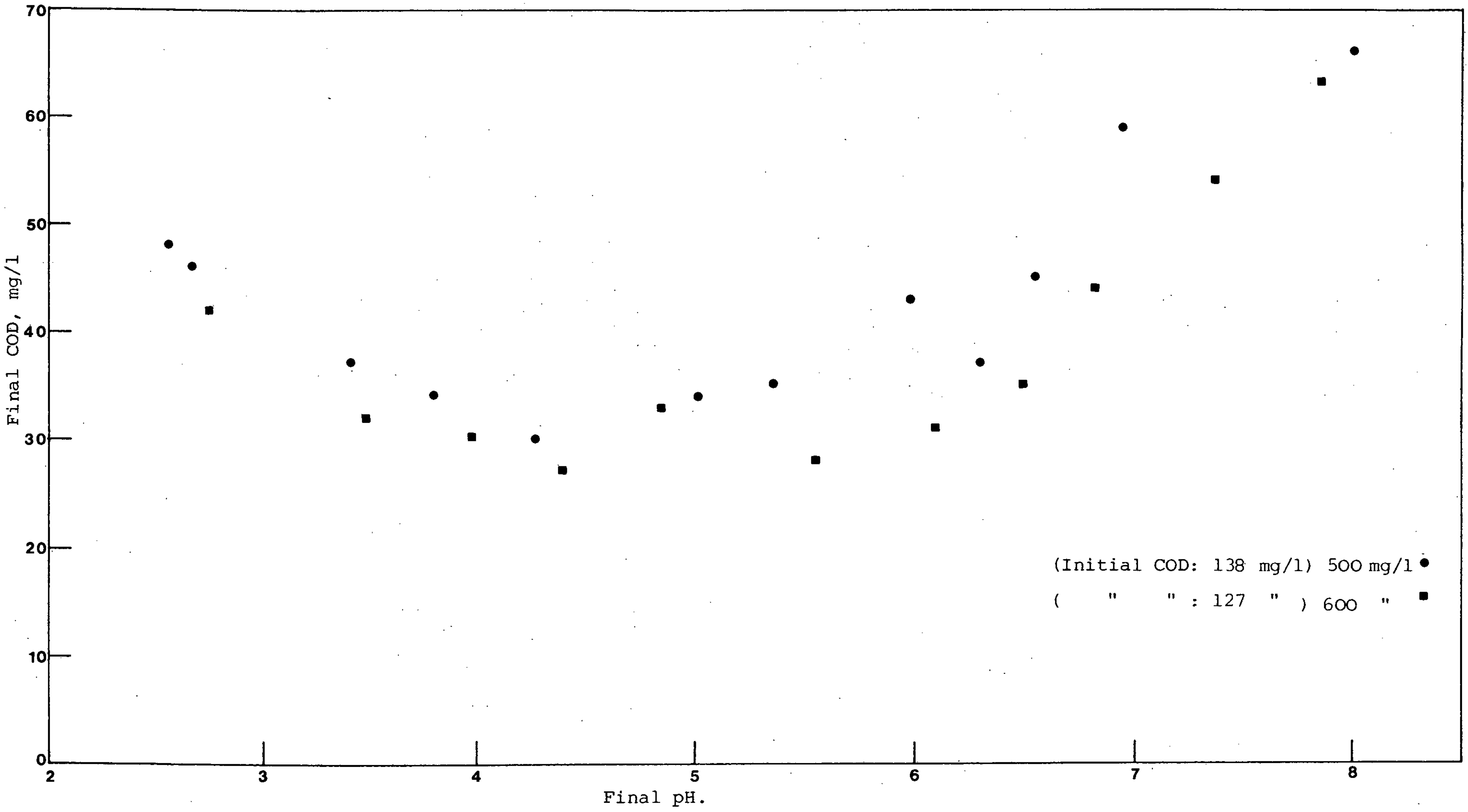


Figure 6.10 Ferric chloride coagulation. Final turbidity is plotted against final pH and coagulant dosage.

Figure 6.11 Ferric chloride coagulation. Final COD is plotted against final pH and coagulant dosage.



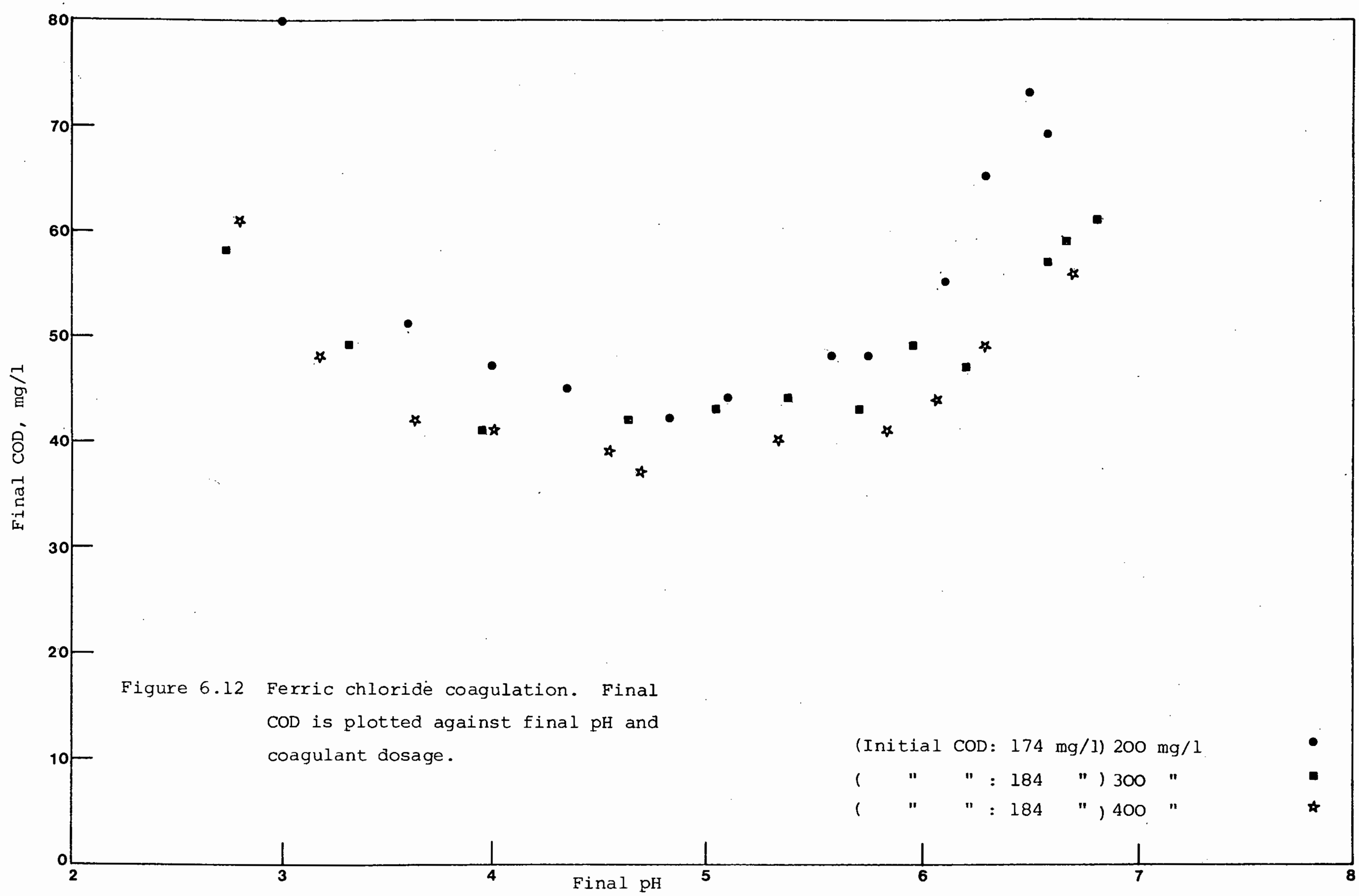


Figure 6.12 Ferric chloride coagulation. Final COD is plotted against final pH and coagulant dosage.

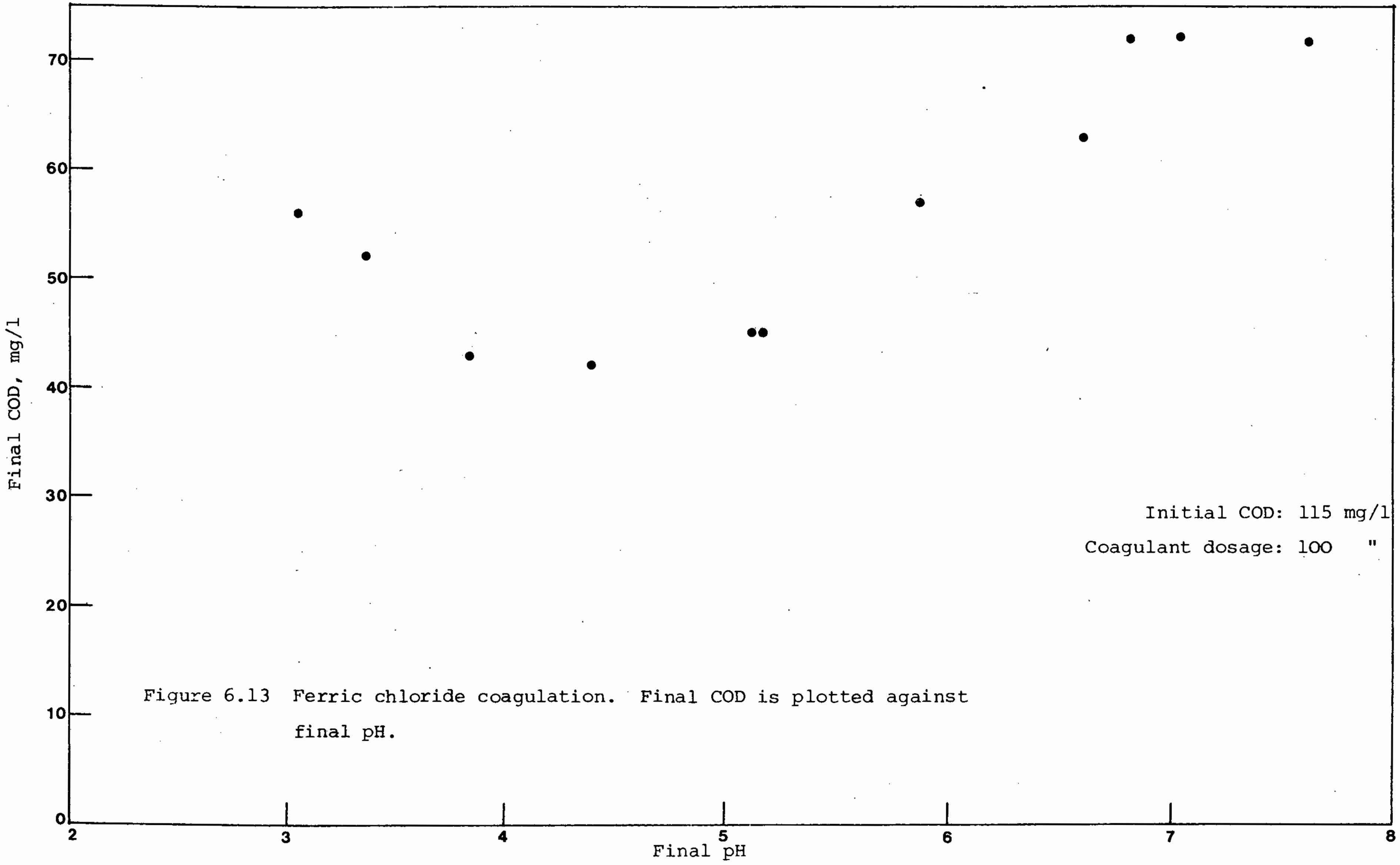


Figure 6.13 Ferric chloride coagulation. Final COD is plotted against final pH.

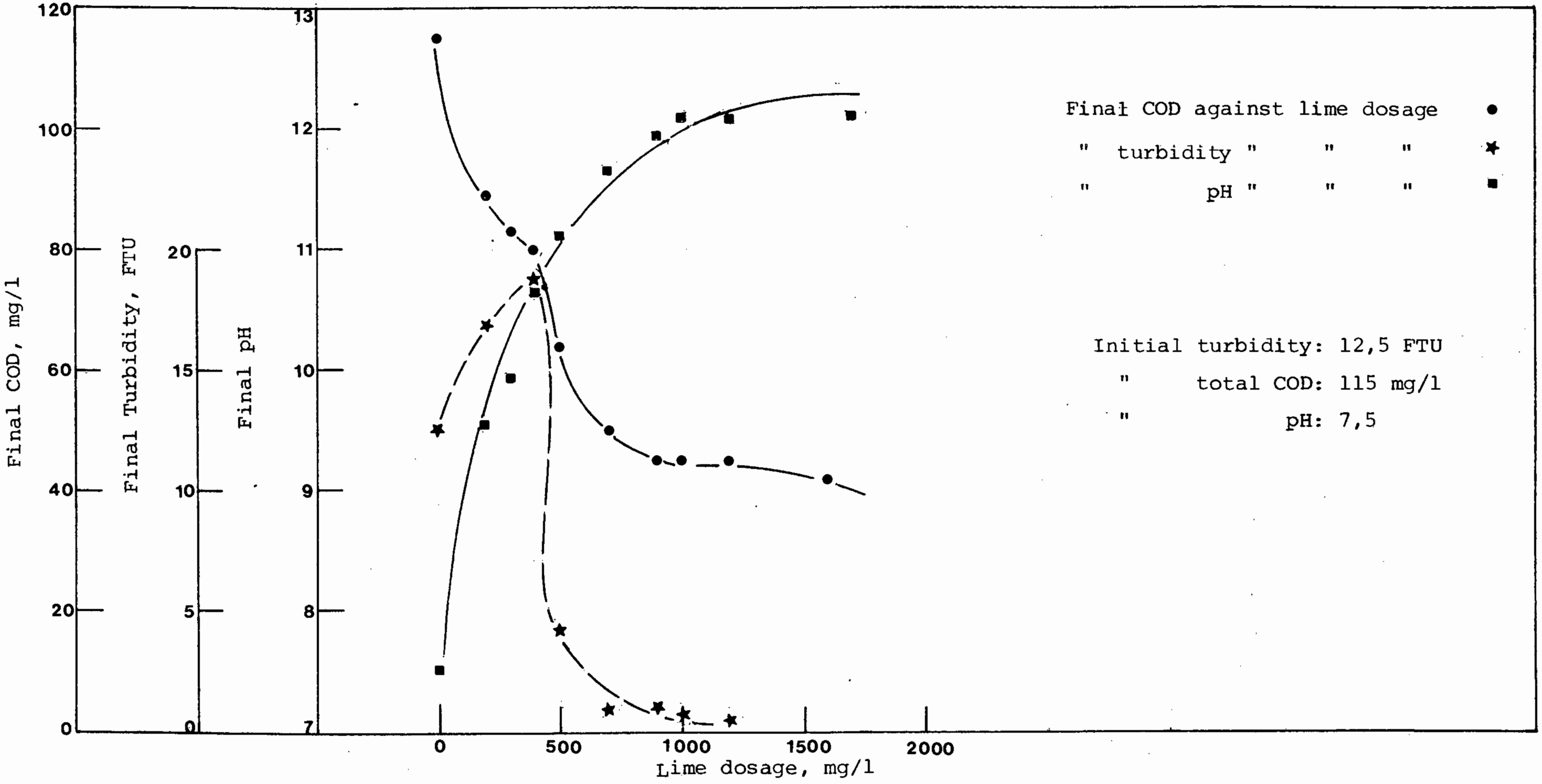


Figure 6.14 Lime coagulation. Final COD, final turbidity and final pH are plotted against lime dosage.

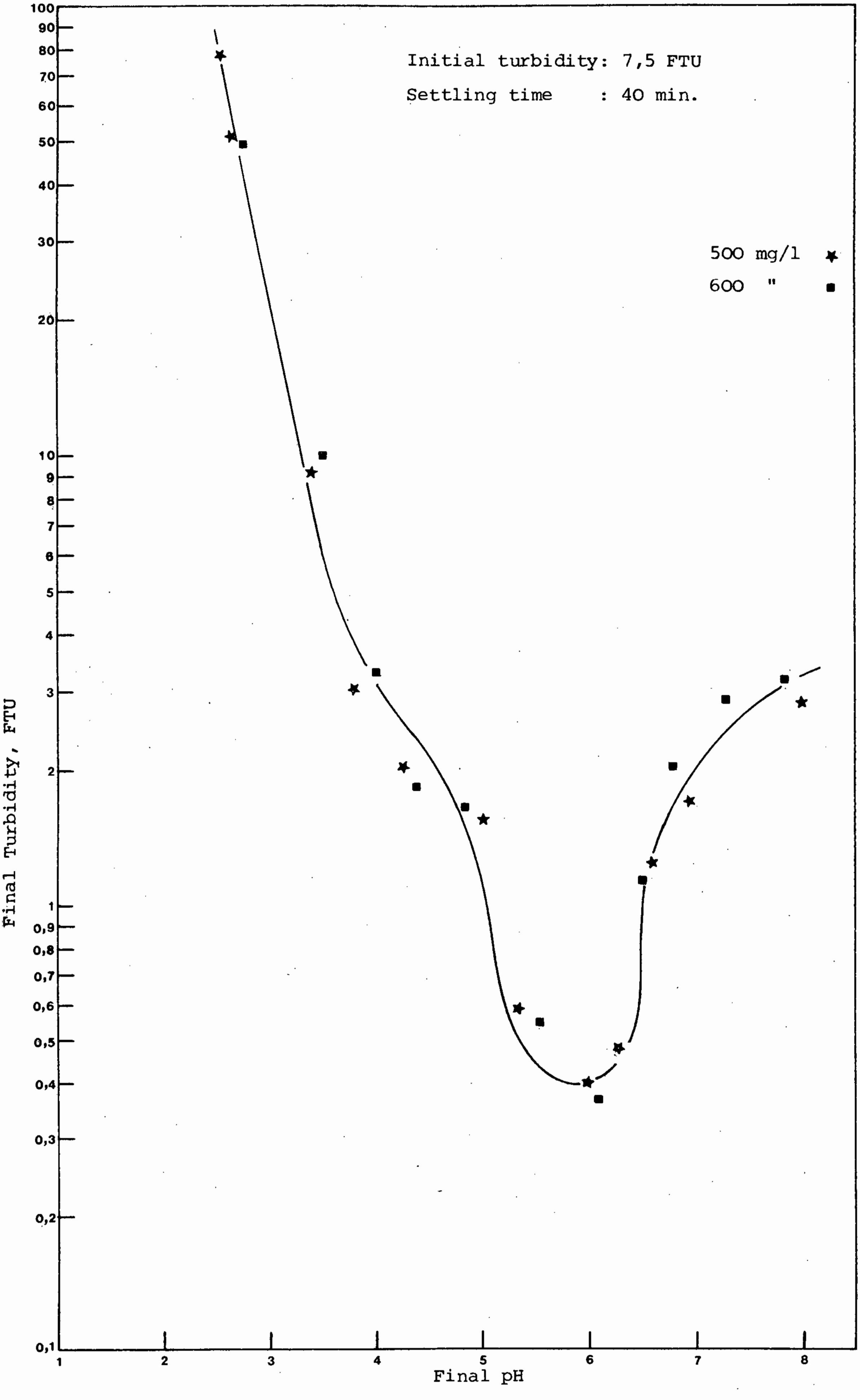


Figure 6.15 Ferric chloride coagulation. Final turbidity is plotted against final pH and coagulant dosage.

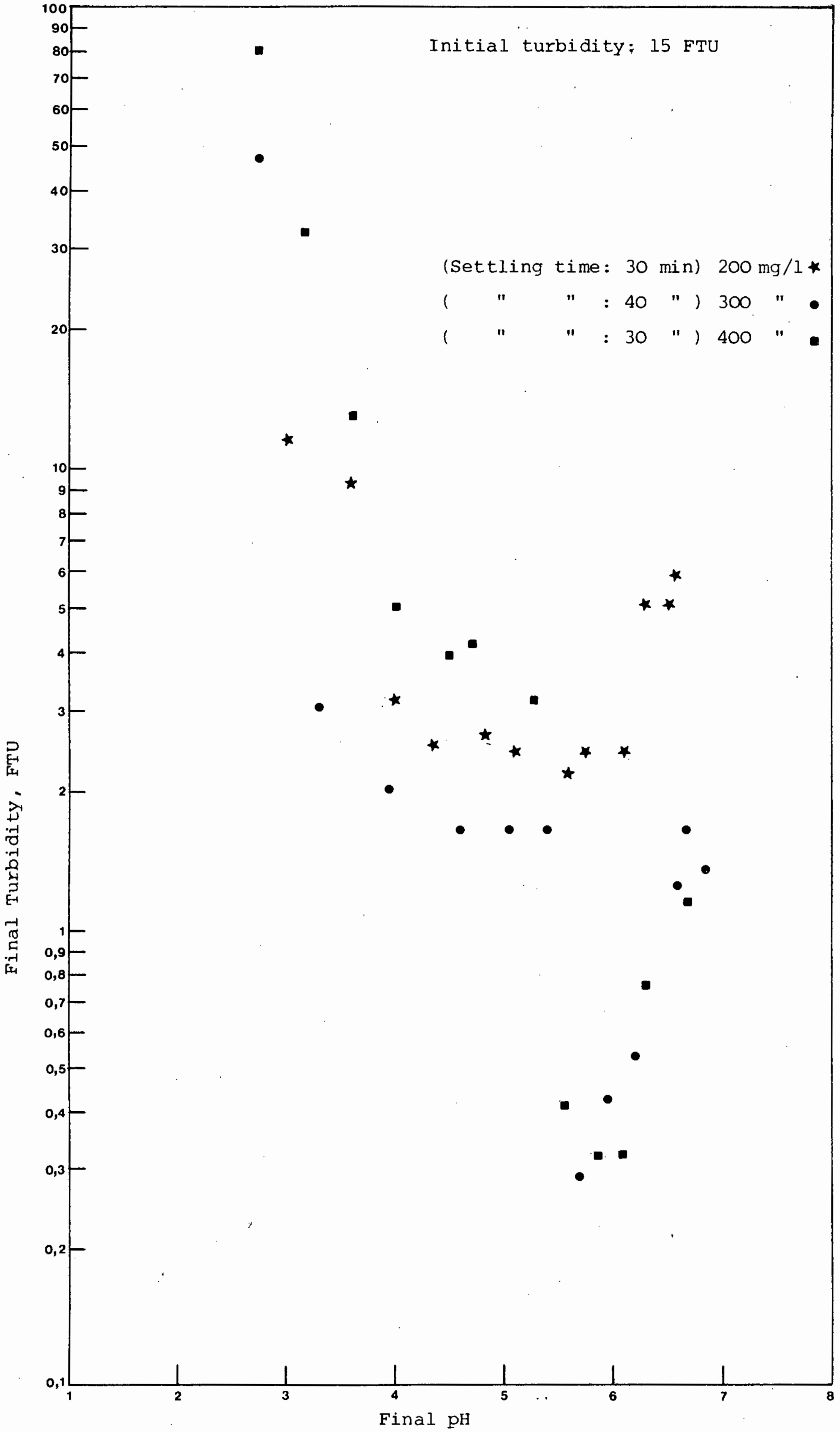


Figure 6.16 Ferric chloride coagulation. Final turbidity is plotted against final pH and coagulant dosage.

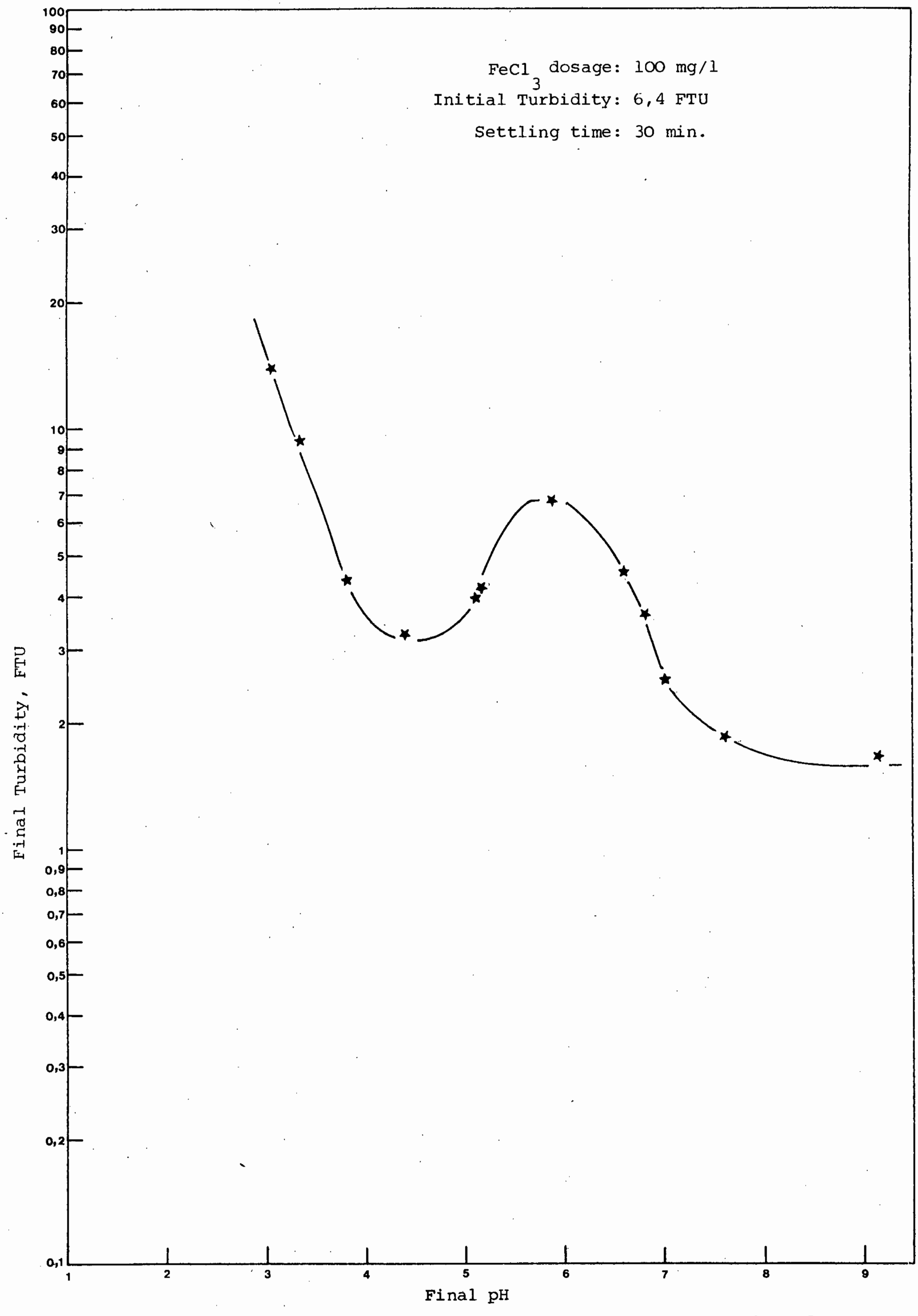


Figure 6.17 Ferric chloride coagulation. Final turbidity is plotted against final pH.

TABLE 6.2

Final Test of the Treatment of the AMP Effluent

The characteristic properties of the raw effluent sample used were:

Turbidity, FTU : 5,9
pH : 7,45
Total COD, mg/l : 12,5
Filtered COD, mg/l : 108
TS, mg/l : 795
TDS, mg/l : 735
TSS, mg/l : 30
TVS, mg/l : 165
Cl^-, mg/l : 220
Na^+, mg/l : 190
Ca^{2+}, mg/l : 33
Fe^{3+}, mg/l : non-detectable
Al^{3+}, mg/l : non-detectable
Colour, absorbance : 0,108

ml IN NaOH added:	1	1	2	2	-	-
Coagulant added :	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$FeCl_3$	$FeCl_3$	$Ca(OH)_2$	$Ca(OH)_2$
Coagulant dosage :	400	400	400	400	2000	2000
Polymer added :	-	N-100	-	N-100	-	AP-273
Polymer dosage :	-	2	-	2	-	2
Final pH :	5,28	5,08	4,98	4,95	12,5	12,5
Final Turbidity (60 min) :	3,14	1,75	1,1	1,25	0,47	0,64
% Turbidity Removal :	46	70	81	79	92	89
Final COD :	41	41	29	29	34	37
% Total COD Removal :	67	67	77	77	73	72
% Filtered COD Removal :	62	62	73	73	68	67
Final Colour :	0,015	0,0155	0,0075	0,0085	0,0135	0,014
% Colour Removal :	86	86	93	92	87	87
Final TDS :	930	940	920	960	1920	1960
Final Ca^{2+} :	-	-	-	-	450	450
Final Fe^{3+} :	-	-	non-detectable		-	-
Final Al^{3+} :	Non-detectable		-	-	-	-
Settling Rate: (cm of depth or % floc removal)						
1 min	1	2	1	4	4	7
2 min	0,5	95%	70%	95%	95%	99%
4 min	60%	-	95%	99%	99%	
5 min		99%				

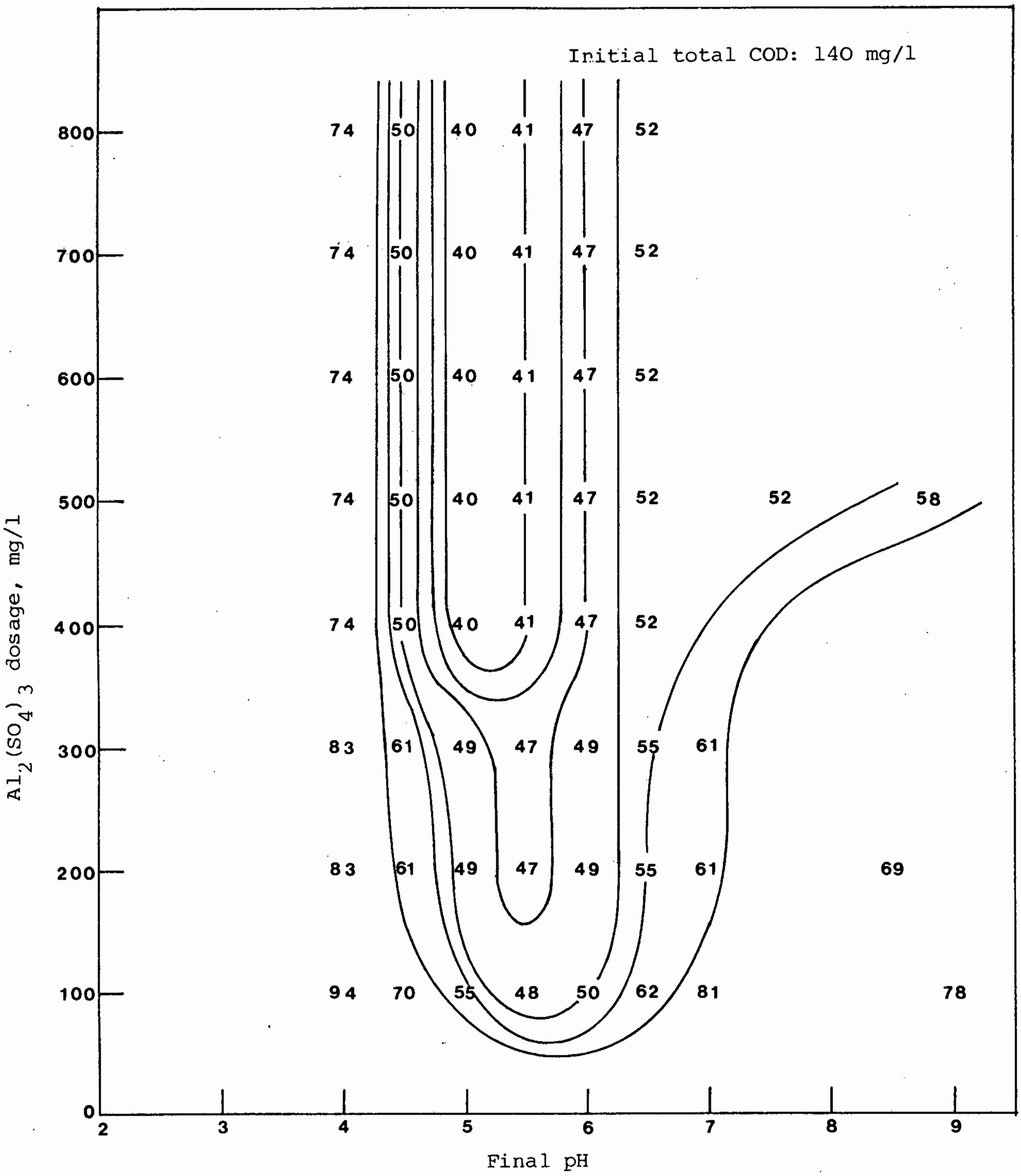


Figure 6.18 Alum coagulation. Variation of final COD with final pH and coagulant dosage.

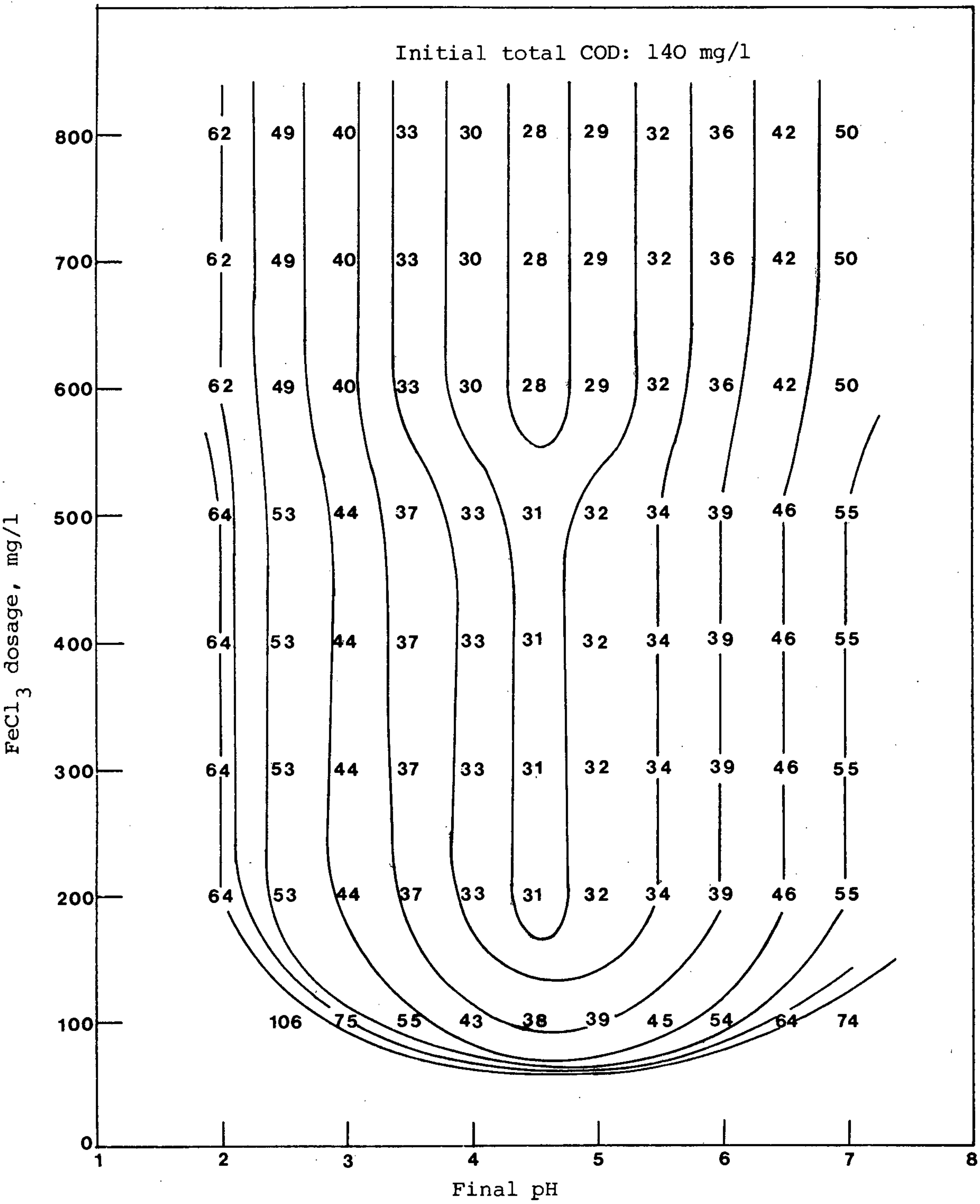


Figure 6.19 Ferric chloride coagulation. Variation of final COD with final pH and coagulant dosage.

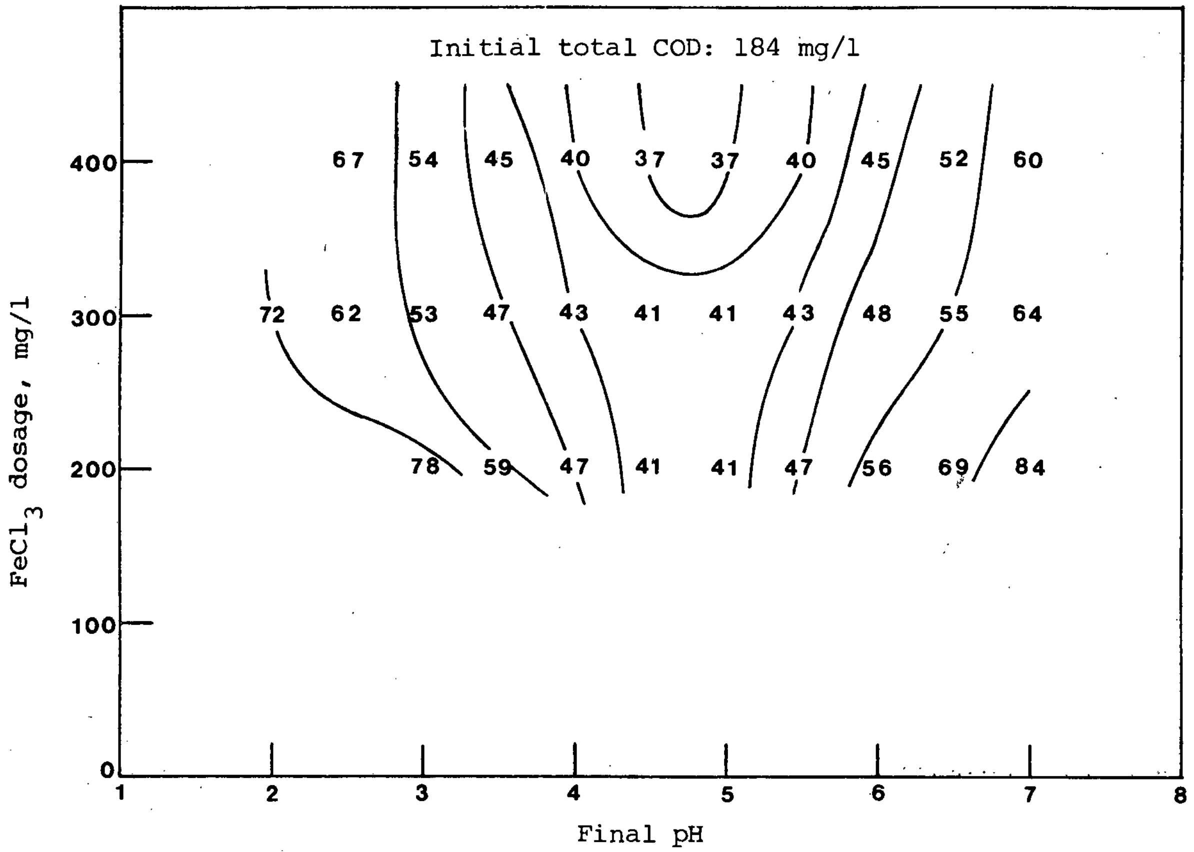


Figure 6.20 Ferric chloride coagulation. Variation of final COD with final pH and coagulant dosage.

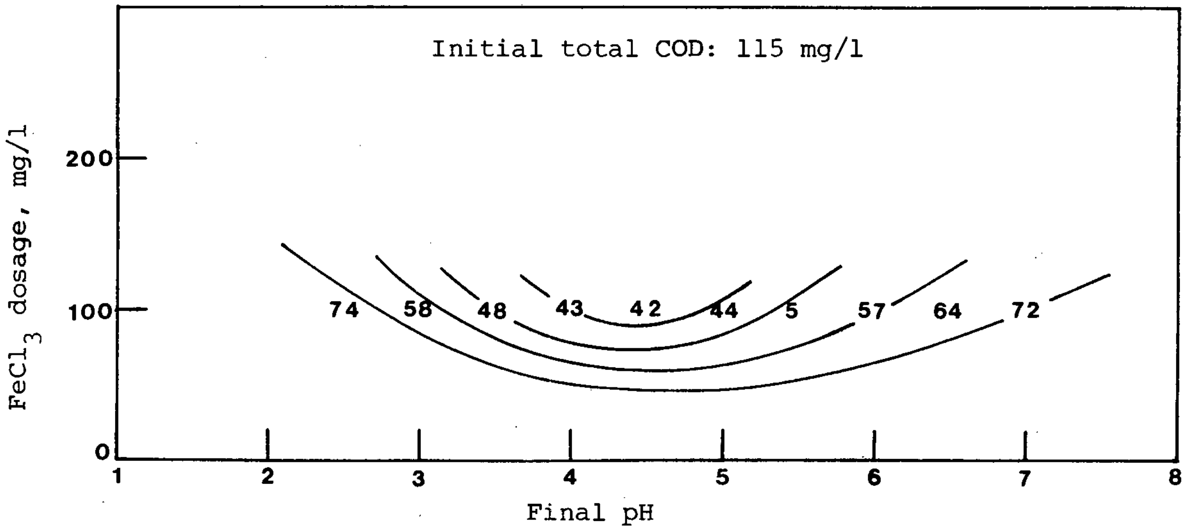


Figure 6.21 Ferric chloride coagulation. Variation of final COD with final pH and coagulant dosage.

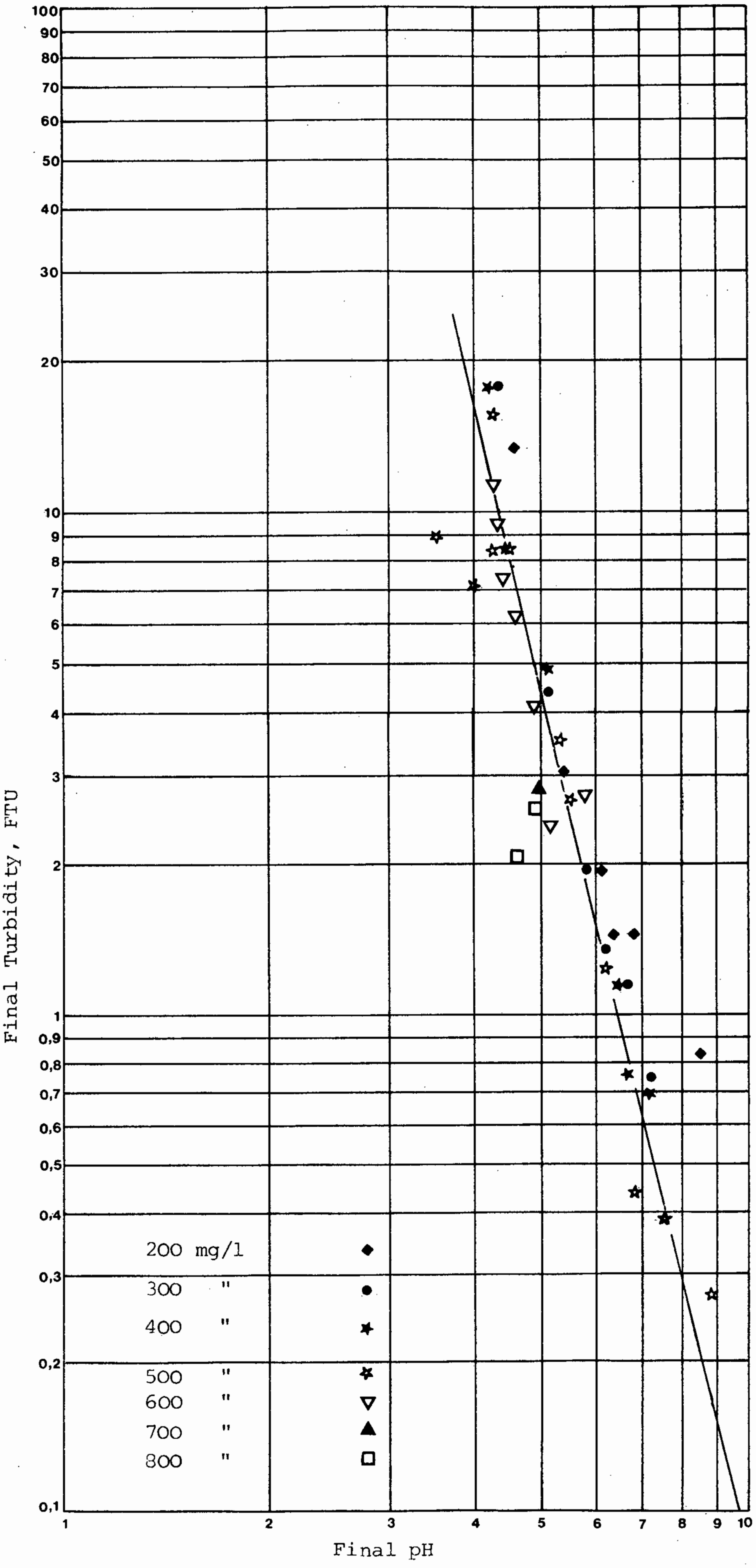


Figure 6.22 Alum coagulation. The final turbidity measured after 60 minutes settling is plotted against final pH and coagulant dosage.

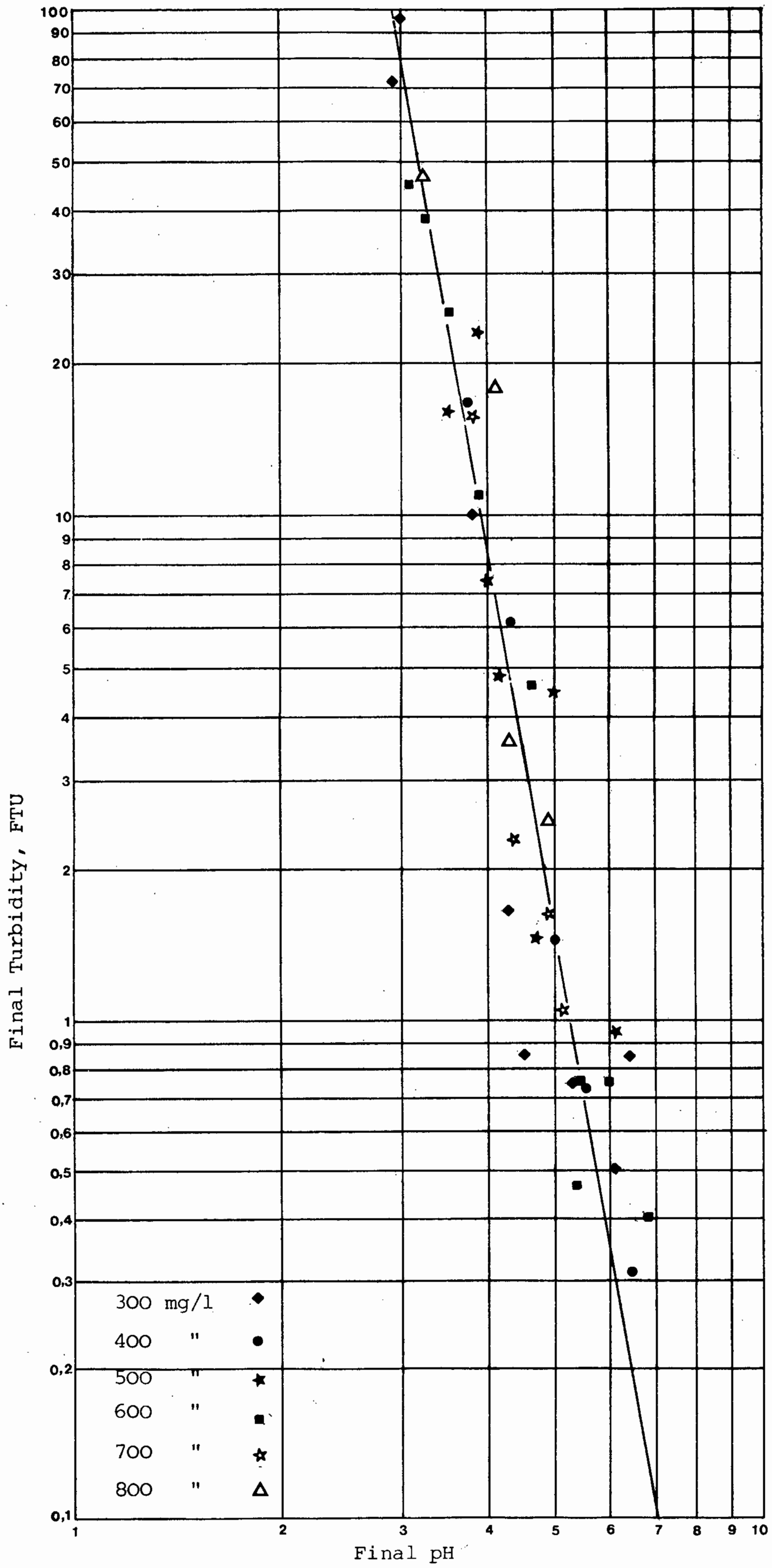


Figure 6.23 Ferric chloride coagulation. The final turbidity measured after 60 min settling is plotted against final pH and coagulant dosage.

6.3.4 Discussion of the Results of the Main Tests

A. COD Removal

A similar pattern to that obtained for COD removal in the cases of MMP and MHT effluents appeared to apply for the AMP effluent, too. This pattern was similar for alum and ferric chloride coagulations. The slightly different optimum pH appearing in Figure 6.18 for alum dosages below 400 mg/l, when compared to that appearing above this dosage, may be attributed to a systematic experimental error - e.g. accidental decalibration of the pH meter used. This difference is not considered as being associated with the mechanism of coagulation.

With an initial total COD of 140 mg/l, approximately 400 mg/l of alum and 600 mg/l ferric chloride were required to achieve maximum COD removal at the optimum pH in each case.

Observing Figures 6.19 and 6.20 it may be concluded that for identical pH and coagulant dosage, the lower the initial COD, the lower the final COD attained. Observing Figures 6.19 and 6.21 it may be seen that this does not quite apply at the optimum pH. This is believed to have been caused by a certain undetermined inhibiting factor.

In the course of this study the effect of prolonged storage periods on the minimum attainable final COD after coagulation was never significant, even if the initial relative COD decrease due to prolonged storage was higher than 5 per cent. This is indicated by the results of Tests 6, 7 and 8 of Section A.I, and Tests 5 and 6 of Section A.II, Appendix K.

Lime was effective at higher than 500 mg/l dosages. The higher the lime dosage, the higher the COD removal.

When the initial total COD of the effluent was 140 mg/l, the minimum remaining COD after coagulation with alum, ferric chloride and lime was 40 mg/l, 28 mg/l and 32 mg/l respectively, (total COD removal was equal to 71, 80 and 77 per cent respectively). These results show that ferric chloride was once more the most effective coagulant for COD removal. Lime could be as effective as alum, if added in excess.

The results of the Final Test - Table 6.2 - show that the relative colour removal was always higher than the relative filtered COD removal for all three inorganic coagulants.

At close to the optimum pH for COD removal, the relative colour removal was 86, 93 and 97 per cent for alum, ferric chloride and lime, respectively. These results show that ferric chloride was the most effective coagulant for colour removal.

The removal of odours was achieved to a large extent with all three inorganic coagulants.

B. Turbidity Removal

The remaining turbidity results shown in Figures 6.9 and 6.10, corresponding to 60 minutes settling, are similar to those obtained in the cases of MMP and MHT effluents under similar conditions. They are relatively independent of the coagulant dosage and the raw effluent's turbidity, being dependent only on the final pH. The explanation for these phenomena has been given in Section 4.3.4 - (B). In the case of AMP effluent - Figures 6.9 and 6.10 - it may be observed that formation of stable colloids also occurred at pH above 7, but their concentration was very low at about pH 9.

For settling periods of less than 60 minutes, increasing remaining turbidity appeared at around neutral pH - Figure 6.9, with 100 mg/l alum. This shows that at neutral pH the rate of precipitation of the metal hydroxide is relatively higher. A similar phenomenon has been found to occur with aluminum hydroxide precipitation at pH 7 by Packham, (14) - Appendix A. Packham has found that maximum precipitation of aluminum hydroxide polymers occurred between about pH 5 and 7,5, but the rate of maximum precipitation was highest at pH 7. The phenomenon of appearance of increased turbidity at a neutral pH is believed to be independent of the phenomenon of stable colloids formation. The nature of the stable colloids has been suggested to be metal hydroxophosphate precipitates, while that of the precipitate appearing at around neutral pH values to be purely metal hydroxide.

Increased remaining turbidity also appeared after ferric chloride coagulation for settling periods of less than 60 minutes. The highest rate of precipitation of ferric hydroxide appeared to be at about pH 8 - Figure 6.15. Webb, (24) has mentioned that the isoelectric point of ferric hydroxide is at pH 8. Although this has not been universally established - see Section 2.3.2 - Webb's statement explains the appearance of increased turbidity at about pH 8 after ferric chloride coagulation.

When small dosages of ferric chloride were applied and the settling period was shorter than 60 minutes, another phenomenon was also observed Figures 6.10 - 100 mg/l $FeCl_3$ -, 6.17 and 5.8 - 100 mg/l $FeCl_3$ - show that the pH for maximum rate of ferric hydroxide precipitation shifted to values lower than pH 8 when low ferric chloride dosages were applied. The cause of this shift is most likely to have been the sulphate ions which were added as sulphuric acid prior to coagulant addition for pH adjustment. This was accomplished by displacement of OH^- ions by SO_4^{2-} ions in the metal hydroxocomplex sheath so that fewer OH^- ions were needed for ferric hydroxide precipitation, which could consequently occur at lower pH.

It may be observed that the slopes of the regression lines shown in Figures 6.22 and 6.23 are similar to those of the lines shown in Figures 4.15, 4.16 and 5.12. Similar conclusions to those drawn in Section 4.3.4 - (B) apply in this case, too.

The effect of pH on the physical characteristics of the floc was marked. At neutral or slightly alkaline pH the floc magnitude was invariably greater than that of the flocs formed at acidic pH.

Lime coagulation completely removed the natural turbidity from the effluent. The flocs formed after lime coagulation were faster in settling than those formed after ferric chloride coagulation, which were, in turn, faster in settling than those formed after alum coagulation.

The results of the Final Test - Table 6.2 - show that 99 per cent floc removal was achieved after 5, 4 and 2 minutes settling with (alum + Superfloc N-100), (ferric chloride + Superfloc N-100), and (lime + Separan AP-273), respectively.

The concentrations of Fe^{3+} and Al^{3+} ions in solution after coagulation were negligible - Table 6.2.

CHAPTER 7

FINAL DISCUSSION, CONCLUSIONS, SUGGESTIONS, AND RECOMMENDATIONS ON THE COD, COLOUR AND TURBIDITY REMOVALS

7.1 FINAL DISCUSSION - COD REMOVAL

7.1.1 Al and Fe(III) Coagulations

7.1.1.1 Discussion of the Experimental Findings

The destabilization of colloids on coagulation with hydrolyzing metal coagulants is brought about by the hydrolysis products of the metal ions and not by the metal ions themselves.

Cationic aluminum polynuclear complexes, which have the approximate composition $Al(OH)_{2,5}$, are formed on coagulation with aluminum salts in the pH range between 4 and 7. The most likely species to predominate in this pH range are $Al_7(OH)_{17}^{4+}$ and $Al_{13}(OH)_{34}^{5+}$ - see Section 2.4.2, Figure 2.3-(a).

Similarly, the cationic species $Fe_2(OH)_2^{4+}$, Fe^{3+} and $Fe(OH)^{2+}$ predominate in the pH range 2 to 7 on ferric coagulation - Figure 2.3-(b).

The shaded areas in Figure 2.3 correspond to approximate ranges of coagulant dosage and pH usually applying in water treatment. For alum coagulation the shaded area shown in Figure 2.3-(a) corresponds to an $Al_2(SO_4)_3$ dosage falling in the range between 1 and 350 mg/l, while for ferric chloride coagulation the shaded area shown in Figure 2.3-(b) corresponds to a $FeCl_3$ dosage falling between 1 and 150 mg/l. In the municipal wastewater treatment practice, however, although the pH range for coagulation has remained unchanged, the applied dosages have, in general, been higher than those mentioned here, because of the higher concentration of polluting matter in wastewaters.

As in water treatment, coagulation in sewage effluents takes place under conditions of pH and coagulant dosage such that oversaturation with respect to the metal hydroxide occurs. On the other hand, the concentrations of the soluble metal species at equilibrium are very small within the pH ranges between 5 and 7 for alum, and between 3,5 and 7 for ferric chloride coagulations - Figures 2.3-(a) and -(b).

During the course of treatment of the AMP effluent, the lowest $Al_2(SO_4)_3$ and $FeCl_3$ concentrations which produced highest COD removals were 400 mg/l and 600 mg/l, respectively. These correspond to concentrations of $Al(OH)_3$ and $Fe(OH)_3$ equal to 1,1 x 10^{-3} mol/l and 3,7 x 10^{-3} mol/l, respectively. Considering aluminum hydroxide precipitation, it may be observed from Figure 2.3-(a) that aluminum hydroxide, at concentration approximately equal to 10^{-3} mol/l, precipitates at a pH higher than 4,5 in pure water. From the results reported in Chapters 4, 5 and 6, however, it may be observed that for $Al_2(SO_4)_3$ dosages equal to, or lower than, 400 mg/l - corresponding to concentrations of $Al(OH)_3$ equal to or lower than, 10^{-3} mol/l - a precipitate appeared even at pH as low as 3,5. According to Figure 2.3-(a), $Al(OH)_3$ precipitates cannot normally be formed at pH 3,5 at such concentrations. Zhukova *et al.*, (23) have mentioned that even at an ionic strength equal to 0,5 mg/l, precipitation of $Al(OH)_3$ has not been observed below pH 4,2. The explanation of this shift of the minimum pH for aluminum hydroxide precipitation towards lower pH is related to the effect the organic substances in the effluent exerted upon precipitation. Specific chemical interactions between the metal hydrolysis species and the co-ordinating sites on the surface of the organic colloids were considered responsible for this shift. These interactions altered the physical and chemical characteristics of the metal hydroxo-polymeric hydrolysis species and, consequently, the solubility characteristics of the precipitate formed.

The results presented in Chapters 4, 5 and 6 as well as those presented in Appendices F, G, H, I, J, K and L clearly show that on coagulation with alum or ferric chloride, a well-defined pattern appeared which was similar for both coagulations and relatively independent of the origin of the sewage effluent. In all cases the removal of the organic waste matter occurred between pH 4 and 7 for aluminum, and between 2 and 7 for ferric coagulations.

In the course of this study it was observed that in order to initiate turbidity removal - and, consequently, COD removal - the appearance of a metal hydroxide floc was in all cases necessary. The soluble metal hydrolysis polymeric species alone did not prove effective in turbidity removal.

In no coagulation experiment was restabilization of either the destabilized particulate or colloidal organic matter observed. At constant pH, any excess coagulant added immediately formed a precipitate which settled rapidly - provided the pH was appropriate for precipitation.

Figures 4.13, 4.14, 5.10, 5.11, 6.18, 6.19, 6.20 and 6.21 show that for any coagulant dosage (horizontal axis), as the pH approaches its optimum - from either left or right - the COD removal increases. Also for any pH (vertical axis), the higher the applied coagulant dosage, the higher the COD removal. In both cases the COD removal occurred up to a certain extent no matter how high the applied coagulant dosage was. A pseudostoichiometric relationship - in the sense defined by Stumm and O'Melia, (15) - existed between the coagulant dosage and the concentration of organics removed as COD at a constant pH. This is more pronounced at the optimum pH.

The previously mentioned Figures also show that the lower the remaining COD after coagulation, the narrower the pH range for further COD removal becomes. Maximum COD removal can only be achieved within a pH range of half a pH unit width. In this pH range the metal coagulant is rendered most effective.

Considering the contours corresponding to 31 mg/l final COD in each of the Figures 4.14, 5.11, and 6.19, concerning ferric chloride coagulations, a plot can be made, as shown in Figure 7.1. Each of the three contours corresponds to one of the three effluents each of which is characterized by its initial filtered COD. From this Figure it may be concluded that, if different effluents were treated to the same extent, the one with the higher initial filtered COD level would require a narrower pH range to achieve the same final COD level. This narrowing occurs towards, and is maximum at, the optimum pH. Figure 7.1 also shows that the higher the initial filtered COD, the higher the coagulant dosage required to achieve a certain final COD level.

A similar plot to that shown in Figure 7.1 was made for alum coagulation. This is shown in Figure 7.2. To make this plot data from Figures 4.13, 5.10 and 6.18 were collected. Conclusions similar to those given above may be drawn here, too.

The contours corresponding to 41 mg/l final COD in Figures 6.19 and 6.20 are replotted in Figure 7.3. Conclusions, similar to those drawn from Figures 7.1 and 7.2 can also be drawn from Figure 7.3. This suggests that the coagulation pattern is independent of the origin of effluent, which, in turn, may imply that the composition of all sewage effluents is basically similar. This could mean that the organic waste matter in sewage effluents is a product of the primary and secondary treatment steps and is, to a large extent, independent of the initial composition of the raw sewage. A similar conclusion has been drawn by Rickert and Hunter, (26), (27) - see Section D.1 of Appendix D.

The variation of the minimum residual COD achieved after coagulation with final pH and effluent is shown in Figures 7.4 and 7.5 separately for each hydrolyzing metal coagulant (for these plots data from Figures 4.13, 4.14, 5.10, 5.11, 6.18 and 6.19 were used).

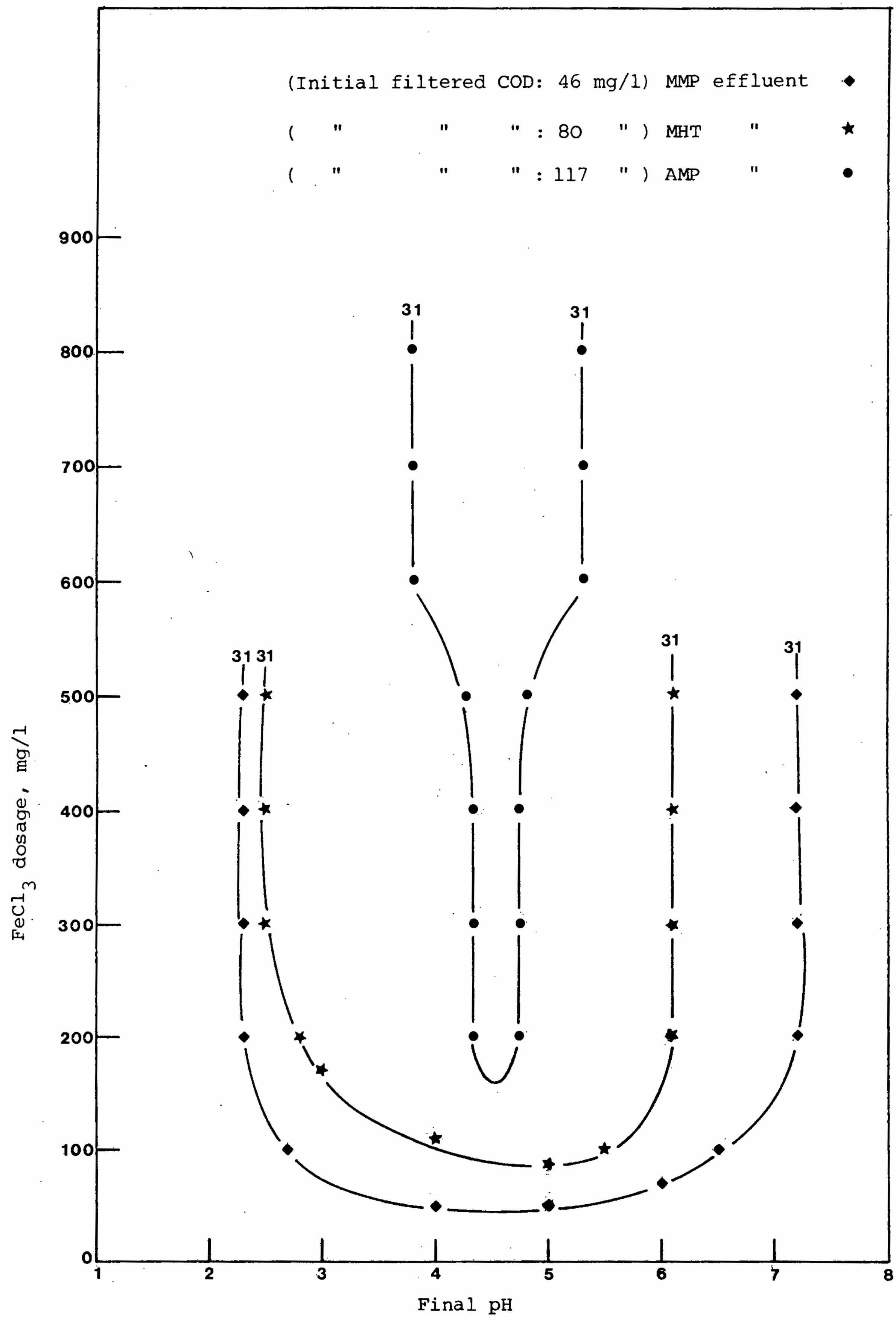


Figure 7.1 Ferric chloride coagulation. Variation of a certain final COD level with coagulant dosage, final pH and effluent.

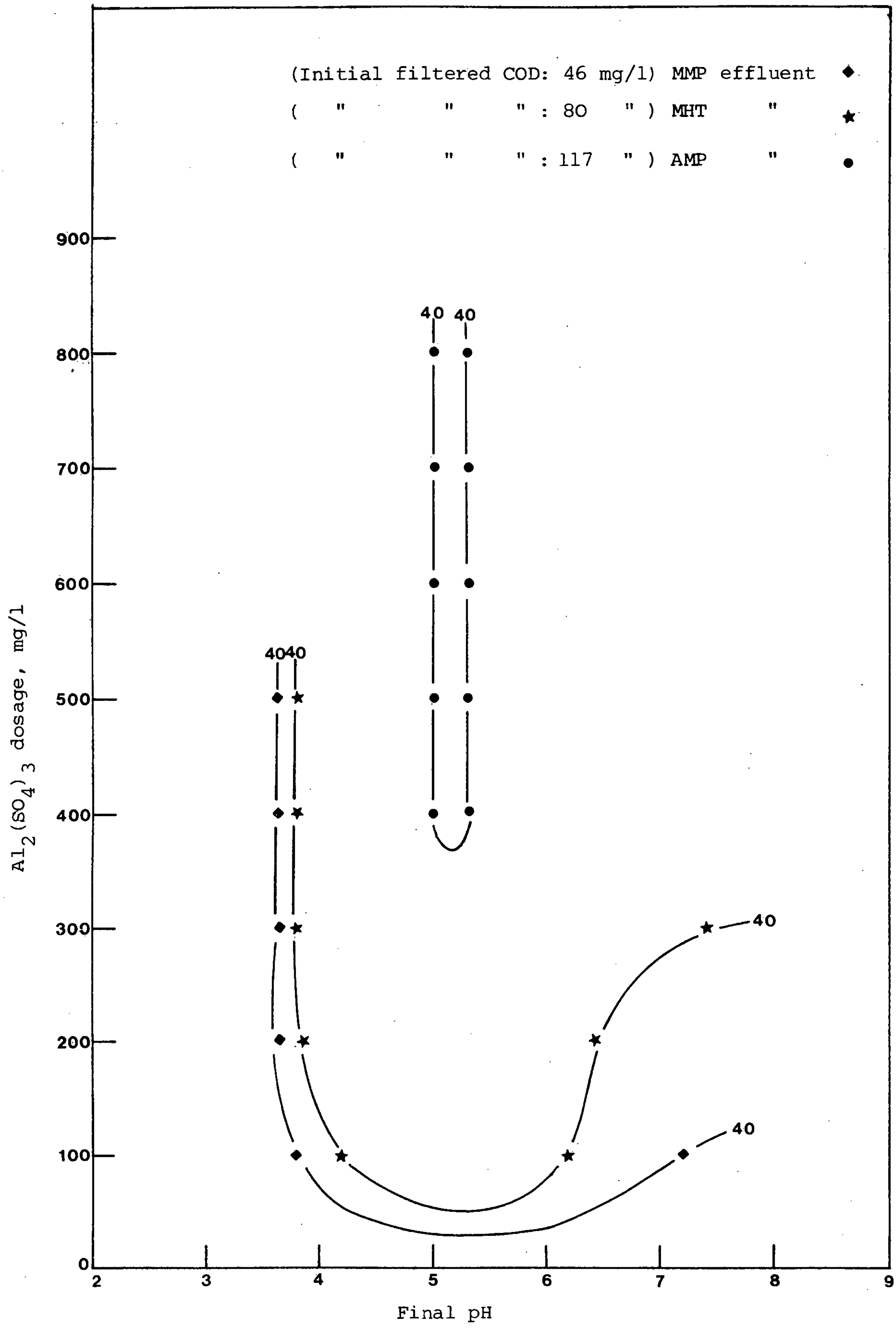


Figure 7.2 Alum coagulation. Variation of a certain final COD level with coagulant dosage, final pH and effluent.

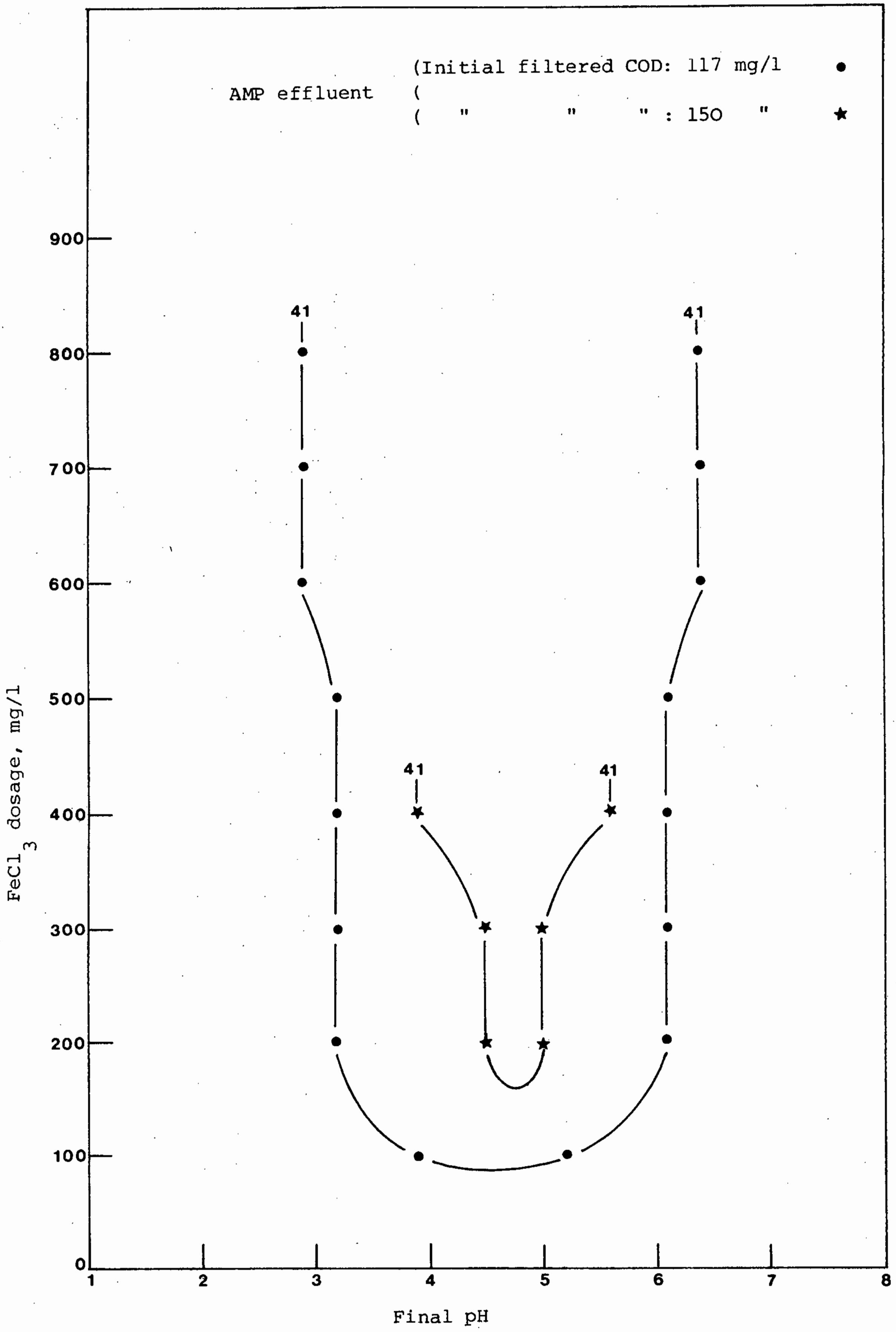


Figure 7.3 Ferric chloride coagulation. Variation of a certain final COD level with coagulant dosage, final pH and initial filtered COD.

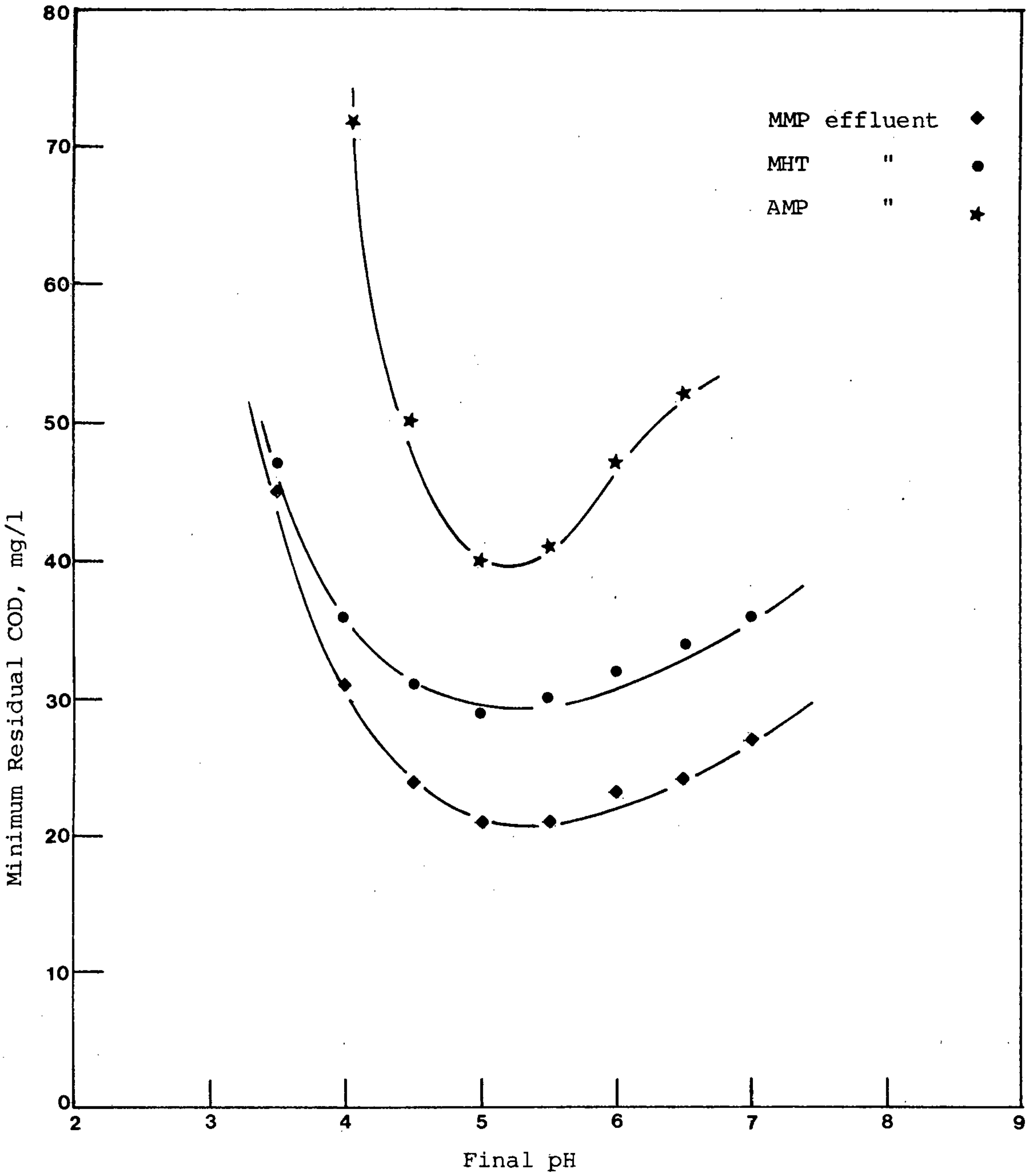


Figure 7.4 Alum coagulation. Variation of minimum residual COD with final pH and effluent.

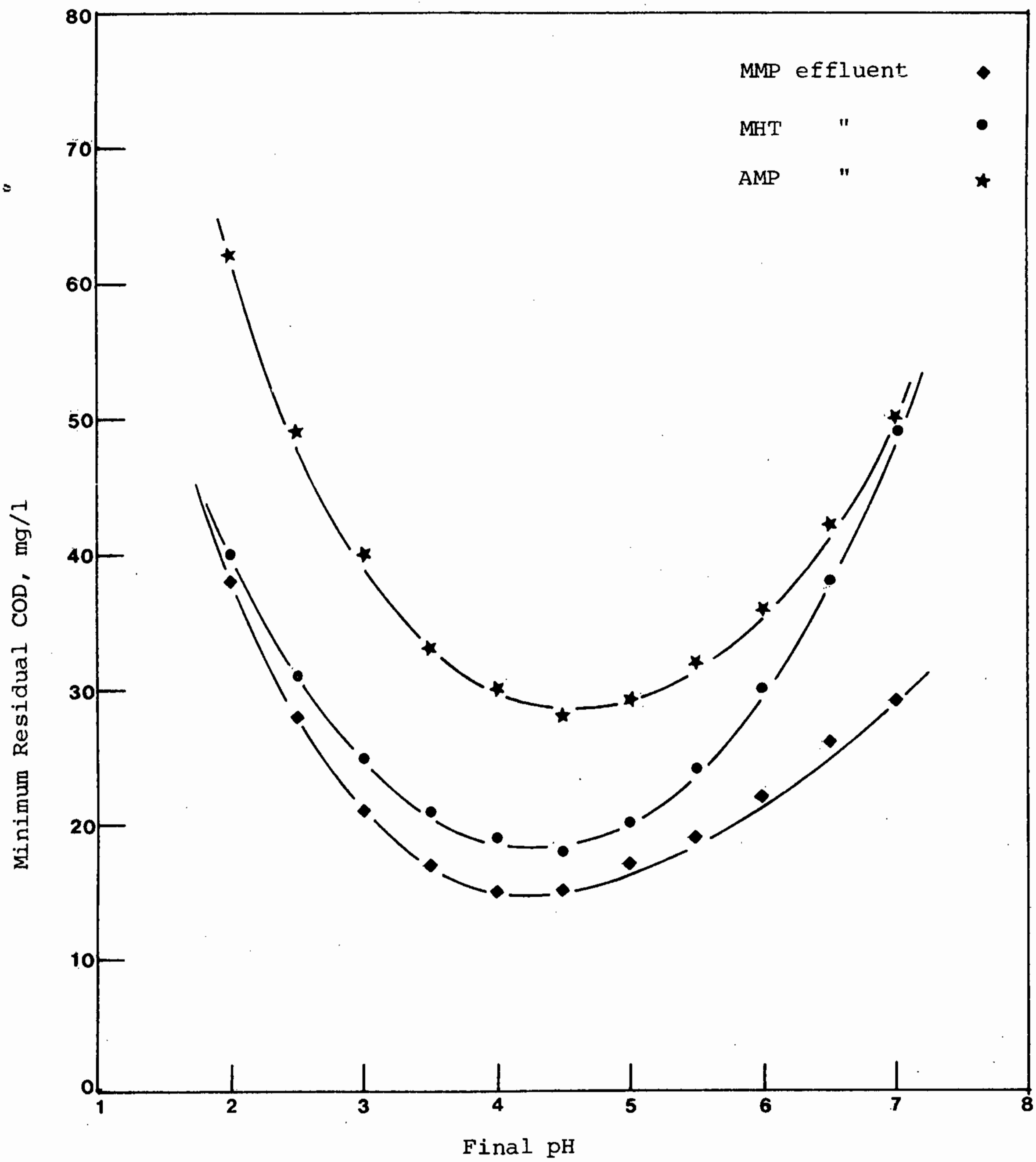


Figure 7.5 Ferric chloride coagulation. Variation of minimum residual COD with final pH and effluent.

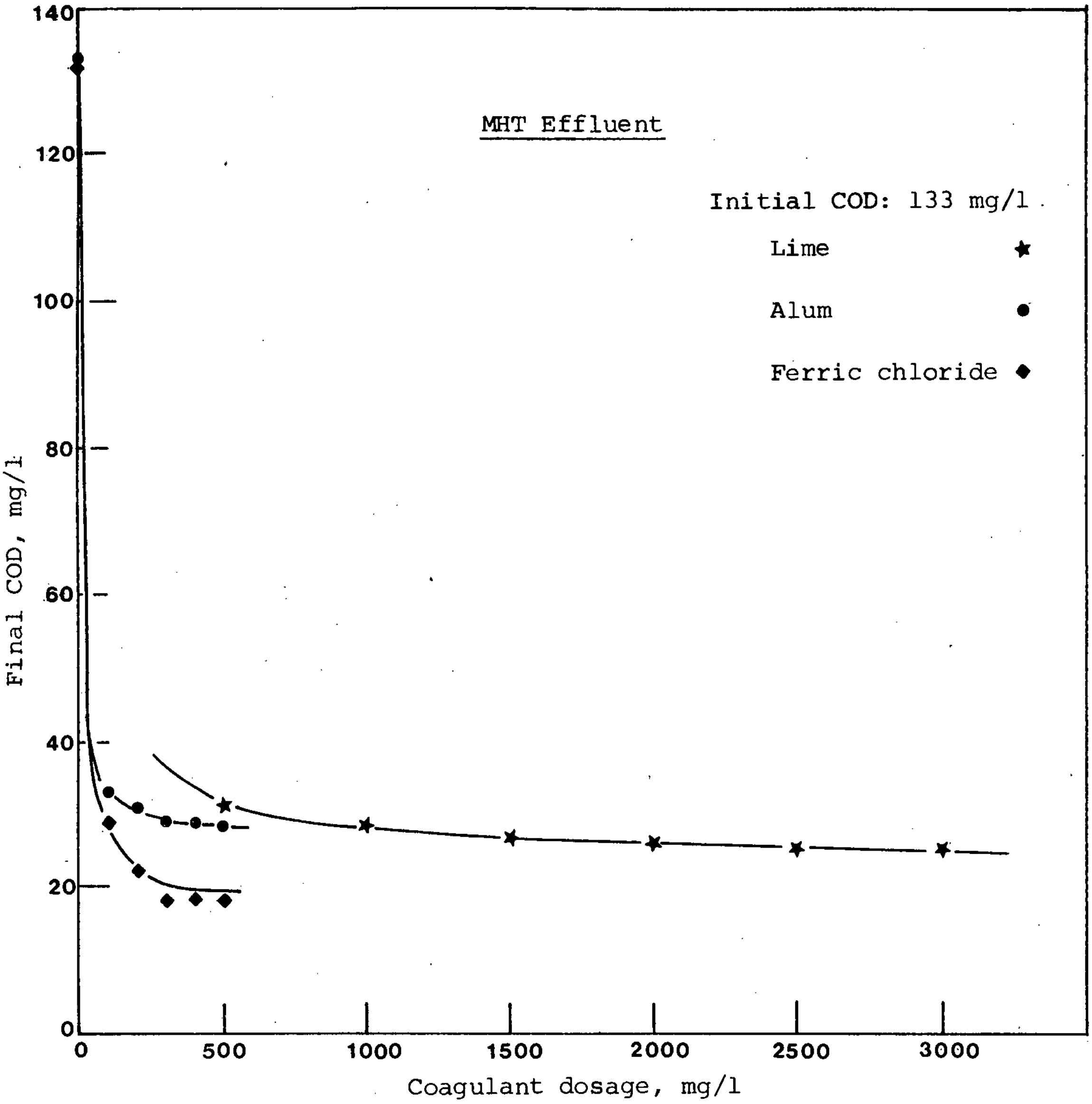


Figure 7.6 The final COD at optimum pH is plotted against coagulant dosage and coagulant.

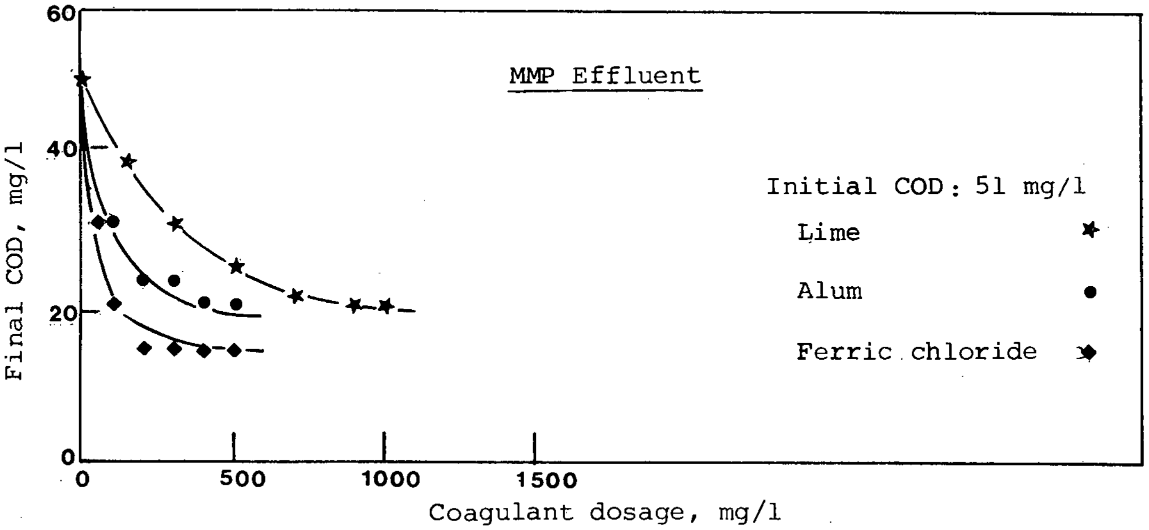


Figure 7.7 The final COD at optimum pH is plotted against coagulant dosage and coagulant.

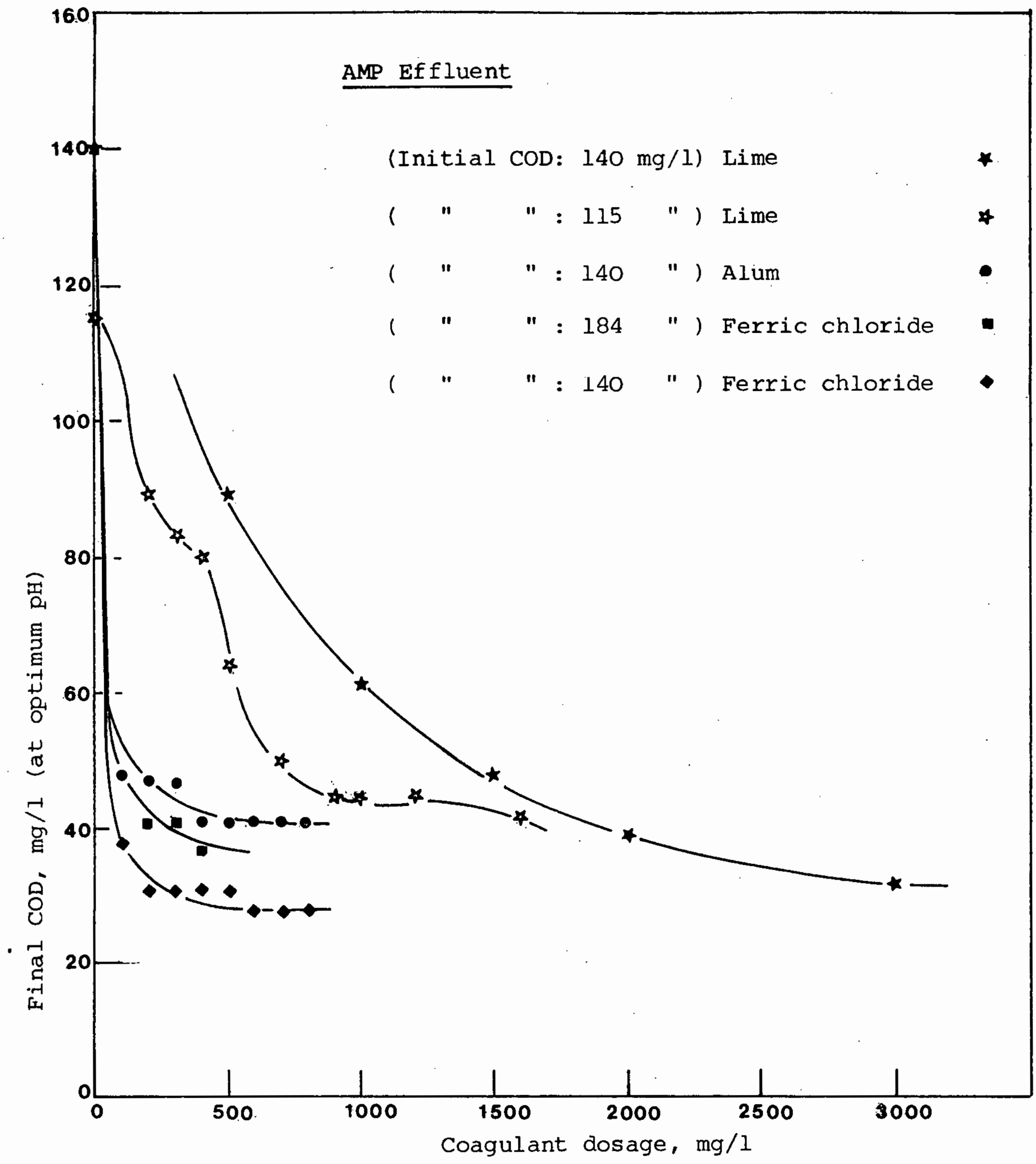


Figure 7.8 The final COD at optimum pH is plotted against coagulant dosage and coagulant.

Figures 7.4 and 7.5 show that for any effluent the optimum pH for COD removal was between 5 and 5,5 for alum, and between 4 and 5 for ferric chloride coagulations. Ferric chloride is clearly shown to be more effective than alum for COD removal. As it is observed, always a certain amount of organic waste matter remained unremoved. This was higher, the higher the initial filtered COD.

This may also be shown by plotting the final COD achieved at the optimum pH against coagulant dosage and coagulant, separately for each effluent. These plots are shown in Figures 7.6, 7.7 and 7.8.

7.1.1.2 Theoretical Discussion

According to what has been mentioned in Appendix A, the pronounced and prominent effect of pH on coagulation with hydrolyzing metal coagulants strongly suggests that specific chemical interactions and not adsorption effects are primarily responsible for the destabilization of the organic colloidal matter in sewage effluents. McLellon *et al.*, (30) have been led to a similar conclusion.

The experimental findings presented in Figures 7.1 to 7.5 are very similar to those obtained by Hall and Packham, (25) on removal of organic colour from water with hydrolyzing metal coagulants. This, associated with the fact that the organics removal, as envisaged in this thesis, was designed to include colour removal, made the author to consider the views of Hall and Packham on the underlying mechanisms of colour removal from water,as applicable to COD removal from sewage effluents.

The views of the author concerning the organics removal from sewage effluents involve three modes of destabilization. These are described, in short, as "enmeshment", "adsorption" and "specific chemical interactions" (SCI), and, associated with a theoretical explanation of the already presented experimental findings, are discussed below:

(a) Removal of the Particulate Matter from Sewage Effluents

The removal of the suspended settleable turbidity is considered for discussion here, because it comprises a portion of the total COD of the effluent.

The slowly occurring phenomenon of the settling of particulate matter could be brought to an end by the addition of a hydrolyzing metal coagulant to such an extent that precipitation occurred. Under such conditions, adsorption of the polynuclear metal hydrolysis species onto the surfaces of the organic particles and subsequent destabilization did not seem to be responsible for accelerating the settling of particulate matter. Any effect other than that attributed to floc formation and subsequent removal of the particles together with the precipitating floc did not seem to be significant. For floc formation to occur, oversaturation with metal hydroxide seemed to be a prerequisite. Adsorption onto the freshly formed "metal hydroxide" floc, which was positively charged, may have been responsible for the turbidity removal up to a certain extent. But, even if this was true, this phenomenon was masked by the subsequent precipitation of amorphous metal hydroxide, which was caused by the continuing coagulant addition and was due to supersaturation effects - as defined by Stumm and O'Melia, (15). The amorphous metal hydroxide precipitate enmeshed and removed the particles. The "sweep floc" phenomenon - see Appendix A - which was associated with the precipitation of amorphous metal hydroxide, has been considered mainly responsible for the removal of the natural turbidity from sewage effluents.

Similarly, Packham, (14) has shown that enmeshment of the dispersed particles in a mass of rapidly forming and precipitating metal hydroxide flocs has been responsible for turbidity removal from water - see Appendix A. Under conditions of rapid precipitation, the precipitate is composed of molecular chains which are particularly effective in forming interparticle bridges. Such conditions are responsible for the formation of a precipitate of almost zero charge and prevail at the isoelectric point of the metal hydroxide precipitate, which is different for aluminum and ferric hydroxides. The isoelectric point of aluminum hydroxide is at pH 7 and the experimental results of this thesis tend to agree with this. That of ferric hydroxide has been reported to be approximately pH 5 - Stumm and Morgan, (10) - while elsewhere has been reported to be pH 6,7 or pH 8 - see Section 2.4.1. The experimental findings of this thesis support pH 8 as being the isoelectric point of ferric hydroxide (see Section 6.3.4 - (B)).

The non-appearance of restabilization phenomena throughout the course of this work was probably due to oversaturation effects which, according to Stumm and O'Melia, (15), inhibit restabilization.

The above discussion suggests that the mechanism proposed by Packham best describes the phenomenon of removal of the particulate matter from sewage effluents.

(b) Removal of the Colloidal Organic Matter from Sewage Effluents

Specific chemical interactions, (SCI) and not adsorption effects have been considered primarily responsible for the destabilization reactions which took place upon the removal of organic colloids from sewage effluents. As mentioned in Appendix A, the SCI mechanism consists of partial substitution of the OH^- ions of the metal hydroxo-polymeric sheath by other complex forming anions which occupy the co-ordinative sites on the surface of organic colloids. This substitution satisfies the co-ordinative requirements of the metal ions for charge neutralization. For the specific co-ordination an adsorption reaction of the metal hydrolysis polymeric species on the surface of the organic colloids seems to be a prerequisite step. The degree of substitution depends on the degree of co-ordination of the anions with the metal ions. The higher the tendency of the anions to compete for OH^- ions, the higher the degree of substitution. The higher the degree of substitution, the lower the concentration of OH^- ions needed to exist in solution in order to satisfy the co-ordinative requirements of the metal ions and, consequently, the lower the pH needed for specific co-ordination, subsequent charge neutralization, and eventual destabilization of the organic colloids.

Assuming constant metal ion concentration, those inorganic colloids with co-ordinative sites showing higher affinity for the metal ion will be responsible for a greater shift of the optimum pH towards acidic values. The higher affinity may be related to a higher degree of ionization of the co-ordinative groups at a certain pH. At the optimum pH the ionization is limited. Thus, only a certain proportion of these groups is able to interact with the metal ions. On the other hand, appropriate metal hydrolysis species should be formed for the specific co-ordination. As the concentration of the metal ion increases, precipitation of the "metal hydroxide" will end the specific co-ordination. Consequently, the optimum pH for COD removal represents a compromise between maximum dissociation of the active co-ordinative groups on the surface of organic colloids and formation of the appropriate metal hydrolysis species required for precipitation of the "metal hydroxide", (25). At the optimum pH for COD removal, the extent of ionization of the co-ordinative groups is fixed, and any additional amount of coagulant in excess to that needed to induce initial precipitation of the metal ion will cause formation of the appropriate hydrolysis species, which will interact with free co-ordinative groups, subsequent precipitation of "metal hydroxide", and further removal of an increasing number of organic colloids. This mechanism will continue functioning until there are no more available co-ordinative sites for interaction.

The above discussion also applies to soluble organic molecules which contain complex forming anions able to substitute OH^- ions in the metal hydroxo-polymeric sheath, and which, consequently, are also amenable to removal by coagulation under certain conditions.

Applying Hall and Packham's conclusions - (25) and Appendix A - to the present case it seems reasonable to suggest that a large number of the active co-ordinative groups on the colloid surface are acidic groups, or, that a large number of the soluble organic substances found in sewage effluents are acidic compounds. This is well supported if what has been presented in Appendix D is taken into consideration and, specifically, the findings of Rebhun *et al.*, (31), Bunch *et al.*, (32), Murtagh and Bunch, (33), and Painter, (34). Furthermore, considering interaction between the metal ion hydrolysis species and those acidic groups it seems reasonable to suggest - as Hall and Packham did - that formation of basic salts of aluminum or iron occurs during coagulation. This is more complete at the optimum pH.

The theoretical explanation of the results plotted in Figures 4.13, 4.14, 5.10, 5.11, 6.18, 6.19, 6.20 and 6.21, which is based on the previous discussion, follows.

For any fixed coagulant dosage, as pH approached the optimum pH, increased ionization of the acidic groups on the colloid surface occurred and the effect of SCI became more prominent. This became most pronounced at the optimum pH, where formation of basic salts occurred. The formation of pure metal hydroxide was most pronounced at the isoelectric point, which was pH 7 for aluminum hydroxide precipitate, and about pH 8 for ferric hydroxide precipitate. At other than optimum pH values, adsorption effects predominated and low COD removal was observed.

For any fixed pH the appeared pseudostoichiometry between coagulant dosage and concentration of organics removed as COD was a phenomenon which was due to simultaneously adsorption and SCI effects. If SCI were only responsible for COD removal, a stoichiometry and not a pseudostoichiometry would have appeared due to formation of basic salts, only.

At any fixed pH the appearance of a limit on COD removal was attributed to the existence of soluble organic substances which could not be removed by coagulation. These could have been substances deficient in acidic groups.

The slightly different optimum pH appearing in Figures 4.13, 5.10 and 6.18 for alum coagulation and, separately, in Figures 4.14, 5.11 and 6.19 for ferric chloride coagulation is attributed to the slightly different composition encountered from effluent to effluent. Also, the slightly different composition among different samples of the same effluent explains the difference in the position of the optimum pH shown in Figures

6.19, 6.20 and 6.21.

From Figures 7.1 and 7.2 it may be concluded that to achieve removal of organics to a certain extent from the highly polluted AMP effluent, SCI were required to take part. This, however, was not the case with the MMP effluent. In the first case, this is indicated by the specificity of the pH range required. For the MMP effluent adsorption effects were adequate. Similarly, Figure 7.3 shows that if an effluent's quality is subject to fluctuations, to achieve a certain low final COD level, conditions which ensure that SCI will occur should be maintained, if the fluctuation is accompanied by a high increase in COD.

Figures 7.4 and 7.5 show that the higher the initial COD of an effluent, the higher the concentration of those substances which cannot be removed by coagulation.

If the minimum residual COD obtained at the optimum pH for COD removal from Figures 7.4, 7.5, 6.11 and 6.12 (corresponding to samples from the same or different effluents) is plotted against the initial filtered COD, separately for each coagulant, the plots (a) and (b) shown in Figure 7.9 are made. These show that, within a certain initial filtered COD range, a more or less linear relationship exists between the initial filtered COD and the minimum residual COD which can be achieved after coagulation at the optimum pH.

Throughout the course of this study, alum has been less effective than ferric chloride, although the mechanism of destabilization was similar in both cases. This can also be shown if plots 7.9 - (a) and - (b) are compared with each other. The similarity of slopes of the lines accounts for the similar destabilization mechanism, while the slight shift of the line under (a) towards increased COD values in relation to that under (b), accounts for the decreased effectiveness of alum to remove COD. Similar conclusions have been drawn by other investigators - e.g. Hall and Packham, (25), McLellon *et al.*,(30), Black *et al.*, (35), etc. This is believed to have been associated with the higher optimum pH which has been obtained on alum coagulations in relation to that obtained on ferric chloride coagulations. Ferric ion is a stronger acid than aluminum ion. According to Hall and Packham, (25) ferric ions show a greater affinity for anions than aluminum ions. The greater affinity between Fe^{3+} and OH^- is indicated by the formation of basic iron salts at a lower pH in the case of ferric coagulations, to that required for the formation of basic aluminum salts, as well as by the higher isoelectric point of ferric hydroxide - pH 8 - in relation to that of aluminum hydroxide precipitate - pH 7. Similarly, the better floc settling characteristics observed after ferric chloride coagulation were the result of

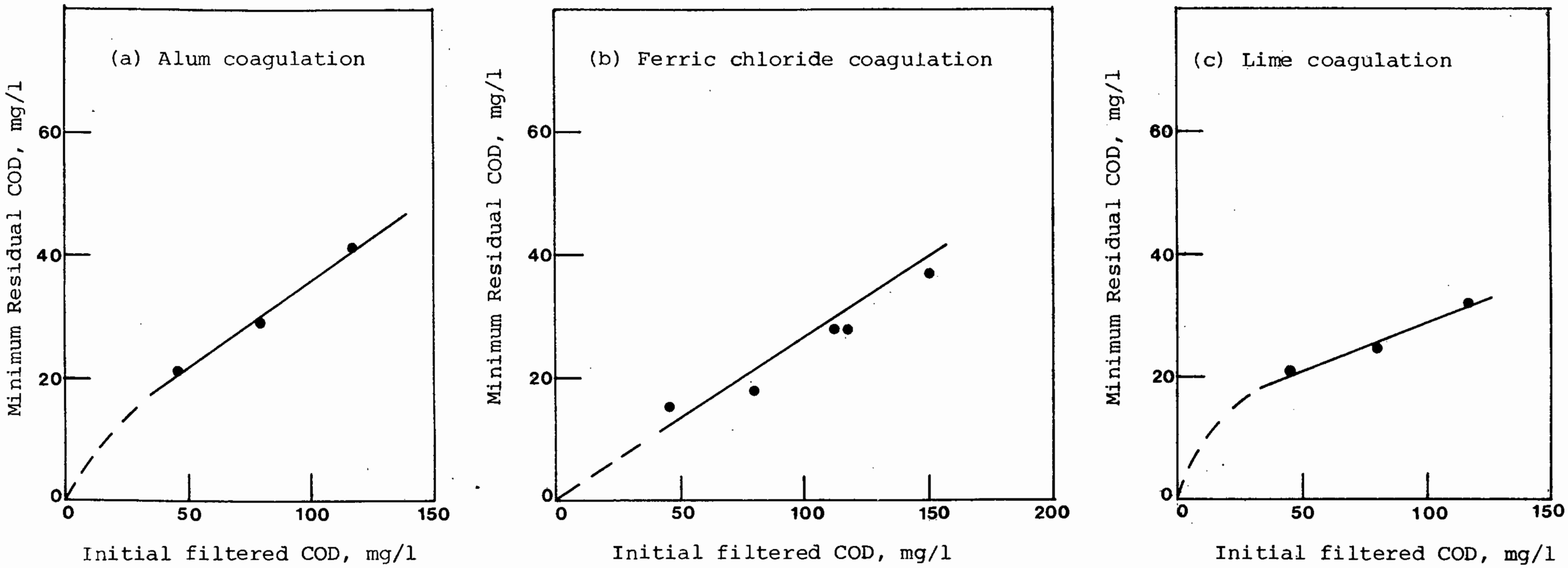


Figure 7.9 Minimum Residual COD is plotted against initial filtered COD separately for each inorganic coagulant.

the higher affinity of ferric ions for anions which altered the physical characteristics of the floc - Stumm and Morgan, (10).

7.1.2 Lime Coagulation

The results presented in Figures 4.10, 5.5, 6.8 and 6.14 concerning final COD were also plotted in Figures 7.6, 7.7, and 7.8 for comparison with the results obtained on coagulation with hydrolyzing metal coagulants.

For lime to become effective for turbidity or COD removal, it should be added in such amounts as to largely neutralize the acidity as well as create a sufficiently high pH for magnesium hydroxide to precipitate. Magnesium hydroxide particles are positively charged and are readily adsorbed on the negative surface of the hydrophilic colloids predominating in sewage effluents. Precipitation of calcium salts accelerates the overall removal, because they act as weighing agents on magnesium hydroxide precipitation.

Figures 7.6, 7.7 and 7.8 show that excessive lime dosages - higher than those required to result in complete magnesium hydroxide precipitation - invariably resulted in a higher COD removal, the higher the lime dosage. This suggests that Ca^{2+} ions might have aided COD removal in those cases. The relatively low magnesium ion concentration of the AMP effluent - about 20 mg/l - cannot account for nor explain the high COD removal observed on coagulation with lime, if precipitated as magnesium hydroxide. The agency of calcium ions is rather necessary to account for the difference. Calcium ions act via charge neutralization on the organic colloids by compacting the electrical double layer and subsequently destabilizing the colloids. The destabilization mechanism associated with the double-layer model is considered responsible for part of the high COD removals which were observed after addition of excessive amounts of lime. The action of calcium ions is aided by the fact that at the high prevailing pH, increased ionization of the active groups of the colloid surface occurs which renders the organic colloids more negatively charged. The magnesium hydroxide destabilization step followed by the calcium ion destabilization step may be observed in Figure 6.4, where the curve relating the lime dosage with the final COD changes slope twice.

A pseudostoichiometric relationship appeared to exist between the concentration of lime added and the amount of organics removed as COD.

A similar plot to those appearing in Figure 7.9 for alum or ferric chloride coagulations was also made for lime coagulation. This is shown under

(c) in Figure 7.9. The COD values considered for this plot were the minimum values obtained after excessive lime treatment of each effluent. It may be observed that a straight line can approximately express the relationship between minimum remaining COD and initial filtered COD. The different slope of the line under (c) in relation to those of the lines under (a) and (b) is related to the different mechanism which applies on lime coagulation.

In summary, the removal of the particulate matter on coagulation with lime occurs by enmeshment of the particles in a mass of precipitating magnesium hydroxide and calcium salts. The removal of the organic colloids occurs by adsorption of the magnesium hydroxide precipitate onto the surface of the colloids and subsequent charge neutralization. At excessive lime dosages compaction of the electrical double-layer surrounding the colloids by calcium ions and subsequent charge neutralization, aid the overall removal.

On lime coagulation both dosage and pH play an important role in removing COD. The required lime dosage is a function of the initial pH, acidity, concentration of pollutants, and concentration of magnesium ion in solution.

7.1.3 Effect of Organic Polyelectrolytes on COD Removal when used Alone

From the discussions developed in Sections 4.2.1, 4.3.4, 5.3.4, 6.2.1 and 6.3.4 it may be concluded that on addition of synthetic cationic polyelectrolytes, a reaction of charge neutralization occurred between them and organic anions in solution. This is supported by the fact that similar results were obtained when cationic polyelectrolytes of widely different M.W. and chemical characters were applied - compare, for instance, the actions of Superfloc C-521, Nalco-607, and Praestol 444-K. Such a reaction probably occurred between the cationic polymers and the organic colloids, too. In any case, the products of these reactions were finally dispersed colloidal particles which did not settle, but gave rise to an increased turbidity at low cationic polymer dosages. Similar results have been obtained by Rebhun *et al.*, (31), and Shelton and Drewry, (36). At increased dosages coagulation began of both the original turbidity and that formed during the charge neutralization reaction.

The above discussion indicates that cationic polyelectrolytes can only remove a certain small portion of the organic waste matter when applied alone.

The synthetic non-ionic and anionic polyelectrolytes were not effective at all in removing either suspended or dissolved organic matter, because they could not cause either charge neutralization or adsorption and subsequent bridging under the conditions they were applied.

Floccotan promised good results initially. Despite, however, the good floc formation, it proved to be ineffective in removing the colloidal organic matter. It was only effective in removing the particulate matter, which accounted for only a small portion of the total COD.

The action of Floccotan consisted rather in enmeshing the suspended particles in a mass of voluminous slow settling flocs.

In general, it may be concluded that the organic polyelectrolytes had little effect in removing the organic waste matter from sewage effluents when applied alone.

7.1.4 Effect of Organic Polyelectrolytes on COD Removal when Used in Conjunction with Inorganic Coagulants

A very slight improvement in COD removal occurred in this case in addition to that achieved by the action of the inorganic coagulants alone. This is believed to have occurred incidentally and was rather due to the better floc settling characteristics the organic polymers induced with their addition (see Section 4.3.4 - (c)).

7.1.5 Cost of COD Removal by Chemical Coagulation

The cost associated with the chemicals required to achieve a certain final effluent quality has been estimated for each coagulant and effluent and has been plotted against final COD. The plots are shown in Figures 7.10, 7.11 and 7.12. The cost estimates are also presented in a tabulated form in Appendix M. For hydrolyzing metal coagulants the costs have been estimated at optimum conditions for COD removal in each case (optimum pH). For lime coagulation two costs are presented. The one corresponds to merely the cost of lime required for coagulation, while the other to the cost of lime required plus the cost of the carbon dioxide required to bring the pH of the treated effluent down to the initial pH before coagulation.

The choice of the optimum solution will be governed by the cost involved and the extent of treatment required - desirable, or according to certain standards. Figures 7.10, 7.11 and 7.12 show that an expense equal to 5 cents per kilolitre of effluent should at least be expected for good COD removal from any effluent (1975 cost).

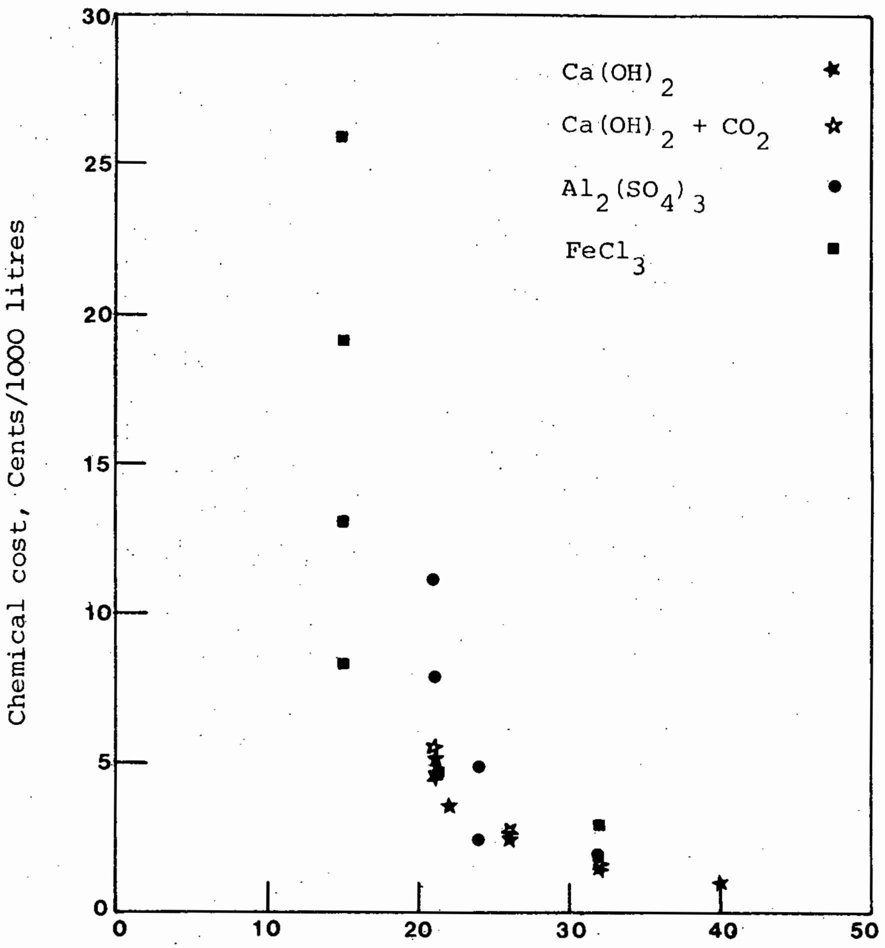


Figure 7.10 MMP effluent, Variation of chemical cost with desirable final COD and coagulant.

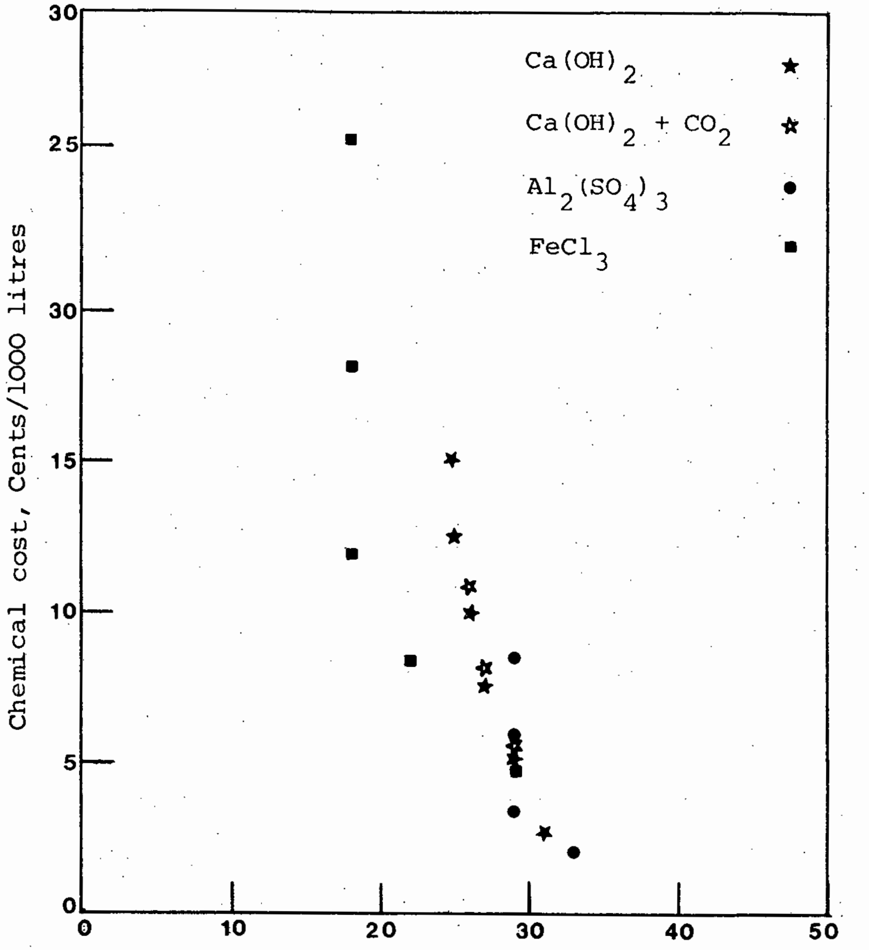


Figure 7.11 MHT effluent. Variation of chemical cost with desirable final COD and coagulant.

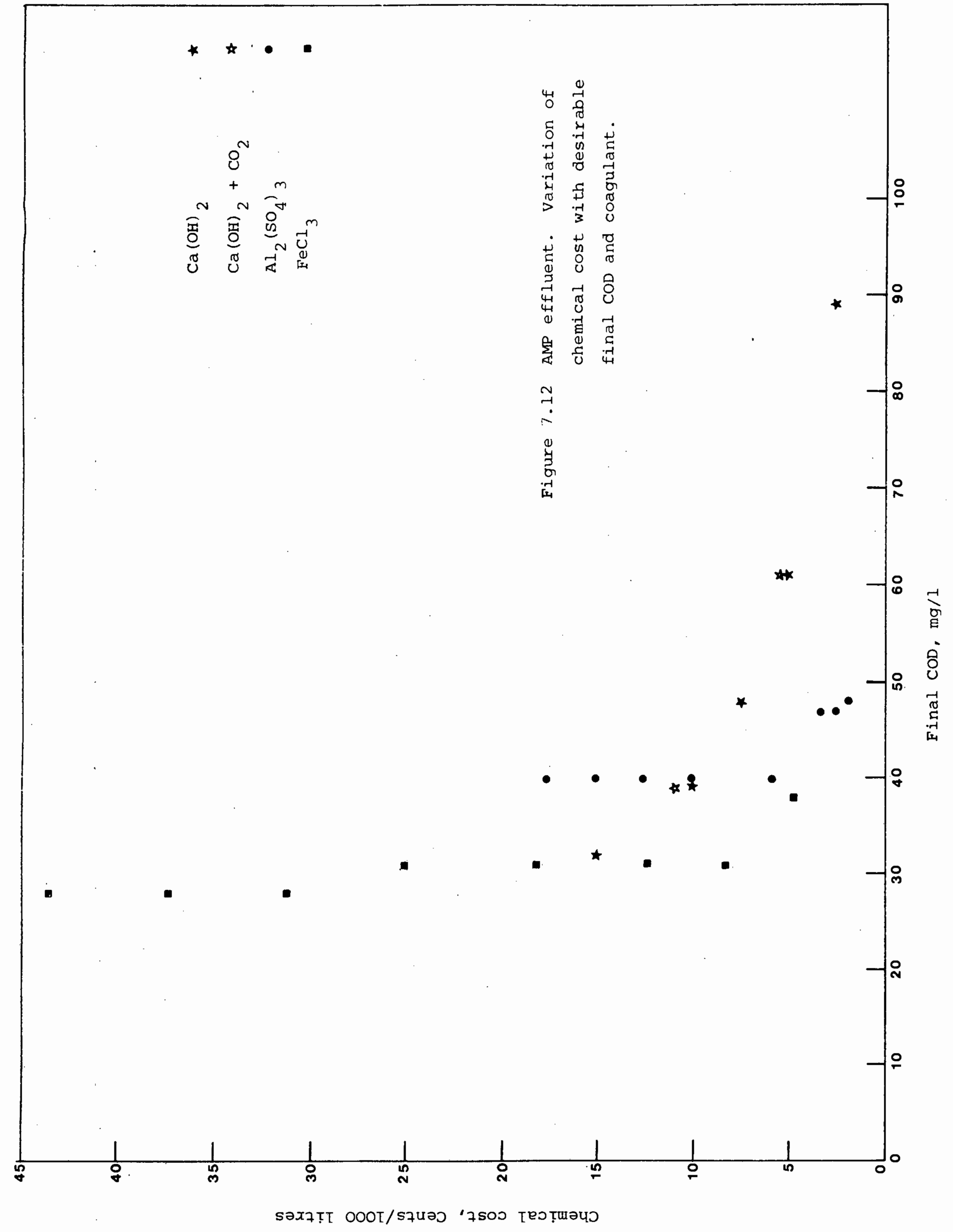


Figure 7.12 AMP effluent. Variation of chemical cost with desirable final COD and coagulant.

7.2 COLOUR REMOVAL

Colour removal constitutes a part of the total COD removal, because colour substances are either colloidal or soluble organic substances - see Appendix D, Section D.2. Consequently, the mechanisms described in Sections 7.1.1.2 - (b) and 7.1.2 concerning COD removal apply to colour removal as well.

Plotting the initial filtered COD and colour values reported in Tables 4.2, 5.2 and 6.2 against each other, the plot shown in Figure 7.13 is made. This Figure shows that the colour concentration is rather directly proportional to the filtered COD. Considering the final colour values reported separately for each coagulant in the above Tables and plotting them against initial colour, the plots (a), (b) and (c) shown in Figure 7.14 are made. Each plot in this Figure suggests that a linear relationship exists between initial and final colour concentrations. Figure 7.14 is similar to Figure 7.9. This occurs because colour substances constitute a portion of the substances responsible for filtered COD.

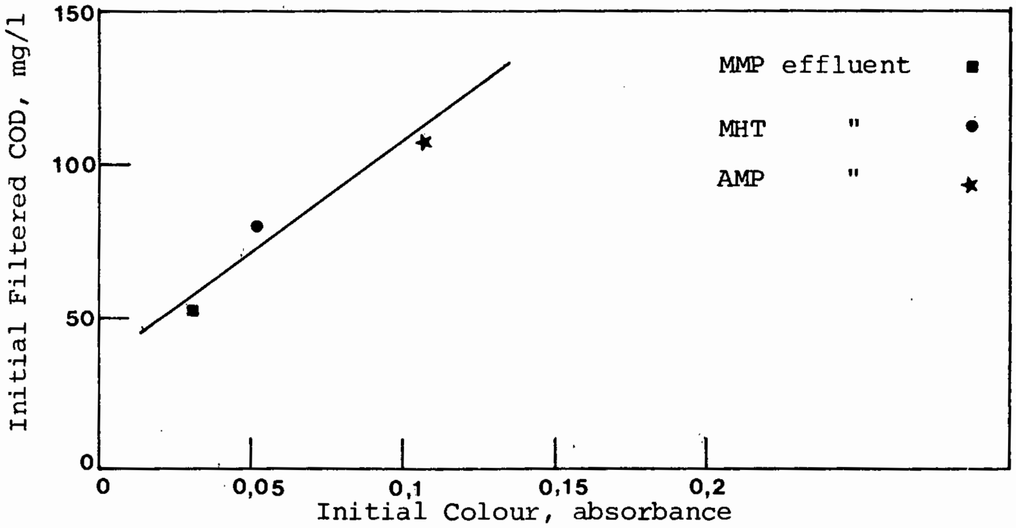
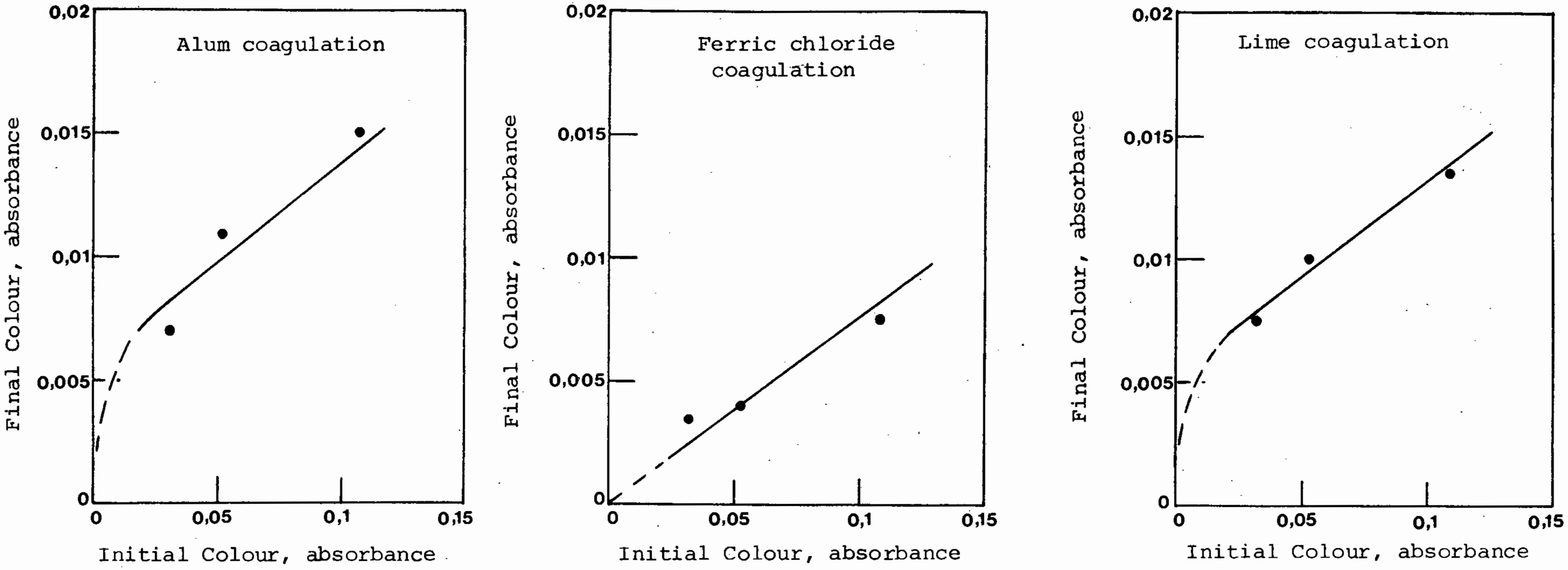


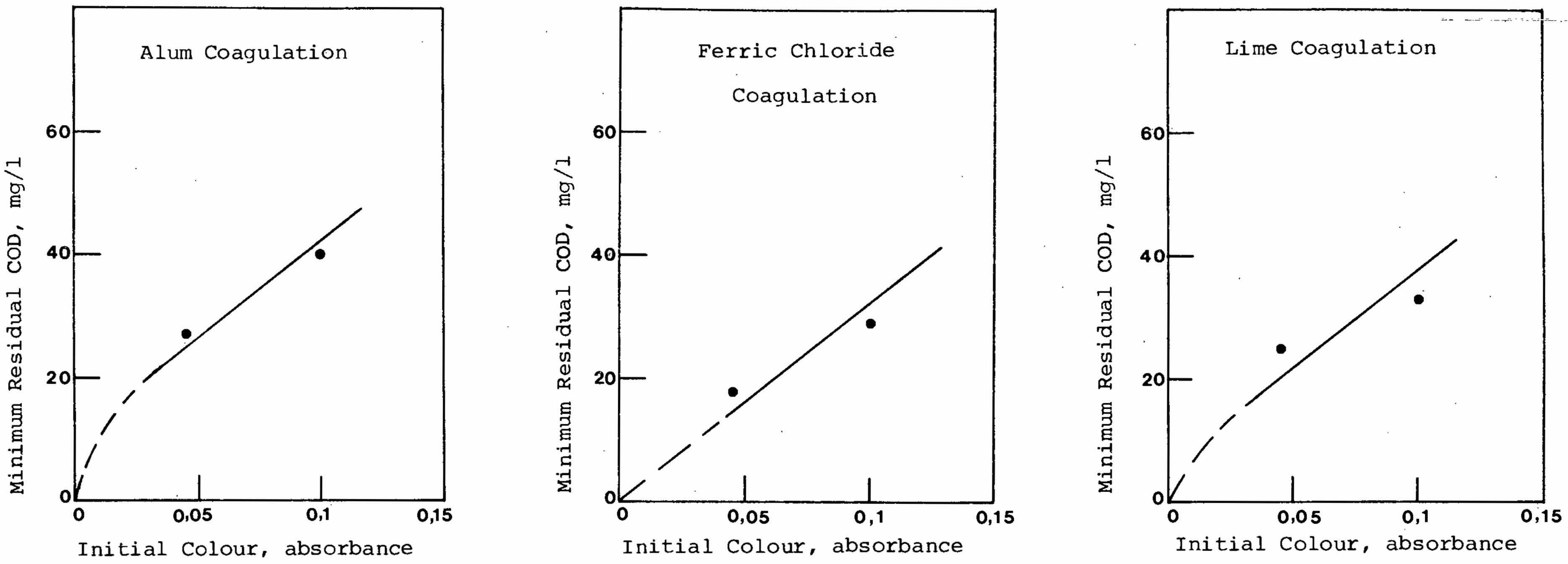
Figure 7.13 Variation of initial filtered COD with initial colour and effluent.

The initial colour determination can be employed to predict the minimum residual COD achievable under conditions of maximum COD removal for each coagulant after coagulation. This can be done by means of the plots (a), (b) and (c) shown in Figure 7.15. These plots are the combination of the plots shown in Figure 7.9 and Figure 7.13. The relationships between minimum residual COD and initial colour will have to be established for a number of different sewage effluents for their use to become widely recommended.



(a) (b) (c)

Figure 7.14 Variation of final colour with initial colour and coagulant.



(a) (b) (c)

Figure 7.15 Variation of minimum residual COD with initial colour and coagulant.

The initial colour determination can also be used to predict the initial filtered COD by means of the plot shown in Figure 7.13. This is particularly useful when the pollutional strength of an effluent is to be determined in terms of COD on a continuous basis. Photometry has already been suggested as a continuous method for COD analysis on effluents, (37).

7.3 FINAL DISCUSSION - TURBIDITY REMOVAL

7.3.1 Hydrolyzing Metal Coagulants

The character of the remaining turbidity after coagulation with hydrolyzing metal coagulants has been discussed in Section 4.3.4. The remaining turbidity after 60 minutes settling has been shown (Sections 4.3.4, 5.3.4 and 6.3.4) to be independent of the amount and character of the natural turbidity of the effluent, and the coagulant dosage applied. It is dependent on the prevailing pH, the character and concentration of the anions in solution, and the chemical character of the trivalent metal coagulant.

As Figures 4.15, 4.16, 5.12, 6.22 and 6.23 show, the remaining turbidity measured after 60 minutes settling lies in a straight line, when plotted against final pH in a log-log scale. This relationship is different for alum and ferric chloride coagulations. If the data presented in Sections L.2, L.4 and L.6 of Appendix L are elaborated as described in Section L.7, a general relationship is formulated for each metal coagulant relating the final turbidity after 60 minutes settling with final pH. This is applicable within a certain pH range which is different for each coagulant, and is represented graphically in Figure 7.16. As it may be observed, each relationship is linear in a log-log scale, both have identical slopes, and the remaining turbidity after ferric chloride coagulation is exactly half of that remaining after alum coagulation, for any pH between 3,5 and 9. Both remaining turbidities are, however, quite low at pH around 7 (below 1 FTU).

7.3.2 Lime Coagulation

As it has been mentioned in Sections 4.3.4, 5.3.4, 6.3.4, and 7.1. 2, on lime coagulation the raw effluent turbidity is removed by enmeshment and simultaneous adsorption in a mass of precipitating voluminous magnesium hydroxide.

7.3.3 Effect of Organic Polyelectrolytes on Turbidity Removal when Used Alone

None of the synthetic organic polyelectrolytes tested alone proved

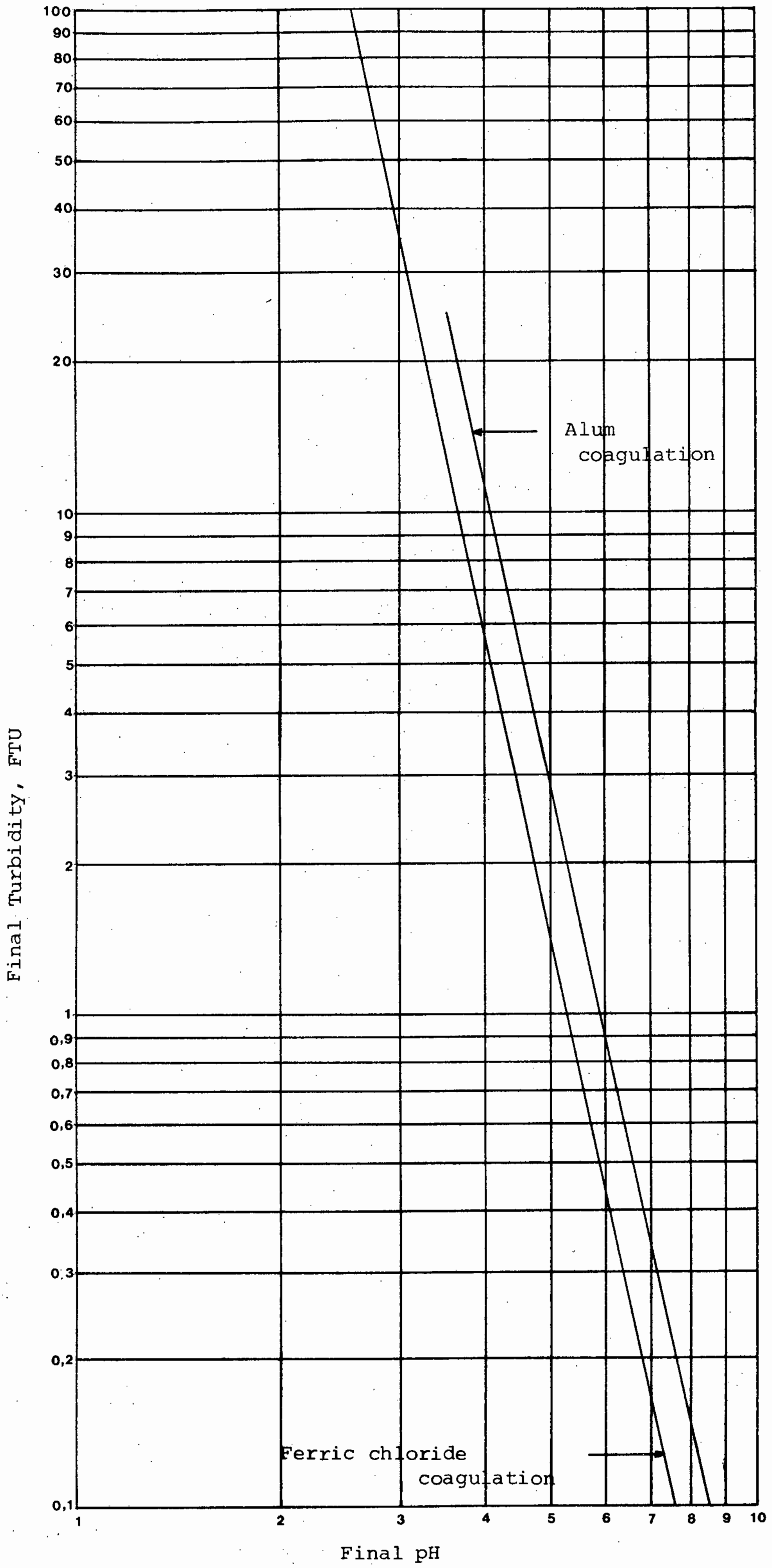


Figure 7.16 Variation of the final turbidity measured after 60 minutes settling with final pH and hyrodlyzing metal coagulant.

capable of completely removing the effluent's turbidity. The cationic polyelectrolytes were effective to a limited extent only.

The natural polymer Floccotan proved capable of completely removing the natural turbidity of the effluent. Its action consisted in enmeshing the particles in a mass of rapidly forming but slowly settling flocs.

7.4 EFFECT OF ORGANIC POLYELECTROLYTES ON FLOC SETTLING CHARACTERISTICS WHEN USED IN CONJUNCTION WITH INORGANIC COAGULANTS

7.4.1 Polyelectrolytes Used in Conjunction with Al or Fe(III) Coagulants.

In general, the use of synthetic organic polymers, especially those of high M.W., resulted in a significant improvement of the floc settling characteristics. Both the floc magnitude and the settling rate were substantially increased.

The mechanism by which the organic synthetic polyelectrolytes act is best described by La Mer's bridging model of flocculation - see Section 2.2.2.

The higher concentrations of the cationic polyelectrolytes in relation to those required for nonionic or anionic polyelectrolytes is explained by either the difference in molecular weight or by the similar charge characteristics of the cationic polyelectrolytes to those of the "metal hydroxide" flocs at the usually acidic pH of coagulation.

Among the polymers tested, Superfloc N-100 was the best flocculating agent when used in conjunction with alum. Both Superfloc N-100 and the negatively charged A-150 showed very good flocculating action when used in conjunction with ferric chloride. Apparently, the higher positive charge of ferric hydroxide flocs accounted for the good flocculating action of Superfloc A-150 in the latter case.

7.4.2 Polyelectrolytes Used in Conjunction with Lime

Among the polyelectrolytes tested, Separan AP-273 was the most effective flocculant aid when used in conjunction with lime. The good flocculating action of this polymer is believed to have been associated with the role calcium ions in solution played on floc aggregation. Their participation in the mechanism is most probably similar to that suggested by Webb, (24) - see Appendix B.

7.5 ERROR ANALYSIS

This is presented in Appendix N.

7.6 FINAL CONCLUSIONS

The results of this thesis have demonstrated that chemical coagulation with hydrolyzing metal salts or lime is capable of substantially enhancing the treatment efficiencies of existing municipal sewage treatment facilities. This is done to a greater extent when chemical coagulation is aided by small amounts of synthetic organic polyelectrolytes.

The relatively good quality of the treated effluents suggests that they could be suitable for use for certain industrial applications - e.g. for once through cooling applications - without perhaps being necessary to apply a demineralization process for the removal of a large part of their dissolved solids fraction. If the latter becomes necessary, the organic load of the coagulated effluents is adequately low for such a process to be applied, presumably without any serious operational implications. (A small amount of coagulated MMP effluent has already been successfully treated through a reverse osmosis system by the author at UCT).

The most effective removals of the organic waste matter were always achieved with ferric chloride coagulation between pH 4 and 5. Aluminum sulphate was less effective within the optimum pH range between 5 and 5,5. Lime was approximately as effective as alum when added at excessive amounts such as to create a pH of at least 12.

The minimum remaining COD achieved with ferric chloride coagulation at the optimum pH was 28±5 mg/l for AMP effluent, 15±5 mg/l for MMP effluent, and 18±5 mg/l for MHT effluent when the raw effluent's COD levels were 140 mg/l, 51 mg/l and 133 mg/l, respectively.

The COD removal achieved after coagulation with any of the inorganic coagulants tested was invariably followed by colour and odour removals.

The removal of the organic waste matter with hydrolyzing metal coagulants was controlled by the following parameters, which are mentioned in descending order of significance:

(i) pH and the associated buffering effects of alkalinity

(Alkalinity becomes significant when pH is not controlled). The coagulation pH is a function of the initial pH, alkalinity, and the chemical character and concentration of the coagulant added. Both the nature of the metal hydrolysis species and the charge of the organic colloids are governed by pH.

(ii) Concentration of the soluble, colloidal and particulate organic waste matter initially present in the effluent,

(iii) Hydrolyzing metal ion concentration,

(iv) Chemical, physical and biological character of the organic waste matter,

(v) Concentration of the suspended and dissolved inorganic waste matter,

(vi) Chemical and physical character of the inorganic waste matter.

The potential of Al and Fe(III) coagulants in removing COD is primarily attributed to that specific chemical interactions take place between the metal ion hydrolysis species and the co-ordinative sites of the colloidal particles.

On lime coagulation the parameters which controlled the removal of the organic waste matter were:

(i) Initial pH and acidity
(ii) Concentration of organic waste matter
(iii) Initial concentration of magnesium ions
(iv) Concentration of calcium ions
(v) Final pH.

The potential of lime in removing COD is mainly attributed to the precipitation of magnesium hydroxide and its subsequent adsorption onto the surface of the colloids. When the precipitation of magnesium hydroxide is complete (pH about 12), the calcium ions are considered responsible for any further COD removal.

The synthetic cationic polyelectrolytes were only slightly effective in removing the organic waste matter from the effluents when applied alone. The synthetic non-ionic and anionic polyelectrolytes were totally ineffective. These were, however, very effective, even at a very small concentration, when used as flocculant aids in conjunction with hydrolyzing metal coagulants. The cationic polyelectrolytes were effective to a lesser extent when used as flocculant aids in conjunction with hydrolyzing metal coagulants besides the fact that much higher dosages were required. The anionic polyelectrolytes were the most effective polyelectrolytes when used as flocculant aids in conjunction with lime.

The natural turbidity of the effluents was completely removed with all the inorganic coagulants. The cationic polyelectrolytes managed to partly remove this turbidity, while the nonionic and anionic polyelectrolytes had no effect.

A method was suggested by which the lowest achievable remaining COD after coagulation can be predicted by determining the initial colour concentration. This is described in Section 7.2.

The cost of the chemicals required for good COD removal was estimated to be at least equal to 5 cents per kilolitre for any coagulant and effluent (1975 prices).

7.7 SUGGESTIONS AND RECOMMENDATIONS

More work done on different sewage effluents could establish or disprove the findings of this work. It is suggested that pilot plant studies be carried out for the determination, study, and solution of the potential problems arising in the large scale operation. These are related to the efficient design of coagulation and flocculation reactors as well as to effective control of the coagulation and flocculation parameters (e.g. control of coagulant, polymer and electrolyte dosing, pH, coagulant and polymer distribution, mixing, floc formation and growth, floc settling) including automatic control for systems designed to operate on a continuous basis.

Taking into consideration the findings of this work as well as information collected from the literature cited, it is recommended that for optimum removal of the different fractions of the organic waste matter encountered in sewage effluents the pH to be maintained at the level or within the ranges reported in Table 7.1.

TABLE 7.1

Fraction of Organic Waste Matter	Coagulant	Recommended pH
Organic particulate matter	Al Salts	7
" " "	Fe(III) Salts	7 - 8
" " "	Lime	> 11
Colloidal and soluble organic matter	Al Salts	5 - 5,5
" " " " "	Fe(III) Salts	4 - 5
" " " " "	Lime	12
Colour	Al Salts	5 - 5,5
"	Fe(III) Salts	4 - 5
"	Lime	12

To remove all fractions of the organic waste matter with hydolyzing metal coagulants as well as to obtain a clear effluent, it is recommended to first adjust the pH prior to coagulant addition to such a level that after the coagulant addition the final pH achieved to be between 4 and 5 for ferric coagulation, and between 5 and 5,5 for aluminum coagulation; second, to add the appropriate amount of coagulant, to allow for a certain time period for the flocs to settle, and to subsequently separate the supernatant from the floc bed; and, third, to adjust the pH to 7 for aluminum coagulation, and between 7 and 8 for ferric coagulation in order to achieve minimum residual turbidity. The last step may be followed by a settling or a filtration step.

LITERATURE CITED

1. Fair, G.M., Geyer, J.C. and Okun, D.A., "Water and Wastewater Engineering", Vol. 1, John Wiley & Sons, New York, 1-2, (1966).

2. Cooper, P., "Physical and Chemical Methods of Sewage Treatment. Review of Present State of Technology", Water Pollution Control, 3 (74), 303, (1975).

3. Eckenfelder, W.W. and Cecil, L.K., "Application of New Concepts of Physical-Chemical Wastewater Treatment", in, "Progress in Water Technology", Vol. I, Pergamon Press, 1972, 91.

4. Daniels, S.L., "A Survey of the Flocculating Agents - Process Descriptions and Design Considerations", AIChE Symposium Series, 136 (70), 266 (1974).

5. La Mer, V.K., "Coagulation Versus the Flocculation of Colloidal Dispersions by High Polymers (Polyelectrolytes)", in "Principles and Applications of Water Chemistry", by Faust, S.D. and Hunter J.V., John Wiley & Sons, New York, (1967), 246.

6. La Mer, V.K., "Coagulation Symposium Introduction", J. of Colloid Science, 19, 291 (April 1964).

7. Coackley, P. and Wilson, F., "Flocculation with Special Reference to Water and Waste Water Engineering", Filtration and Separation 8 (1), 61 (Jan/Feb. 1971).

8. O'Melia, C.R., "Coagulation in Water and Wastewater Treatment", in, "Water Quality Improvement by Physical and Chemical Processes", by Gloyna, E.F. and Eckenfelder, W.W., Jr., University of Texas Press, Austin and London,(1970), 219.

9. EPA Report, "Coagulant Aids for Water Treatment", J. AWWA, 67 (8), 468 (1975).

10. Stumm, W. and Morgan, J.J., "Chemical Aspects of Coagulation", J. AWWA, 54, 971 (1962).

11. Packham, R.F., "The Theory of the Coagulation Process - A Survey of the Literature. 2. Coagulation as a Water Treatment Process", Water Treatment and Examination, 11, 106 (1962),

12. Packham, R.F., "The Coagulation Process - A Review of Some Recent Investigations", Soc. for Water Treatment and Examination, Proceedings, 12, 15 (1963).

13. Packham R.F., "The Coagulation Process. I. Effect of pH and the Nature of the Turbidity", J. of Applied Chemistry, 12, 556 (1962).

14. Packham, R.F., "The Coagulation Process. II. Effect of pH on the Precipitation of Aluminum Hydroxide", J. of Applied Chemistry, 12, 564 (1962).

15. Stumm, W. and O'Melia, C.R., "Stoichiometry of Coagulation", J. AWWA, 514 (May 1968).

16. La Mer, V.K. and Healey, T.W., "Adsorption-Flocculation Reactions of Macromolecules at the Solid-Liquid Interface", Reviews of Pure and Applied Chemistry, 13, 112 (Sept. 1963).

17. Narkis, N. *et al.*, "Ferric Chloride or Lime for Chemical Treatment", Water and Sewage Works, p. 43 (Jan. 1975).

18. Loewenthal, R.E. and Marais, G.v.R., "The Carbonic System in Water Treatment", Published by the Department of Civil Engineering, University of Cape Town (1973).

19. Folkman, V. and Wachs, A.M., "Removal of Algae from Stabilization Pond Effluents by Lime Treatment", Water Research, 7, 419 (1973).

20. Fair, G.M. and Gemmell, R.S., "A Mathematical Model of Coagulation", J. of Colloid Science, 19, 360 (1964).

21. Harris, S.H., Kaufman, W.J. and Krone, R.B., "Orthokinetic Flocculation in Water Purification", Proceedings of the American Society of Civil Engineers, J. of Sanitary Engineering Division, 92, No. SA6, 95 (1966).

22. Herbert, E. and Hudson, Jr., "Physical Aspects of Flocculation", J. AWWA, 885, (Jul. 1965).

23. Zhukova, L.A., Chikov, V.S. and Rachinskii, V.V., "Precipitation of Metal Hydroxides at Constant and High Ionic Strength of the Solution" (S-Kh. Akad. im. Timiryazeva, Moscow, USSR), Kolloid. Zh. 1973, 35(1), 158-160 (Russ.). Extract from Chemical Abstracts, 35651W, V.79, 1973.

24. Webb, L.J., "A Study of Conditioning Sewage Sludges with Lime", Water Pollution Control, 192 (1974).

25. Hall, S.E. and Packham, R.F., "Coagulation of Organic Colour with Hydrolyzing Coagulants", J. AWWA, 57, 1149 (1965).

26. Rickert, D.A. and Hunter, J.V., "Colloidal Matter in Wastewaters and Secondary Effluents", J. WPCF, 44, 134 (1972).

27. Rickert, D.A. and Hunter, J.V., "General Nature of Soluble and Particulate Organics in Sewage and Secondary Effluents", Water Research, 5, 421 (1971).

28. APHA, WPCF, AWWA, (1971), Standard Methods for the Examination of Water and Wastewater, 13th edition, New York.

29. Matijevic, E., "Charge Reversal of Lyophobic Colloids", in Principles and Applications of Water Chemistry", Faust, S.D. and Hunter, J.V., John Wiley & Sons, (1967), 328.

30. McLellon, W.M., Keinath, T.M. and Chao, C.J., "Coagulation of Colloidal-and Solution-Phase Impurities in Trickling-Filter Effluents", W.P.C.F. Journal, 44, 77 (1972).

31. Rebhun, M., Narkis, N., and Wachs, A.M., "Effect of Polyelectrolytes in Conjunction with Bentonitic Clay on Contaminants Removal from Secondary Effluents", Water Research, 3, 345 (1969).

32. Bunch, R.L., Barth, E.F. and Ettinger, M.B., "Organic Materials in Secondary Effluents", J. WPCF, 33, 122 (1961).

33. Murtaugh, J.J. and Bunch, R.L., "Acidic Components of Sewage Effluents and River Water", J. WPCF, 37, 410 (1965).

34. Painter, H.A., "Organic Compounds in Solution in Sewage Effluents", Chemistry and Industry, 17, 818 (1973).

35. Black, A.P., Singley, J.E., Whittle, G.P. and Maulding, J.S., "Stoichiometry of the Coagulation of Colour Causing Organic Compounds with Ferric Sulphate", J. AWWA, 1347 (Oct. 1963).

36. Shelton, S.P. and Drewry, W.A., "Tests of Coagulants for the Reduction of Viruses, Turbidity and Chemical Oxygen Demand", J.AWWA, 627 (Oct. 1973).

37. Thorsen, T. and Oen, R., "How to Measure Industrial Wastewater Flow", Chem. Engineering, 95,(Feb. 17, 1975).

38. Hanna, G.P. and Rubin, A.J., "Effect of Sulphate and Other Ions in Coagulation with Aluminum (III)", J. AWWA, 315 (1970).

39. "Coagulation and Color Problems", Research Committee on Coagulation and Research Committee on Colour Problems", Joint Report, J. AWWA, 311 (1970).

40. Black, A.P. and Vilaret, M.R., "Effect of Particle Size on Turbidity Removal", J. AWWA, 209 (1969).

41. Tenney, M.W., Echelberger, W.F., Jr., Schuessler, R.G., and Pavoni, J.L., "Algal Flocculation with Synthetic Organic Polyelectrolytes", Applied Microbiology, 18 (6), 965 (1969).

42. Echelgerger, W.F., Jr. and Tenney, M.W., "Wastewater Treatment for Complete Nutrient Removal", Water and Sewage Works, 116, 396 (1969).

43. Kane, J.C., La Mer, V.K. and Linford, H.B., "The Filtration of Silica Dispersions Flocculated by High Polymers", J. of Physical Chemistry, 1977 (Oct. 1963).

44. Michaels, A.S., "Aggregation of Suspensions by Polyelectrolytes", Ind. and Eng. Chemistry, 7 (46), 1485 (1954).

45. Edgerley et al, "The Application of Oxidizing Chemicals to Organic Compounds", in "Principles and Applications of Water Chemistry", Faust, S.D. and Hunter, J.V., John Wiley and Sons (1967), 405.

46. Rebhun, M. and Narkis, N., "Advanced Treatment of Effluents from Municipal Waste Water Treatment Plants for Re-Use", Extract from Abstracts in Proceedings of XXXVI Meeting of Israel Chemical Society, Israel, J. of Chemistry, 4, 99 (1966).

47. A.P.H.A., WPCF, AWWA (1965), Standards Methods for the Examination of Water and Wastewater, 12th Edition, New York.

48. Zuckerman, M. M., "Chemical Versus Biological Wastewater Treatment in the Production of High-Quality Re-Use Water", Thesis, New York University, Dissertation Abstracts, 30, B, 1729 (1969), Extract from Water Pollution Abstracts, 43, No. 1573 (1970).

49. Al-Layla, M.A. and Middlebrooks, E.J., "Effect of Temperature on Algal Removal from Wastewater Stabilization Ponds by Alum Coagulation", Water Research, 9, 873 (1975).

50. Rebhun, M. and Manka, "Classification of Organics in Secondary Effluents", J. Environ. Science and Technology, 5, 606 (1971), Extract from Water Pollution Abstracts, 44, No. 2089 (1971).

51. Murtaugh, J.J. and Bunch, R.L., "Sterols as a Measure of Fecal Pollution", J. WPCF, 39, 404 (1967).

52. Ghassemi, M. and Christman, R.F., "Properties of the Yellow Organic Acids in Natural Waters", Limnol. Oceanogr., 1968, 13, 583-597. Extract from Water Pollution Abstracts, Vol. 42, No. 1767 (1969).

53. Clark, J.W. and Viessman, W., Jr., "Water Supply and Pollution Control", International Textbook Co., (1965), 341.

54. Shindala, A. and Stewart, J.W., "Chemical Coagulation of Effluents from Municipal Waste Stabilization Ponds", Water and Sewage Works, 118, 100 (1971).

55. Van Vuuren, L.R.J. and Van Duuren, F.A., "Removal of Algae from Wastewater Maturation Pond Effluent", J. WPCF, 37, (9), 1256 (1965).

56. Middlebrooks et al, WPCF, 12 (46), 2678 (1974).

57. Balmér, P. and Frederiksen, O.F., "A Pilot-Plant Scale Evaluation of Potential Precipitants in the Secondary Precipitation Process", Water Research, 9, 721 (1975).

58. Ide, T., Matsumoto, N. and Arimitsu, H., "The Utilization of Municipal Wastewaters in Japan", Chem. Eng. Progress Symp. Series, 63 (78), 46 (1967).

59. Malhotra, S.K., Lee, G.F. and Rohlich, G.A., "Nutrient Removal from Secondary Effluent by Alum Flocculation and Lime Precipitation", J. Air and Water Pollution, 8, 487 (1964).

APPENDICES

APPENDIX A

Al AND Fe(III) COAGULATIONS - EXPERIMENTAL FINDINGS IN RELATION TO THE MECHANISMS OF DESTABILIZATION

Selected information concerning those experimental findings which are related to the coagulation and flocculation mechanisms was collected from the literature cited. This was transferred and discussed in the present Appendix as well as in Appendices B and C, in order to present a clear picture of the stage of development the theories of destabilization and particle aggregation have reached.

Packham, (13), (14), has conducted investigations on the precipitation of aluminum hydroxide following the addition of alum into artificially prepared solutions containing sodium bicarbonate, sodium hydroxide and sodium chloride with and without minerals in suspension. He found that the optimum pH for coagulation of dilute clay suspensions with alum ccrresponded to that in which aluminum hydroxide was most rapidly precipitated and coagulated in the absence of clay - pH 7. He showed that the alum dosage required to halve turbidity was minimum at pH 7 and independent of the nature of the suspended mineral matter and the presence of appreciable quantities of contaminating organic matter. In the discussion that takes place in the end of reference (12), Packham has stated that his work on the precipitation of aluminum hydroxide had suggested that the initial product of the reaction between aluminum sulphate and water containing alkalinity was invariably colloidal. The rate of coagulation of this colloidal product controlled the rate of coagulation as a whole, and was influenced by coagulant dosage and pH, amongst other variables. He confirmed that aluminum residuals in the zone of rapid coagulation were a function of pH only.

Hanna and Rubin, (38) studying the effect of anions upon coagulation with Al(III), have found that coagulation of Escherichia coli with alum was more effective in the presence of aluminum hydroxide precipitate floc. They proposed that enmeshment of the dispersed phase in precipitating gelatinous aluminum hydroxide occurred. They confirmed that soluble aluminum hydrolysis products play only a minor role in the "sweep floc" zone - see Figure A.1 - since their coagulating action is relatively slow.

Folkman and Wachs, (19), however, have reported that Ives has found that when Al or Fe(III) salts are used to coagulate algae, the basic mechanism consists of mutual attraction and charge neutralization of the negative charge of the algae by the positive charge of the hydroxide coagulant.

The results of alkalimetric titration experiments conducted with Al and Fe(III) salts by Stumm and Morgan, (10) have revealed that the aquo groups which are attached to the coagulant metal ions are displaced by anions in solution, which form complexes with the coagulant metal ions. When these complex forming co-ordinating anions are absent, hydroxyl ions will tend to satisfy the co-ordinative requirements of the metal ion. When they are present, they will compete with hydroxyl ions for the available sites, and they may completely or partly substitute the hydroxyl ions in the charge neutralization reactions of the metal cations, which lead to the formation of a basic metal precipitate. Consequently the co-ordinating anions may have a marked effect on the pH of optimum precipitation. If other co-ordinating anions - except OH^- - are present, less OH^- will have to enter into the lattice resulting in a lower pH for optimum coagulation in the absence of these anions. A definite dependence of the pH for optimal coagulation exists upon the anion present. This effect is clearly demonstrated in the presence of phosphate in solution, (10), (12).

This discussion indicates that specific chemical interactions can, under certain conditions, be responsible for the removal of certain substances such as phosphate, phenolate, and certain aliphatic and aromatic carboxylic acids, upon chemical coagulation initiated by hydrolyzing metal coagulants.

The incorporation, however, of co-ordinating anions into the basic precipitates might also significantly alter their solubility. This occurs when adequate amounts of strongly complex forming anions are present. In this case, soluble metal ion complexes are formed and, as a result, the optimum coagulant pH may be shifted to higher pH values. This occurs with oxalate and salicylate, (10).

The transport step of the coagulation process - flocculation - may also be affected by the presence of certain anions. This is due to the considerable influence which the inclusion of certain anions might have on the physical character of the floc. Stumm and Morgan, (10) state that it has been demonstrated that the presence of succinate, selenate, formate, oxalate, or benzoate leads to very dense floc precipitates which settle at high rates. They also state that "if the temperature, concentration, chemical composition and the manner of mixing are well defined and remain constant, the extent of coagulation will depend primarily upon the nature of the coagulant metal ion species present under these conditions."

According to Stumm and Morgan, (10) the stability of the hydrophilic colloids is highly affected by the valency of the polyvalent cations. Other factors, however, such as the nature of the colloids and the ions in solution are important. The stability of the hydrophilic colloids is strongly influenced by pH and the composition of the ionized groups. For a given metal ion concentration, the pH is the most important control parameter determining which particular polymeric species predominates, and also the charge and, consequently, the stability of the hydrophilic colloids.

Hanna and Rubin, (38) report that Miller has investigated the influence of sulphate, chloride, phosphate, and oxalate upon coagulation with aluminum salts. He has found that the pH of coagulation was dependent upon the anion present. Chloride at high concentrations shifted the pH of optimum coagulation slightly to the acid side. Sulphate widened the range of rapid coagulation towards the acid side, the widening effect becoming more pronounced with increasing concentration of sulphate ion. A somewhat different and even more pronounced effect was found with phosphate.

The effects of anions upon coagulation with aluminum salts have been reviewed by Hanna and Rubin (38), who have also conducted investigation on the coagulation of Escherichia coli with alum. They concluded that the mechanism of coagulation in this case was strongly affected by the type and concentration of anions present in solution.

Stumm and O'Melia, (15) state that under favourable solution conditions (pH, temperature, applied metal ion concentration, time of aging), the hydrolysis products of iron and aluminum salts are adsorbed more readily at particle water interfaces. According to them, the destabilization brought about by these hydrolysis products is greatly influenced by three parameters: coagulant dosage, pH, and colloid concentration. The effect of these parameters has been studied by these investigators for colloid-silica dispersions. At constant pH the relationship between Fe(III) dosage and colloid concentration of surface is represented schematically in Figure A.1, (15). This Figure shows that at low colloid concentrations coagulation is brought about by large amounts of hydroxide precipitate which induce a "sweep floc" phenomenon. The coagulant dosage

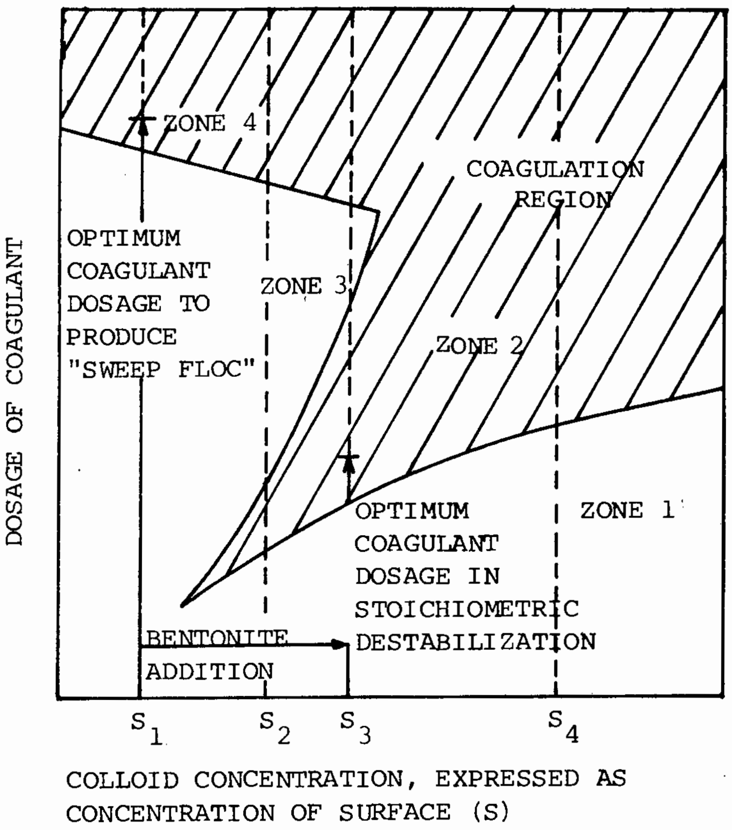


FIGURE A.1

required in systems containing low colloid concentrations can be decreased, if additional surface is provided (e.g. by means of bentonite addition). At larger concentrations of colloid particle surface (S_2 and S_3 in Figure A.1), a smaller coagulant dosage is required than that required to produce precipitation of the metal hydroxide. In that region the required coagulant dosage increases proportionately to the colloid concentration. This phenomenon is named by Stumm and O'Melia the "Stoichiometry of Coagulation", (15).

At very large colloid concentrations the required coagulant dosage may exceed the dosage required for the "sweep floc" coagulation, (8).

In general, if adsorption of hydroxometal species onto the colloid surface influences destabilization, the surface concentration of the solid phase must influence coagulation and restabilization. Restabilization, however, can be retarded or eliminated in solutions which are highly oversaturated with respect to the metal hydroxide, (15). With an increase in pH the OH^- ions bound per Fe^{3+} ion increase and, thus, the net positive charge of the hydrolysis species decreases. In this case, restabilization is more unlikely to occur. In addition, the increased rate of ferric hydroxide precipitation may compete successfully with the adsorption of incipiently formed soluble iron (III) species. Under these circumstances restabilization does not occur and Zone 3, Figure A.1, disappears.

In all of the experiments conducted by Stumm and O'Melia the "stoichiometric" coagulation region - Zone 2 in Figure A.1 - appeared in systems which were oversaturated with respect to ferric hydroxide. Oversaturation of the solutions does not necessarily imply that precipitation of the metal hydroxide occurs rapidly. Some degree of supersaturation must be exceeded before rapid precipitation occurs. As it is shown in Zone 4 - Figure A.1 -,when this degree of supersaturation is exceeded, amorphous precipitates are formed, which are capable of enmeshing colloidal particles, (15). The subsequent settling of this precipitate removes these colloidal particles from the suspension. The critical supersaturation necessary for rapid precipitation could,in fact,decrease with increasing surface concentration, because the colloidal particles can provide interfaces for localized oversaturation.

Stumm and O'Melia, (15) have given an alternative explanation for the existence of Zone 4 - Figure A.1. They consider mutual coagulation of negatively charged colloids with small particles of amorphous precipitates. This explanation presupposes that at low colloid concentrations an insufficient number of particles is present to provide the necessary contact opportunities in a reasonable time. The formation of additional particles by metal hydroxide precipitation can therefore shorten the time required for efficient aggregation. This explanation implies that coagulant dosage will decrease with increasing particle number in the raw water.

These investigators have also emphasized that in actual water-treatment practice both the pH and alkalinity of the water are decreased by the addition of metal ion coagulants. In such a case the addition of a hydrolyzing metal coagulant to water is equivalent to an acidimetric titration of the water, (15).

Finally, they concluded from relevant tests that for dispersions containing large concentration of surface,removal of alkalinity can produce a significant reduction in the requisite coagulant dosage to bring about coagulation. For waters containing lower concentrations of surface, a low alkalinity can produce a narrow or perhaps a non-existent stoichiometric region. In such a case, coagulation is brought about by a "sweep floc" only. For such systems the addition of alkalinity may permit stoichiometric destabilization, or, at least, may lower the coagulant dosage required to produce sweep coagulation, (15).

This adsorption model provides an explanation why the removal of alkalinity can enhance coagulation in sludge conditioning and, also, why the addition of alkalinity can improve coagulation in water purification.

McLellon *et al.*, (30) experimenting on pollutants removal from sewage effluents with hydrolyzing metal ions have claimed that pH and the associated buffering effects of alkalinity primarily controlled the destabilization reactions in these effluents. Stoichiometric considerations, as those observed and defined by Stumm and O'Melia, (15), were found to be of minor importance. McLellon et al have supported the mechanism of specific chemical interactions as being responsible for the removal of the organic waste matter from sewage effluents. These interactions occurred between the hydroxy-metallic polymers and ionogenic groups of the hydrophilic colloids in the effluent, as well as between these polymers and organic anions in solution. Agglomeration of the destabilized particles, then, occurred by subsequent chemical bridging.

These investigators confirmed Stumm and Morgan's conclusion experimentally, that most rapid precipitation of ferric hydroxide occurs at the isoelectric point of the floc matrix, which was found to be at about pH 5 by Stumm and Morgan. However, although McLellon et al did observe most rapid precipitation to occur at pH 5, they did not take into consideration the fact that their result was the result of experiments on wastewater and not on distilled water, as was the case of Stumm and Morgan's experiments. Experimentation with wastewater may result in a marked shift of the optimum pH of precipitation of the metal hydroxide towards acidic pH values as well as in a change of the solubility characteristics of the floc, according to Stumm and Morgan's findings, (10).

Hall and Packham, (25) have conducted extensive research on the coagulation of organic colour from water with hydrolyzing metal coagulants. They found that, in contrast to clay turbidity removal, the minima within which coagulant efficiency is optimum - when it is expressed in terms of amount removed per unit concentration -, narrow and shift to more acidic pH values as the concentration of humic substance is increased. The coagulant dose was also found to be approximately proportional to the concentration of humic or fulvic acid, except at low pH values. They found that the minimum residual concentration of humic material increased with the original concentration and was significantly greater for fulvic than for humic acids. With humic acids minimum residual concentrations were achieved by coagulating in the pH range 5 to 7. With fulvic acids the pH range narrowed as the original fulvic acid concentration increased. In their experiments the results obtained with ferric chloride coagulant were similar to those obtained with aluminum sulphate. In general, ferric chloride gave lower residual colour concentrations with humic acid, but lower pH values were required to achieve this. This showed that the minimum dosages of the two coagulants were of similar order, when expressed as equivalent concentrations, and they expressed the opinion that there is no essential difference in the mechanisms of colour removal, if this is brought about by Al or Fe(III) coagulants.

They concluded that the organic colour and clay turbidity are removed by totally different mechanisms. The coagulation of clay suspensions with Al or Fe(III) coagulants has been shown to be primarily dependent on the rapid precipitation of aluminum or ferric hydroxide, (14). Based on the fact that the optimum pH for colour removal was significantly lower than that for the coagulation of clay, they suggested that chemisorption of colour on hydroxide floc is not a significant factor. Instead, they emphasized that the effect of increasing concentrations of humic substances on the optimum coagulation pH, was similar to that brought about by increasing concentrations of phosphate on the coagulation of clay dispersions.

Relating their own experimental results with theory, they postulated that, upon coagulation with aluminum salts, formation of basic salt occurs. These salts have an approximate empirical formula $Al(OH)_{2,5}X$ in which HX is some acidic function of the humic substance. From electrophoretic studies which they conducted, they concluded that, under given conditions, the maximum degree of colour removal will be determined by the solubility of aluminum hydroxide and by the degree of ionization of the carboxylic groups of the colour molecules. Thus, the optimum pH for colour coagulation represents a compromise between maximum dissociation of these groups and the formation of the aluminum species required for precipitation.

The views of Hall and Packham on the mechanism of water coagulation with aluminum sulphate were, first, that aluminum hydroxide, the main product at near neutral pH values, plays the main role in the coagulation of the dispersed minerals and plant detritus constituting turbidity in natural water. Aluminum hydroxide is most effective for this purpose under conditions leading to its most rapid precipitation. It acts by precipitating both in the bulk solution and on the mineral particles, so that they rapidly become enmeshed in a mass of flocculating aluminum hydroxide. Second, that a polynuclear complex ion (or ions) that is strongly adsorbed on mineral particles, aluminum hydroxide, and other aluminum precipitates, and whose formation is at a maximum at or near pH 5, aids the removal of the dispersed minerals from water by reducing their zeta potential. Third, that another ion (or ions) having approximately the same Al:OH ratio as the polynuclear complex (1:2.5), is able to react with the anions of the coloured humic and fulvic acids, forming insoluble basic aluminate humates or fulvates, which precipitate. The extent to which humic substances are removed in coagulation is determined by the availability of the appropriate basic aluminum ion and the extent and type of ionization on the humic acid molecule.

In a review of the mechanisms involved in the coagulation of colour from water with hydrolyzing metal coagulants, (38) it is mentioned that consideration of specific chemical interactions gives the most satisfactory explanation to the phenomena observed upon colour removal.

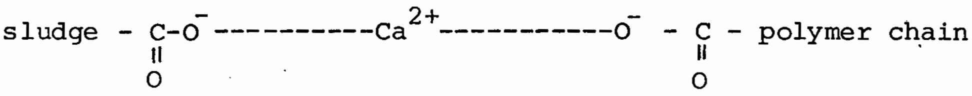
APPENDIX B

LIME COAGULATION - EXPERIMENTAL FINDINGS RELATED TO THE COAGULATION MECHANISMS

Folkman and Wachs, (19) report that when lime was added to algal suspensions made separately in $Mg(HCO_3)_2$ and $Ca(HCO_3)_2$ solutions, algal removal in the suspension containing Mg^{2+} was more effective than in the suspension containing Ca^{2+}. The cause could be related to the findings of Larson and Boswell. They found that magnesium hydroxide is positively charged, while calcium carbonate is negatively charged (even in the presence of calcium hydroxide). This could mean that magnesium hydroxide plays a definite role in the removal of algae via charge neutralization.

Zhukova *et al.*, (23) have found from studies on lime precipitation that calcium hydroxide precipitates at constant ionic strength equal to 0,5 M above pH 11,5. The minimum solubility of calcium hydroxide was $(1,8 \pm 0,2) \times 10^{-3}$ M, and maximum precipitation was obtained at pH above 13.

Webb, (24) investigating sewage sludge conditioning with lime and synthetic polyelectrolytes states that the high pH caused by the addition of lime increases the negative zeta potential of the particles and renders them more amenable to interaction with positively-charged species (including cationic polyelectrolytes which might be added) but, simultaneously, the cationic character of these species is reduced by the presence of increasing quantities of hydroxyl ions. Webb also reports that the anionic polymers used in conjunction with lime, should be fully ionized in alkaline solution and, consequently, could not be expected to be effective unless the calcium ion can act as a link between the negatively-charged polyelectrolytes, and the negatively-charged particle surface. He suggests that the calcium ion is linked via ionized carboxylic groups on both polymer and sludge surface, as shown below:



$$\text{sludge} - \underset{\substack{\| \\ O}}{C}\text{-}O^{-}\text{----------}Ca^{2+}\text{----------}O^{-} - \underset{\substack{\| \\ O}}{C} - \text{polymer chain}$$

APPENDIX C

ORGANIC POLYELECTROLYTES - EXPERIMENTAL FINDINGS RELATED TO THE MECHANISMS OF COAGULATION OR FLOCCULATION

Research of Black and Vilaret, (40) has revealed the effect of particle size on turbidity removal by organic polyelectrolytes. For their investigation they used artificially made latex suspensions of different particle size. They found that the optimum cationic polymer dosage is quantitatively related to the surface area of the colloidal dispersions. The surface area of the dispersion is, in turn, related to the size of particles. They also found that a mixture of dispersions of different particle size tends to widen the required dosage range for good turbidity removal. They then established the above findings with experiments on silica and clay suspensions.

Black and Vilaret concluded that the Kinetics of the destabilization process is definitely affected by the particle size, the smaller the particle size,the faster the destabilization.

When a non-ionic polymer was used in conjunction with a metal coagulant, a qualitative relationship was observed to exist between the particle size and polymer dosage for optimum destabilization. The smaller particles required higher polymer dosages. With only hydrolyzing metal coagulants, on the other hand, particle size was also found to have a qualitative effect on the required dosages to bring about coagulation.

Rebhun *et al.*, (31) have conducted research on the effect of polyelectrolytes in conjunction with bentonitic clay on contaminants removal from secondary effluents. When they added a cationic polyelectrolyte to an effluent they observed formation of additional turbidity. This increased turbidity appeared after addition of the polyelectrolyte at low dosages only. At adequately high polyelectrolyte dosages, however, flocs appeared which managed to remove the initially existing and the additionally created turbidity. After addition of the cationic polyelectrolyte, a small increase in colour was observed. A similar increase in the total COD was also observed after addition of low cationic polyelectrolyte amounts.

Adding bentonitic clay to the effluent prior to the cationic polyelectrolyte addition, however, improved the turbidity removal and no increase in colour at low polyelectrolyte dosages was observed.

Rebhun and co-workers explained the above phenomena in the following way:

"The addition of cationic polyelectrolytes, which are hydrophilic colloids and contain positive functional groups, results in a reaction of charge neutralization between these groups and the organic and inorganic anions in solution - e.g. phosphates. The reaction products are finely-dispersed colloidal particles which do not settle and which give an increased turbidity at low cationic polyelectrolyte dosage. The degree of dispersion of the reaction products depends on several factors such as their particle size and solvatation which, in turn, depends on the presence of non-ionic and ionic chemical groups which can aid dispersion. An excess of a hydrophilic colloid of one type may be adsorbed by the product of its reaction with a second colloid and, thus, stabilize the particle in the dispersion. This could happen in spite of the fact that the size of the resulting combined particle is larger than that of the suspended particles in the effluent before the reaction. In this way, settling of the reaction product can be hindered."

The notable effect of bentonitic clay in improving removal of the various components from the effluent was explained by these investigators by the fact that this hydrophilic colloid, having a large available surface area, adsorbs the products of the reaction between the cationic polyelectrolyte and anionic components of the effluent. The clay particles serve as nuclei for coagulation, resulting in formation of large rapidly settling flocs. Therefore, reaction products which were finely dispersed and could not be made to settle after flocculation, did indeed settle from the suspension in the presence of clay.

Tenney *et al.*, (41) have investigated algal coagulant with synthetic organic polyelectrolytes. They found that cationic polyelectrolytes (polyamines) were effective in algal removal. But, no algal coagulation was achieved with anionic (polystyrene), and non-ionic (polyacrylamide) polyeletrolytes. They also found that up to a cationic polyelectrolyte concentration of about 3 milligrams per litre, the polyelectrolyte was attached on the algal surface, while above this concentration, increasing amounts of it were observed in solution.

They concluded that the action of the cationic polyelectrolytes is best explained by the bridging model of destabilization - see section 2.2.2 - while the bonding of anionic and non-ionic polymers to the algal surface is controlled by chemical rather than electrostatic forces.

Tenney *et al.*, (41) have also studied the effects of pH, algal concentration, and algal growth phase on the requisite cationic polyelectrolyte dosage.

They state that the prevailing pH will influence the action of the polyelectrolyte - e.g. extent of coiling, degree of ionization, charge density - and the surface charge density of the colloid. They showed that within the pH range from 2 to 4, algal coagulation was effective when 10 mg/l of cationic polyamine was used.

They expressed the opinion that a definite stoichiometry exists between algal concentration and cationic polyelectrolyte dosage for optimal coagulation. Consequently, the extent of polymer coverage of the active sites on the algal cell surface is a factor that directly controls chemical coagulation in this case, provided algal cell bridging can occur. They found that optimal algal coagulation occurred at about 50 per cent algal cell surface coverage, with destabilization and restabilization reactions occurring at lower and higher surface coverage ratios, respectively.

Echelgerger and Tenney, (42) have employed the bridging model to explain the mechanism of coagulation of bacteria from a two-stage activated sludge process by cationic polyelectrolytes. They have also discussed the parameters which qualitatively influence the optimum polyelectrolyte dosage.

Coackley and Wilson, (7) in a review of the theories of coagulation, state that La Mer's bridging model of flocculation leads to a quantitative expression for the polymer dosage necessary to give the maximum filtrate rate. Under conditions which lead to bridge formation, La Mer has shown that a plot of refiltration rate versus polymer dosage gives rise to a maximum refiltration rate at a specific concentration of polymer. This maximum is considered to be caused by the floc achieving its maximum degree of flocculation. As the polymer dosage is increased above that corresponding to the maximum refiltration rate, the floc disperses, closer packing occurs, the extended segments physically interfere with bridge formation, and, at higher dosages, the polymer covers the particles and stabilizes them against bridging.

Among others, Kane *et al.*, (43) have confirmed the existence of a single optimum polymer concentration for maximum filtration rate. However, as Coackley and Wilson,(7) report, the correlation of the shape of the refiltration versus dosage curve with the theoretical predictions has been considered by Slater to be due more to the existence of uncertain factors in the theoretical equation than due to exact description of a real system by La Mer's model. According to Coackley and Wilson "Slater has also critically examined the concept inherent in the theory of La Mer, that the greatest degree of bridging occurs at the optimum polymer dosage. Experimenting with a fluospar suspension, he has shown that at low concentrations of a non-ionic polyacrylamide, the filter cake permeability increased with increasing filter cake thickness, supernatant clarity, initial settling rate and height of settled bed. The maximum refiltration rate, however, occurred after the maximum height of settled bed had been reached and considerably before the maximum settling rate and height of consolidated filter cake. Supernatant clarity showed a broad maximum which overlapped the maximum filtration rate. Slater has therefore suggested that the optimum permeability of a filter cake does not reflect a maximum degree of flocculation."

Coackley and Wilson,(7) state that in La Mer's theory as the number of segments available for adsorption increases, the dosage of polymer required to achieve the optimum filtration rate decreases. La Mer has shown that for molecular weights of $M = 10^6$ and $M = 5x10^6$, the optimum dosage (mole/g) decreases by almost two orders of magnitude. It is not always appreciated, however, that as the optimum dosage decreases, the optimum filtration rate also decreases. This has been shown by La Mer to be very significant. Consequently, according to the above discussion, a small dosage of a high molecular weight polymer, is not really interchangeable with a high dosage of a low molecular weight of another polymer of the same ionic character and chemical nature.

Michaels, (44) has studied the aggregation of mineral suspensions by organic polyelectrolytes. He observed the following:

(i) Under given conditions the aggregating capacity of polymers of acrylamide is higher, the higher the molecular weight,

(ii) This aggregating capacity reaches a maximum at a degree of hydrolysis of about 28 to 35 per cent,

(iii) At low polymer concentrations a minimum appears in aggregating ability at a low degree of hydrolysis, and

(iv) The ionic groups in the polymer play an important role in the coagulating or flocculating processes.

Michaels has explained the coagulating and flocculating action of the cationic, non-ionic and anionic polymers of acrylamide, (44).

On the basis of the bridging model and appropriate experimental evidence O'Melia, (8) has made the following statements:

(i) Efficient destabilization is often achieved with polymers having a charge similar to that of the colloidal particle.

(ii) Optimum destabilization occurs when only a fraction of the available adsorption sites on the surface of the colloidal particles are covered.

(iii) Dosages of polymer which are sufficiently large to saturate the colloidal surfaces produce a restabilized colloid, since no sites are available for the formation of polymer bridges.

(iv) Under certain conditions a system which has been destabilized and aggregated can be restabilized with extended agitation, due to the breaking of polymer surface bonds and the folding back of the extended segments on the surface of the particles.

(v) Of principle importance, a direct relationship exists between the available surface area in the colloidal system and the quantity of polymer required to produce optimum destabilization.

APPENDIX D

NATURE OF THE ORGANIC IMPURITIES IN SEWAGE EFFLUENTS

D.1 NATURE OF THE SUSPENDED AND DISSOLVED ORGANIC IMPURITIES (EXCEPT COLOUR) IN SEWAGE EFFLUENTS

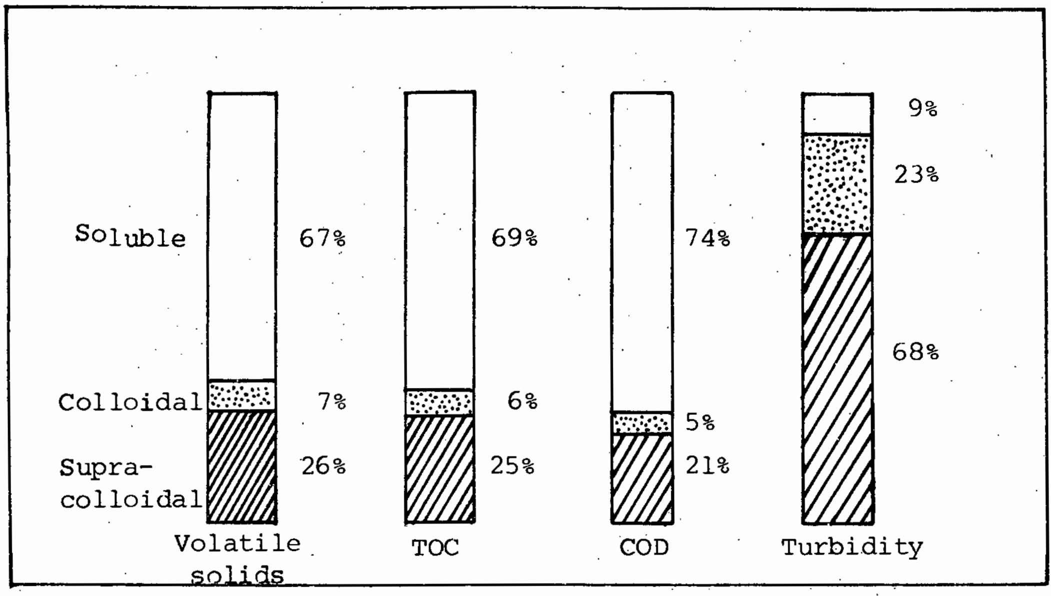
The nature of the organic matter found in secondary sewage effluents is not completely different from that in natural waters. Edgerley *et al.*, (45) have discussed the origin of organic matter in surface waters. The amount of organic matter in these waters is relatively small. The sewage effluents, however, due to their higher degree of pollution and contamination, contain a wider variety of organic substances, a lot of which exist in appreciable concentrations.

As it will become clear later in this Section, the nature of the suspended matter in sewage effluents is mainly organic, while the nature of the dissolved matter is mainly organic. The dissolved organic fraction, however, is relatively larger than the corresponding fraction in an equal volume of natural surface water.

The organic constituents of a sewage effluent that has received biological treatment exist either in a soluble or in a suspended (settleable or non-settleable) form. The particle-size boundary that defines whether the scattered matter is in soluble or in suspended non-settleable forms has not been clearly set out and, usually, different authors establish it in a different way. This is due to the fact that it is a rather arbitrary task to set a boundary limit of particle size between the above two forms, since, in fact, there is not any such particle-size limit below which the particles to fall into the sphere of soluble substances. The solubility of a substance does not only depend on its size. Steric effects and chemical factors are important, too. Therefore, a short survey on how different authors have defined both soluble and suspended matter has been considered necessary to be included here. This is done in Section D.3 of the present Appendix.

Rickert and Hunter, (26), (27) have investigated the percentage distribution of fractions in a secondary effluent which had received activated sludge treatment, to the volatile solids, TOC, COD and turbidity. Their results are shown in Figure D.1, (27).

The colloidal fraction accounted for a very small portion of the total organic content. The COD attributable to the soluble matter was 74% of the total COD. Of a total of 7,7 JTU (Jackson Turbidity Units) turbidity content, 5,9 JTU was due to supracolloidal matter, 2 JTU to



Percentage contribution of secondary effluent fractions to the volatile solids, TOC, COD, and turbidity.

Figure D.1

colloidal matter and 0,8 JTU to soluble matter.

The above investigators concluded that the solid particles contained in the secondary effluent were highly organic in character. But, since the soluble solids constituted the largest portion of the total solids, the soluble fractions contained the bulk of the organic matter in the effluent. The soluble solids themselves were, however, predominantly inorganic in character.

The inorganic content of the effluent constituted mostly of soluble matter (97 per cent, the supracolloidal and colloidal fractions accounting for the rest).

The colloidal matter in the effluent was found to consist of mainly bacterial cell walls and cellular debris, according to electron micrograph studies. The remainder included viruses, phages and detached flagellae. Rickert and Hunter suggested that the colloidal matter in sewage effluents is mostly formed during biological treatment in the treatment plants.

McLellon *et al.*, (30) have mentioned that according to the results of an investigation undertaken by Pipes (1970), most organics discharged from conventional wastewater treatment plants have been found to be present in the particulate and not in the soluble form. This conclusion, however, contradicts that drawn by Rickert and Hunter, (27).

McLellon et al, (30) as a result of their own investigations on sewage effluents, have suggested that all the organic waste matter removed by coagulation had been present as colloidal particulate matter in the wastewaters.

Rebhum and Narkis, (46) have stated that the effluents from municipal sewage treatment plants contain residues of organic matter in dissolved and colloidal forms, phosphates, detergents, and other undegradable components.

Shindala and Stewart, (43) as a result of experiments conducted on filtered and unfiltered samples collected from stabilization ponds, have concluded that, on average, more than 50 per cent of the COD content of pond effluents was due to algal populations.

Rebhun et al, (31) have reported that secondary effluents contain many organic constituents most of which are anionic compounds. Some of these were found to be organic acids dissociated at a neutral or alkaline pH. They have stated that, in sewage effluents, carbohydrates, amino saccharides, amino acids and some polypeptide exist, and that the materials which are responsible for colour in sewage effluents, are part of the refractory organics group. According to these authors, the suspended solids in a sewage effluent are mainly organic in character with hydrophilic surface properties.

Bunch et al. (32) working with secondary trickling filter and activated sludge effluents, have found that the amount of suspended solids was fairly small, but this amount accounted for 20 to 30 per cent of the total COD. For their investigation they have defined the COD of the dissolved organic matter in sewage effluents to be the COD of the fraction that passes through a Whatman No. 5 filter paper. According to their results, most of the COD is due to the soluble organic fraction. This conclusion is in agreement with that of Rickert and Hunter's, [26] concerning the percentage of the total COD attributable to the soluble organic fraction. Filtration through an asbestos mat in a Gooch crucible was the method of separation of suspended solids in the investigation of Bunch and co-workers, (47). The diffusibility of the effluents was determined by dialysis through a cellulose membrane. The identified fractions of the effluents by Bunch *et al.*, are shown in Figure D.2, (32). The approximate composition of the soluble organics (observed after filtration through Whatman No. 5 filter paper) is shown in Figure D.3, (32). As can be seen from Figures D.2 and D.3, more than half of the ether extractable matter falls in the strong acid classification. It was found that most of the constituents contributing to soluble COD were dialyzable, and about 40 per cent of this material was of rather high M.W. (because it resisted dialysis through the semipermable cellulose mebrane).

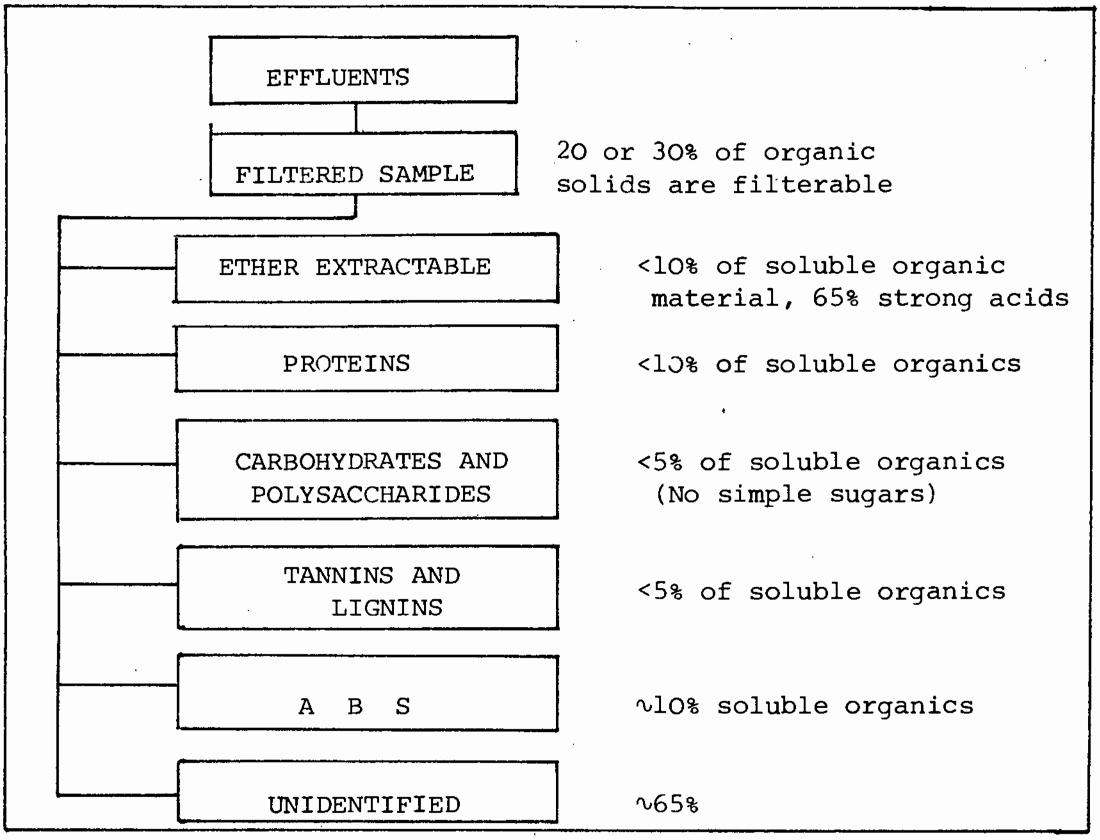


FIGURE D.2
Profiles of approximate behaviour and composition of secondary effluents.

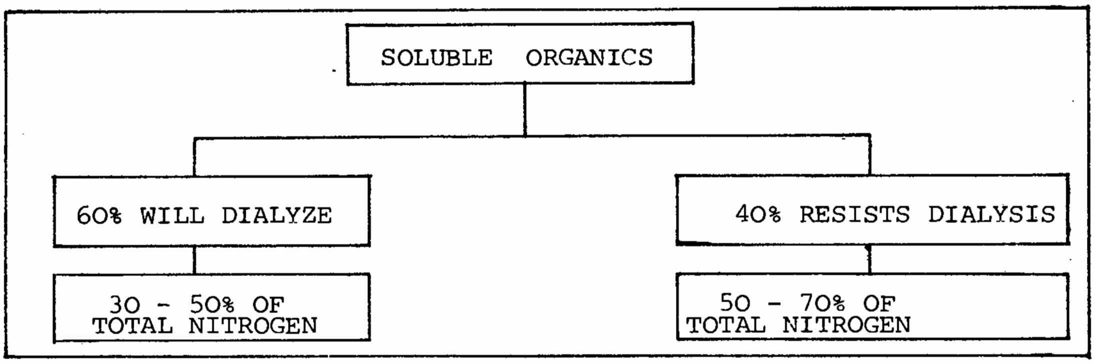


FIGURE D.3

Breakdown of soluble organics in secondary effluents.

Consequently, according to the above investigators, about 40 per cent of the soluble COD was due to organic material composed of large molecules like protein or other polymeric substances.

Murtaugh and Bunch, (33) investigating the acidic components of sewage effluences from trickling filter and activated sludge plants, have found that the percentage of COD corresponding to the soluble organic material extracted by ether (organic acids) averaged 46. The soluble fraction was obtained after centrifuging the raw sample in their case.

Zuckerman, (48) has reported that in effluents from biological treatment plants the soluble organics are of high M.W.

Al-Layla and Middlebrooks, (49) have found that samples from a wastewater stabilization pond contained essentially the same genera distribution of algae. Fifteen (15) per cent of the samples were found to contain debris - mainly dead algal and bacterial slime -,5 per cent were found to contain diatoms, and 80 per cent Chlamydomonas sp.

Painter, (34) has stated that the soluble organic matter in secondary sewage effluents is composed of soluble non-biodegradable and biodegradable organic matter. More specifically, he has considered the following groups of substances: (a) Easily biodegradable compounds such as sugars and amino acids, which are either products of the biological treatment or exist in the raw sewage itself escaping complete oxidation, (b) Biodegradable substances which completely escaped biodegradation for one reason or another through the plant, (c) Products of the microbial metabolism and microbial activity, (d) Compounds produced after the death and lysis of living cells, and (e) Non-biodegradable substances.

Painter discusses previous findings and shows that directly opposite conclusions have been drawn concerning the origin of the soluble organic matter in sewage effluents. The one conclusion has been that the soluble organic matter in sewage effluents comes from the sewage itself (it already exists in the raw sewage), and the other that the soluble organic matter is created during the biological treatment. He suggests that the true state lies somewhere in between these two extremes.

Painter has extensively studied the composition of the soluble organic fraction which he obtained after ultrafiltration of different secondary sewage effluents. He reports, (34) that more than half of the organic compounds were of high M.W. (greater than 10 000), since they did not diffuse through the dialysis membrane. A much larger portion of carbon has been accounted for in the dialyzable fraction (greater than 80 per cent) than in the non-dialyzable fraction (10 per cent). These results were compatible with those from earlier works, according to Painter, except with the results reported by Rebhun and Manka, (50) , who found that a much higher proportion of carbohydrate and protein was present in the meat manufacture effluent on which they experimented (Rebhun and Manka, (50) have also shown that 40-50 per cent of the soluble organic matter in sewage effluents were humic substances. The remaining fractions consisted of about 8 per cent organic acids, 14 per cent anionic detergents, 11 per cent carbohydrates, 22 per cent proteins,and 2 per cent tannins).

Painter, (34) states that the number of positively identifed soluble compounds in sewage effluents is small and is much smaller than that found in sewage. He states: "except in the special cases of detergents and pesticides, the present available evidence is not enought for a sufficient distinction to be drawn between organic matter of natural origin and that made by man."

Although a large part (greater than 80 per cent) of the smaller dialyzable fraction has been classified into general groups - see above -, only about 10 per cent of the large non-dialyzable has been so classified. Since the non-dialyzable fraction consists of substances of higher M.W., it should be expected to be more amenable to removal by coagulation.

The list in Figure D.4 deals with the soluble substances positively identified in well treated sewage effluents.

Compound		Concentration (μg/l)
Glucose		2-50
Fructose		
Sucrose		
Mannose		
Allulose		
Xylose		
Raffinose		
Formic acid		10
Acetic acid		20
Propionic acid		5
Butyric acid		10
Iso-butyric acid		10
Iso-valeric acid		50
Caproic acid		10
Uric acid		10
Pyrene	10 hydrocarbons in all	1 (total)
Perylene		
Benzpyrenes		
DDT		0,1 (each)
BHC		
Dieldrin		

FIGURE D.4

Substances positively identified in sewage effluents

Among the ten polycyclic aromatic hydrocarbons reported in Figure D.4, five were carcinogenic under the conditions of standards tests.

The pesticides DDT, BHC and dieldrin were each found at concentration of around 0,1 µg/l. The sterols, coprostanol and cholesterol, were found to be present at 100 and 50 µg/l, respectively, in trickling filter effluents, but only at concentrations 8 and 15 µg/l respectively, in activated-sludge effluents, (51).

The data reported in Figure D.4 concern good quality effluents, in the sense that they have received a quite extensive biological treatment. In bad quality effluents, the concentrations which have been reported were a lot higher. An example of this kind are the effluents on which Murtaugh and Bunch, (33) have conducted experiments.

Shelton and Drewry, (36) have reported that Kelly *et al.*, found Coxsackie virus in 47 per cent of the sewage systems they examined. They also found that standard sewage treatment plants do not destroy the virus. Hence, sewage is a definite mode of transport for enteric-virus populations.

D.2 NATURE OF COLOUR IN SEWAGE EFFLUENTS

Painter, (34) has suggested that a portion of the non-classified high M.W. fraction of the soluble matter in secondary effluents could be humic and fulvic acids.

Hall and Packham, (25) have stated that humic substances are rather formed in the soil by a polymerization of polyphenolic units derived from either bacterial synthesis or the breakdown of lignin residues. Their precise molecular constitution is not yet known. Alcoholic, phenolic, carboxyl, methoxyl and quinonoid groupings have been shown to exist in addition to variable proportions of nitrogenous compounds such as amino acids and poly-peptides.

In a review of the nature of colour in effluents, (39) it has been stated that most authors since 1917 have concluded that organic colour in water is colloidal. Packham and Shapiro, however, have suggested that it may be in true solution. Hall and Packham, (25) have stated that a proportion of the colour molecules are sufficiently large to exhibit colloidal properties.

Stumm and Morgan, (10) state that organic impurities of biological origin found in water or wastewater, such as colour, proteins and carbohydrates, may be present in true solutions as single molecules or reversible aggregates of them and, thus, do not necessarily possess a phase boundary. "Solutions of such molecules are frequently called macromolecular or hydrophilic sols, because the weights of such macromolecules often fall within the range of particle weights, which has been arbitrarily chosen as belonging to the special sphere of colloid science", (10).

Ghassemi and Christman, (52) applying gel chromatography techniques, have found that the apparent molecular weight of the colour-producing molecules in natural waters relative to dextrans was in the range 700 - 10 000, with the molecular weight of one fraction in excess of 50 000.

D.3 SURVEY ON DEFINITIONS OF SOLUBLE AND SUSPENDED MATTER

According to Clark and Viessman, (53) the particle size boundary that defines if the scattered matter is in soluble of suspended form is above 10^{-6} mm (1 mμ). The particle size boundary that defines if the suspended matter is in settleable or non-settleable forms is about 10^{-3} mm (1 μ). Not all particles of this approximate size form stable colloidal systems, since factors other than size must also be taken into account. Turbidity is produced by particle sizes of 10^{-4} mm (0,1 μ) and larger, whereas smaller particles (primary colloids) impart colour, tastes and odours. In summary, the particle size of the suspended particles falls into the range 10^{-7} to 0,1 mm, according to these authors.

Rickert and Hunter, (26), (27) have defined the ideal limits of the various fractions of the solids in secondary effluents as follows:

Fraction	Particle Size	
Settleable	> 100μ	(10^{-1} mm)
Supracolloidal	1-100μ	(10^{-3} - 10^{-1} mm)
Colloidal	1mμ-1μ	(10^{-6} - 10^{-3} mm)
Soluble	< 1 mμ	(10^{-6} mm)

The above authors have stated that, frequently, the "soluble matter" in wastewaters and sedondary effluents is defined as the matter that passes a membrane filter with 0,45 μ pores. The "soluble fraction" obtained by this method generally contains a considerable amount of colloidal-sized organic matter. The membrane filtration procedure is usually performed on the settled portions of a sample and, consequently, the material removed during filtration should roughly correspond to the material in the upper half of the colloidal size range fraction plus the entire supracolloidal fraction. According to Standard Methods, (47) this material could be defined as non-settleable suspended matter.

Rickert and Hunter themselves, however, have employed a different procedure for the separation of the above-mentioned four different fractions encountered in a sewage effluent. This consisted of the following three steps, (26), (27):

Step 1 : Sedimentation (Imhoff cone)
Step 2 : Supercentrifugation (4800 g)
Step 3 : Supercentrifugation (62500 g)

According to the above investigators, electron microscopy studies confirmed that Steps 1 and 2 attained the ideal boundary limits for the fractionation of secondary effluents. Electron microscopy studies also revealed that Step 3 approached but did not attain the ideal boundary limit between the colloidal and soluble fractions. It was found that Step 3 removed all particles above 0,2μ and that most of the remaining particles were smaller than 0,05μ in size. The authors concluded that the fraction in the supernatant obtained from Step 3, should be an excellent approximation to a true soluble fraction of a secondary effluent.

In Standard Methods, (28) the total suspended solids level is determined by filtering the wastewater through a GF/C filter disc in a Büchner funnel or Gooch crucible. The filtrate is supposed to contain only dissolved matter. A good example of the confusion that may arise when separation of colloidal substances is carried out, is the one associated with the colour measurement. According to Standard Methods, (28) the true colour of an effluent is considered to be the colour of the light transmitted by the waste solution after the suspended material has been removed, including the pseudo-colloidal particles. A micrometallic filter crucible of average pore size 40μ, and a calcined filter aid are suggested to be used for the removal of the suspended material. If what has been stated previously in this Section is taken into account, this filtrate should include a considerable amount of supracolloidal particles. Rebhun *et al.*, (31) have distinguished among "true turbidity", "true colour", and "apparent turbidity". The "true turbidity" is removed after centrifuging at 8000 rpm for 2 min. The colour of the centrifuged sample is the "true colour".

The above discussion indicates that confusion may arise when different authors define the suspended and soluble fractions of organic matter in a different way and draw conclusions about constituents of effluents that have been obtained by the application of different separation methods.

APPENDIX E

PREVIOUS RESEARCH ON THE REMOVAL OF ORGANIC WASTE MATTER FROM SECONDARY EFFLUENTS BY CHEMICAL COAGULATION

According to Shindala and Stewart, (54) among the conventional physical separation methods applied to separate suspended matter from water, chemical coagulation seemed to be the best for the removal of suspended matter from sewage effluents. The reason is that it has the potential to remove not only mineral suspensions, but also COD, BOD, nitrogen, phosphorus and algae. These investigators have investigated the extent of the potential of chemical coagulation to remove algae and to improve the quality of an effluent originated from a stabilization pond. They found that when the initial COD of the raw effluent was equal to 142 mg/l, the final COD attained after treatment was 20 mg/l (50 per cent of the times occurred). The effluent was treated with 175 mg/l alum. When the initial COD was 250 mg/l, the final COD was reduced to 30 mg/l (90 per cent of the times). They also found that when the effluent was treated with alum or ferric sulphate, the optimum pH for COD removal was 5,5, when alum was the coagulant, and 4,8 when ferric sulphate was the coagulant. Chemical coagulation under the above conditions resulted in a marked reduction of the coliform content. To estimate the algal contribution to COD, the above investigators conducted tests on filtered and unfiltered samples of stabilization pond effluents. Their results have indicated that, on average, algae contributed more than 50 per cent to the total COD.

Folkman and Wachs, (19) have investigated the removal of algae from stabilization pond effluents by lime treatment. They state that different investigators have performed tests on excess lime-soda softening at times, which have resulted in arrested activity to at least 99,95 per cent of the viruses. This virus content reduction occurred for different initial hardness levels. The precipitation of magnesium hydroxide had a specific effect. When only magnesium hydroxide was precipitated, 99,999 per cent of the viruses were removed at pH 10,5. When calcium carbonate was precipitated the viral removal was only partial.

Folkman and Wachs, (19) have confirmed earlier conclusions related to the mechanism of viable cell removal initiated by lime treatment. According to this mechanism the principal factor in the algae coagulation process are the positively-charged magnesium hydroxide particles.

The calcium and magnesium ions and the negatively charged calcium carbonate particles play only a minor role. This mechanism, therefore, functions via charge neutralization of the negatively charged algal cells by the positively charged magnesium hydroxide particles.

In the above process, pH plays an important role, because magnesium hydroxide starts precipitating at pH 10 and only at pH 11 have most of the magnesium ions in solution precipitated. The negative potential on the surface of the algal cells is also influenced by pH. It becomes highest at about pH 10 and only when pH approaches 11, the zeta potential decreases. Consequently, at pH 10 coagulation cannot occur, because magnesium hydroxide has not precipitated, and above pH 10 the zeta potential of the algal cells is too high to be neutralized by the magnesium hydroxide particles. Only at about pH 11, where the zeta potential has dropped, can good coagulation occur. Under these conditions, the higher the COD level of the substrate, the higher the required magnesium hydroxide precipitate. To obtain enough magnesium hydroxide precipitate adequate amounts of lime should be added to increase the pH to 11 (provided enough magnesium is present in the system).

Folkman and Wachs have also found that the required pH for algal charge neutralization by magnesium hydroxide depends upon the zeta potential of each type of algae. Good coagulation was attained in all cases at a pH around 11. A residual opacity was observed after the tests. This was attributed to the fine calcium carbonate suspension resulting after the lime treatment and, also, to the colloidal organic matter that was not removed by this treatment.

Van Vuuren and van Duuren, (55) have investigated the removal of algae from wastewater maturation pond effluents with chemical coagulation. They concluded that chemical coagulation yields an acceptably clear and colourless water. Polyelectrolytes, which were used in conjunction with lime or alum, were found to be ineffective. Al-Layla and Middlebrooks, (49) state that the effect of the polyelectrolytes in the above work of van Vuuren and van Duuren was probably masked by the high alum and lime doses used. Alum and excess lime, were both found to yield good results.

Al-Layla and Middlebrooks, (49) state that Golueke and Oswald have conducted a series of experiments to investigate the relation of pH to algal coagulation with cationic polyelectrolytes. They found that coagulation was most extensive at pH 3. They obtained algal removal ranging from 80 to 90 per cent. Algal removal efficiencies were not affected in the pH range between 6 and 10 by cationic polyelectrolytes.

The above investigators also state that the California Department of Water Resources reported (1971) that out of 60 polyelectrolytes tested, 17 compounds were effective in the coagulation of algae. Generally, less than 10 mg/l of the polyeletrolytes were required for effective coagulation.

Al-Layla and Middlebrooks, (49) studying the effect of temperature on algal removal from wastewater stabilization ponds by alum coagulation have concluded that the effect of temperature on the coagulation of algae is quite significant. The effects of paddle speed, alum dosage, flocculation time, and settling time on the algal removal are influenced by temperature variations. They have suggested that more alum should be added in warm seasons in relation to the amount required in cold seasons to obtain the same efficiency. Alum is more effective at low temperatures (10°C) at any dosage level. The removal of algae is favoured when floc sedimentation and stirring occur at low temperatures. They state that the influence of temperature on algal removal by coagulation was the most significant parameter, but they have not considered the effect of pH at all. The coagulation pH in all of their experiments varied between 7,75 and 6 (this variation in pH was not intentional, but simply accompanied the alum addition only.

Shelton and Drewry, (36) have reviewed past research on virus removal from wastewaters by chemical coagulation or precipitation. Among others, they have reported the following:

Thayer and Sproul have found that 99,999 per cent T2 virus inactivation occurred when magnesium hydroxide was the only precipitate formed upon water softening. Among the other precipitates, magnesium hydroxide was the most effective.

Inactivation and removal of viruses from water by coagulation with polyelectrolytes have been studied by Thorup et al. They found that cationic polyelectrolytes were more effective than anionic and nonionic ones in virus removal. The highest removal achieved was 94 per cent when polymers were applied. When the polymers were used in conjunction with ferric sulphate or alum, did not result in further decrease of the virus concentration from that achieved by the primary coagulants.

Berg *et al.*, of the Cincinnati Water Research Laboratory have found that lime coagulation of poliovirus I from secondary effluent yielded up to 99,86 per cent removal of virus.

Chaudhuri and Engelbrecht have been convinced that chemical coagulation techniques can accomplish bacterial virus removals as high as 99 per cent. They found that virus removal was proportional to turbidity removal. They also found that cationic polyelectrolytes used either as primary coagulants or as flocculant aids could greatly improve the process efficiency.

York has been involved in a study to determine the efficiency of a wide range of coagulants and coagulant aids in virus removal. He has found that alum and ferric chloride were the most effective primary coagulants among all those which had been tested. Cationic polyelectrolytes showed to be moderately effective as primary coagulants. On the whole, however, they were unsatisfactory because of their ineffectiveness in removing COD, colour, and turbidity. The efficiency of alum coagulation, on the other hand, was not significantly increased when polyelectrolytes of all the ionic characters were used in conjunction with alum as flocculant aids.

Shelton and Drewry, (36) have concluded the following as the result of their survey:

"(1) Virus (1 mμ approximate diameter) removal occurs through the phenomenon of cationic co-ordination with the carboxylic groups in the virus-coat protein, and the virus-cationic complex thus formed becomes linked to the floc and precipitates.

(2) Virus inactivation is not accomplished through the formation of the ionic complex, since infectious RNA remains viable in the floc.

(3) The effectiveness of polyelectrolytes as coagulants and coagulant aids varies with the virus type used and is virtually a virgin area of study with many virus types."

(4) "Non-ionic and anionic polyelectrolytes are not suitable for direct virus removal, since the virus-ion link is dependent upon positive molecular charge. However, some increased removals incidental to the electrokinetic properties of the polyelectrolytes may be possibly due to better floc formation or settling characteristics."

Shelton and Drewry, (55) have also conducted research into the effectiveness of different chemical coagulants and polyeletrolytes in virus removal from a secondary effluent and raw surface water, and on how well the effective coagulants and polyeletrolytes exhibit their action on polluted waters.

They found that alum was slightly more effective than ferric salts for virus removal.

A cationic polymer was used with unsatisfactory results when it was applied as primary coagulant. Its use resulted in poor floc formation and settling characteristics, while the virus removal was only moderate. Anionic and non-ionic polymers broadened the effective dosage range of inorganic primary coagulants for good virus, turbidity, and COD removals. These polymers improved the floc characteristics and, consequently, produced only incidental improvements on virus removal. When the non-ionic polymers were used as coagulant aids, usually gave moderately better results, which were attributable to their ability to form more dense and "sticky" flocs.

Echelgerger and Tenney, (42) investigating the coagulation of microbial populations of an effluent from a two-stage activated-sludge treatment plant have found that the microbial populations can be effectively removed by cationic polyelectrolytes. They commented that the bacterial coagulation is a result of formation of a three-dimensional matrix consisting of bacteria bridged together by polymer chains. The optimum polymer dosage is the one at which adequately strong matrices form which can withstand shear agitating forces, and which do not result in extensive coverage of the available bacterial surface sites to inhibit bridge formation. This dosage is influenced by pH, because it affects the charge of both the bacteria and the polyelectrolytes, the microbial concentration, bacterial growth phase, degree of agitation, temperature, method of polymer dosing, and ionic composition of wastewater.

Middlebrooks *et al.*, (56) have reported that McGarry has studied the coagulation of algae in stabilization pond effluents. He found that alum was effective for algae coagulation from high rate oxidation pond effluents. The time of polyelectrolyte addition had no significant effect when the polyelectrolyte was used in conjunction with alum.

Balmer and Frederiksen, (57) have done a pilot-plant scale evaluation of potential coagulants, applying chemical coagulation to presettled domestic wastewater. They used alum, ferric iron and lime as coagulants. With alum coagulation, the COD removal was around 70 per cent in the favourable pH range (below 6). With ferric iron coagulation the COD removal averaged 60 per cent, while with lime coagulation it averaged 55 per cent.

McLellon and co-workers, (30) state that coagulation with subsequent flocculation has been shown to be suitable for removal of particulate matter as well as solution-phase organic and inorganic impurities.

Investigating the coagulation of colloidal and solution-phase impurities existing in trickling filter effluents, they found that with ferric chloride coagulation, the best possible treatment resulted in remaining turbidity in the supernatant equal to about 5 JTU (measured after 30 minutes of settling). They found that residual turbidities were relatively independent of initial turbidity levels. The efficiency of treatment was,then,concluded to be greater for trickling filter effluents having higher turbidity.

The above investigators applied coagulation to effluents from secondary clarifiers (humus tanks) as well. Treatment with ferric chloride resulted in a final COD as low as 20 mg/l. In similar studies, residual COD levels have ranged from 10 to 25 mg/l. These results represented removal efficiencies of carbonaceous material that varied between 70 and 90 per cent. Based on the above data they concluded that the pollutional load of the organic waste material discharged to receiving bodies could be reduced by a factor of five by the application of chemical coagulation.

In the work of McLellon *et al.*, the optimum dosage of Fe^{3+} applied to remove turbidity (which was measured after 30 minutes of settling) corresponded precisely to the optimum dosage required for COD removal. This resulted in the optimum pHs for COD and turbidity removals to be identical when the pH was not controlled. However, this finding can be misleading, because, if the settling period was altered, the optimum pH for turbidity removal could also be altered.

Examination of the relative removals of turbidity and organic colour revealed that, while 80 per cent of the organic carbon was removed (as COD) by ferric chloride, only about 70 per cent of the turbidity was removed at the optimum coagulant dosage. Similarly, in other studies,COD removal varied from 70 to 90 per cent, while removal of turbidity varied between 50 and 80 per cent. The appearing difference in the relative removals indicated that some soluble organic substances were removed from the solution in excess of the colloidal matter to which the turbidity was attributed. This removal of soluble organic substances was due to the effect of specific chemical interactions, according to these authors.

McLellon *et al.* concluded that in all cases the pH and the associated buffering effets of akalinity mainly controlled the coagulation mechanism. Good removals of COD - between 70 and 90 per cent - were obtained with Fe^{3+} coagulant. Variations in waste strength and composition had no significant effect on the final quality.

The bacterial cells in the above effluents were destabilized and removed from the water simultaneously during the removal of other colloidal matter. About 99,9 per cent of the viable bacteria, which were present initially, were removed with ferric coagulant under optimum removal conditions (final pH 4,4).

Ide *et al.*,(58) have found that alum and ferric chloride were the most effective coagulants for the removal of turbidity and colour from municipal effluents. These two coagulants showed a similar effect. For COD or phosphate removals, however, ferric chloride was found to be more effective than alum.

Malhotra *et al.*,(59) investigating nutrients removal from secondary effluents with the aid of lime and alum have found that better COD removal was achieved with alum coagulation when the initial pH was adjusted at 6, than that achieved at the natural pH of the effluent (about 8). About 55 per cent of the COD was removed at pH 6, while about 25 per cent at pH 8, with an alum dosage of 250 mg/l applied in both cases. The addition of 300 mg/l bentonite as well as up to 25 mg/l Separan NP-10 (non-ionic polymer) did not markedly improve the removal efficiency (the alum dosage was 100 mg/l). The addition of Separan NP-10 increased the size and settleability of flocs, but also increased the COD and organic nitrogen concentration of the sample.

Rebhun and Narkis, (46) have investigated the efficiency of coagulation when initiated by alum and organic polyeletrolytes to remove pollutants from municipal sewage effluents. Reduction of 92 per cent of the effluent's turbidity, 68 per cent in COD, and a BOD of less than 1 mg/l were obtained. 96 per cent of the synthetic detergents were removed by cationic polyelectrolytes. Addition of bentonitic clay prior to the addition of coagulants, improved the efficiency of the process. Settling rates and relative removals were improved.

Rebhun *et al.*,(31) have investigated contaminants removal from secondary effluents with the use of polyeletrolytes in conjunction with bentonitic clay. They state that the use of coagulant aids such as anionic polymers by other investigators to improve the floc formed did not cause significant removals of soluble organic matter. Their research on effluents revealed that 50 mg/l of cationic polyeletrolyte (polyethyleneimine) or, alternatively, about 300 mg/l of alum were required for complete turbidity removal from secondary effluents. They observed a difference in floc magnitude in the two cases. The resulting flocs from the addition of the cationic polyelectrolyte were small and their settling velocities low. Those, however, resulting from the addition of alum were larger. They also observed that on addition of cationic polyelectrolyte to the effluent, additional turbidity appeared. This was rather due to a reaction occurring between the cationic polymer and various components of the solution. The additional turbidity appeared at low polymer dosages only. At increased polymer dosages, coagulation occurred during which both the initial and the additional turbidity were removed. When bentonitic clay was added to the effluent prior to the polymer addition, the removal of turbidity was improved. The resulting flocs were larger and their settling velocities were higher. The turbidity, however, did not increase in the presence of bentonitic clay at low cationic polyelectrolyte dosages. At such dosages a small increase in colour was also observed. In the presence of clay no increase of colour was observed at low polymer dosages. These observations were explained in the following way by the above investigators:

When the cationic polyeletrolyte was added, reactions took place between the polyeletrolyte and various components of the effluent. The products of these reactions were stable colloids which added to the existing turbidity. Some of them could be so finely dispersed that centrifugation - which the investigators applied to remove turbidity in order to be able to measure the true colour - could not cause their separation.

The effect of bentonitic clay was attributed to that the particles of this hydrophobic colloid adsorbed the products of the above-mentioned reactions, due to their large surface area, and served as nuclei for coagulation. Thus, formation of large rapidly settling flocs occurred. It seemed that the main task of bentonite was to aid the settling of the suspended particles.

On the contrary, treatment of the effluent with the cationic polyeletrolyte, without the addition of clay, did not result in COD removal for dosages up to 20 mg/l. As a result, an increase in total COD appeared at low polyelectrolyte dosages (the polyelecyrolyte came into solution, while settling did not occur). At higher dosages, however, coagulation occurred and the total COD was decreased by about 40 per cent. The cationic polyelectrolyte resulted in higher soluble COD removal at increasingly higher dosages, which indicated that it reacted with soluble organic matter. The resulting reaction products were insoluble and could be removed by centrifugation.

The presence of bentonite clearly improved the COD removal, which was as high as 90 per cent after the addition of the cationic polyelectrolyte.

Where clay was only added, the extent of adsorption of organic substances onto the surface of the bentonitic clay particles was such as to result in 36 per cent removal of the total COD (measured after initial settling of the raw effluent). (The 36 per cent figure would correspond to 74 per cent total COD removal, if settling were not allowed to occur and the effluent were treated as soon as it was sampled). This resulted in 50 per cent removal of the soluble COD measured after centrifuging the sample.

A non-ionic polymer of acrylamide, which was tested, was not effective in removing the organic substances present in the effluent.

Lime treatment showed that colour, suspended solids, and coliform bacteria could be efficiently removed.

The above discussion implies that mineral suspensions need very small dosages of cationic polyelectrolytes for efficient removal. The high dosages required in the above case revealed a high demand for the polyeletrolyte, which was attributed to the existence of the soluble organic components. This conclusion has also been verified in another study on coagulation of clay dispersions in the presence and absence of humic and fulvic acids (Narkis *et al.*, 1968), as Rebhun *et al.*, (31) report.

APPENDIX F

MILNERTON MATURATION POND EFFLUENT - PRELIMINARY TESTS

I. INORGANIC COAGULANTS

I.1 Alum Tests

Test 1

	Turbidity		pH	COD*			
Initial values :	1,5		7,2	54			
$Al_2(SO_4)_3$ dosage :	0	20	40	100	200	400	1000
F. pH :	7,2	7,18	7,03	6,7	4,9	4,47	4,19
F.T. (60 min.) :	1,2	0,83	1,2	1,45	4,85	5,05	31,5
% Turbidity Removal :	20	44,7	20	3	-223	-236	-2000
F. COD* :	53	52	47	40	36	27	36
% COD Removal :	2	3,7	13	26	33	50	33

The final turbidity results are shown graphically in Figure 4.2.

Note: When the COD values are accompanied by one asterisk, they have been determined by means of the autoanalyzer. These are approximate values, because they have been approximately corrected by subtracting 40 mg/l from the values given by the autoanalyzer - this was the increase in reading due to Cl^- interference - see also Section 3.6-(1).

The addition of chemicals occurred according to the sequence in which they are reported. The final pH is denoted as F.pH while the final turbidity as F.T. and the final COD as F.COD. The settling period applied in each test is reported together with the final turbidity in parentheses.

Test 2

	Turbidity		pH	COD		
Initial values :	1,5		7,2	45		
ml 1 N H_2SO_4 :	1,85	1,7	1,5	1,2	0,6	-
$Al_2(SO_4)_3$ dosage :	100	100	100	100	100	100
F. pH :	4,54	4,82	5,27	5,71	6,18	6,6
FT (120 min.) :	0,68	0,59	0,31	0,2	0,2	0,14
% Turbidity removal :	54	61	79	86	86	91
F. COD :	30	26	30	30	34	32
% COD Removal :	33	42	33	33	24	28

The above test results are shown graphically in Figure 4.3.

Test 3

	Turbidity		pH			
Initial Values :	2,5		7,5			
ml 1 N H_2SO_4 :	2,6	1,95	1,75	1,55	1,25	0,6
$Al_2(SO_4)_3$ dosage :	100	100	100	100	100	100
F. pH :	3,95	4,87	5,19	5,56	5,87	6,24
FT (40 min.) :	5,9	3	2,6	2,3	2,15	1,95

The above test results are shown graphically in Figure 4.4.

I.1.1 Alum with bentonite

Test 1

	Turbidity		pH	COD*		
Initial values :	1		7,8	43		
Bentonite dosage :	10	10	10	100	100	100
$Al_2(SO_4)_3$ dosage :	20	50	200	20	50	200
F. pH :	7,75	7,51	6,5	7,15	7,1	5,85
FT (30 min.) :	1	1,95	7,2	1,55	1,75	7,25
F.COD* :	40	35	22	35	35	23

I.2 Effect of NaOH when added alone or after the addition of bentonite

Test 1

	Turbidity	pH	COD*	Ca^{2+}	Mg^{2+}
Initial Values :	1,6	8,4	56	55	60
Bentonite dosage :	100	200			
ml 1 N NaOH :	12,2	12,2			
F. pH :	12	12			
FT (30 min.) :	0,48	0,05			
F.COD* :	33	32			
F. Ca^{2+} :	0	0			
F. Mg^{2+} :	0	0			

Test 2

	Turbidity	pH	COD*
Initial values :	1,8	8,3	61
ml 1 N NaOH :	12		
F. pH :	12		
FT (10 min.) :	0,78		
F. COD* :	37		
Remaining colour concentration :	High		

I.3 Ferric chloride tests

Test 1

	Turbidity	pH	COD
Initial values :	1,6	8,1	54

$FeCl_3$ dosage :	0	20	40	100	200	300	400
F. pH :	8,1	7,1	6,83	6,16	3,3	2,7	2,5
FT (60 min.) :	0,8	0,39	0,31	0,43	2,35	34	45
% Turbidity removal :	50	75	80	73	-47	-2025	-2712
F. COD :	52	46	44	35	23	28	30
% COD removal :	4	14	18	35	57	48	44

The final turbidity results are shown graphically in Figure 4.5, and the final turbidity results together with the final COD results in Figure 4.6.

Test 2

	Turbidity	pH	COD*
Initial values :	0,88	7,1	62

$FeCl_3$ dosage :	20	40	100	200	400
F. pH :	7,1	6,95	6,45	3,8	2,77
FT (40 min.) :	1,45	1,05	1,2	2,55	58
% Turbidity removal :	-65	-19	-36	-168	-6490
F. COD* :	39	39	29	24	25
% COD removal :	37	37	53	61	59

The final turbidity results are shown graphically in Figure 4.7.

I.4 Lime tests

Test 1

	Turbidity	pH	COD*	Ca^{2+}	Mg^{2+}
Initial values :	1	7,55	40	60	56

$Ca(OH)_2$ dosage :	60	100	150	300	450	600	800	1000
F.pH :	9,25	9,95	10,49	11,17	11,35	11,74	12,1	12,27
FT (60 min.) :	0,6	0,4	0,26	0,36	0,75	0,8	0,15	0,13
F. COD* :	40	35	30	25	20	18	18	18
F. Mg^{2+} :	55	53	49	21	3	0,5	0	0
F. Ca^{2+} :	63	73	68	85	110	160	230	265
F.[Ca^{2+}+Mg^{2+}] as ppm $CaCO_3$:	385	400	370	300	285	400	575	662

I.5 Comparison of effects of lime, alum and bentonite

Test 1

	Turbidity	pH	COD*	Ca^{2+}	Mg^{2+}	Na^{+}
Initial values :	1,6	8,5	48	68	60	300
Bentonite dosage :	-	100	-	200		
$Al_2(SO_4)_3$ dosage :	-	-	200	-		
ml 1 N NaOH :	-	-	-	12,2		
$Ca(OH)_2$ dosage :	600	600	-	-		
F. pH :	11,95	12	4,95	12		
FT (60 min.) :	0,6	0,23	3,05	0,27		
F. COD* :	25	20	25	34		
F. Ca^{2+} :	150	150	68	0		
F. Mg^{2+} :	0	0	60	0		
F. Na^{+} :	290	280	295	520		

II ORGANIC POLYELECTROLYTES

II.1 Polyelectrolytes used alone

Test 1

	Turbidity	pH	COD*				
Initial Values :	0,63	7,6	46				
Polymer added :	444-K	C-110	MG-200	N-100	A-150	AP-273	C-521
Dosage (up to..) :	20	20	20	20	20	20	20
Flocs Appeared :	Yes	No	No	No	No	No	Yes
Flocs Settled :	No	-	-	-	-	-	No
Appearance of supernatant :	Turbid	Clear	Clear	Clear	Clear	Clear	Turbid
$Al_2(SO_4)_3$ dosage :	40	40	40	40	40	40	20
Flocs Appeared :	Yes	No	No	No	Yes	No	Yes
Flocs Settled :	Partially	-	-	-	Yes	-	Yes
F.COD*	34	56	62	60	42	42	37

Test 2

	Turbidity	pH	COD*
Initial values :	0,63	7,6	46

Polymer added :	444-K	C-110	MG-200	N-100	A-150	AP-273
Polymer dosage :	10	10	10	10	10	10
Flocs appeared :	Yes	No	No	No	No	No
Flocs settled :	No	-	-	-	-	-
Bentonite dosage :	100	50	50	100	100	100
Flocs appeared :	Yes	Yes	Yes	Yes	Yes	Yes
Flocs settled :	No	Yes	Yes	Yes	Partially	Partially
F. COD* :	-	42	45	42	51	50

Test 3

	Turbidity	pH	COD*
Initial values :	0,63	7,6	46

Bentonite dosage :	50	50	50	50	50
Polymer added :	444-K	MG-200	N-100	A-150	AP-273
Polymer dosage :	5	5	5	5	5
Flocs appeared :	Yes	Yes	Yes	Yes	Yes
Flocs settled (60 min.) :	No	Yes	Yes	No	No
F. COD* :	42	44	42	45	42

II.2 Alum with organic polyelectrolytes

Test 1

	Turbidity	pH	COD*
Initial values :	0,93	8,05	46
$Al_2(SO_4)_3$ dosage :	50	100	200
Polymer added :	AP-273	AP-273	N-100
Polymer dosage :	1	1	1
F. pH :	6,5	6,55	6,05
F. COD* :	36	32	25
Flocs settled :	Yes	Yes	Yes
Supernatant's appearance :	Clear	Clear	Clear

Test 2

	Turbidity	pH	COD*
Initial values :	0,63	7,6	46
$Al_2(SO_4)_3$ dosage :	100	100	200
Polymer added :	A-150	AP-273	Ap-273
Polymer dosage :	2	1	5
F. pH :	6,65	6,65	4,8
Flocs appeared :	Yes	Yes	Yes
Flocs settled :	Yes	Yes	Partially
Appearance of supernatant :	Clear	Clear	Turbid
F. COD* :	32	32	-

Test 3

	Turbidity	pH	COD*	
Initial values :	1,2	8	50	
$Al_2(SO_4)_3$ dosage :	200	100	100	200
Polymer added :	-	C-521	AP-273	N-100
Polymer dosage :	-	20	1	1
Flocs settled :	Yes	Yes	Yes	Yes
F. pH :	5,75		6,35	5,65
FT (60 min.) :	3,25		0,72	1,55
F. COD* :	30	27	30	25

Test 4

	Turbidity	pH	COD*
Initial values :	1,5	8	57
$Al_2(SO_4)_3$ dosage :	200	300	400
Polymer added :	N-100	N-100	N-100
Polymer dosage :	1	1	1
F.pH :	5,6	4,6	4,4
FT (2,5 min) :	0,77	1,35	1,65
F. COD* :	26	24	23

II.2.1 Alum with polymers and bentonite

Test 1

	Turbidity	pH	COD*
Initial values	1,2	8	50
Bentonite dosage	100	300	
Polymer added	N-100	N-100	
Polymer dosage	1	1	
FT (5 min.)	2,15	2,15	
F. pH	5,6	4,6	
F. COD*	24	22	

Test 2

	Turbidity	pH	COD*
Initial values	0,93	8	46
Bentonite dosage	100		
$Al_2(SO_4)_3$ dosage	100		
Polymer added	N-100		
Polymer dosage	1		
Flocs appeared	Yes		
Flocs settled	Yes		
F. COD*	32		

II.3 Ferric chloride with organic polyelectrolytes

Test 1

	Turbidity		pH	COD*		
Initial values	1,5		7,5	51		
ml 1 N NaoH	-	-	-	0,25	0,95	2,9
ml 1 N H_2SO_4	1,7	0,95	-	-	-	-
$FeCl_3$ dosage	50	100	158	200	300	600
Polymer added	A-150	A-150	A-150	A-150	A-150	A-150
Polymer dosage	0,5	0,5	0,5	0,5	0,5	0,5
F. pH	5,24	4,98	4,93	5,05	5,19	5
FT (15 min.)	0,58	0,65	0,75	0,65	0,59	1,25
F. COD*	43	34	31	(not reliable values)		

II.4 Lime with organic polyelectrolytes

Test 1

	Turbidity	pH	COD*	
Initial values	0,93	8,05	46	
Ca(OH)$_2$ dosage	200	400	200	100
Polymer added	AP-273	AP-273	444-K	AP-273
Polymer dosage	1	1	5	1
Flocs appeared	Yes	Yes	Yes	Yes
Flocs settled	Yes	Yes	Yes	Yes
F. pH	11	11,5	11	9,8
F. COD*	34	25	34	37

Test 2

	Turbidity		pH	COD*	
Initial values	1,4		8,5	45	
Ca(OH)$_2$ dosage	150	200	250	300	400
Polymer added	AP-273	AP-273	AP-273	AP-273	AP-273
Polymer dosage	0,5	0,5	0,5	0,5	0,5
F. pH	10,5	10,7	10,75	10,9	11,2
FT (15 min.)	0,43	0,36	0,17	0,22	0,3
F. COD*	35	32	32	31	31

Comment: after the addition of the polymer the flocs were aggregated into bigger flocs which settled faster.

II.5 Lime with bentonite and polyelectrolyte

Test 1

	Turbidity	pH	COD*
Initial values	0,93	8,05	46
Bentonite dosage	100		
Ca (OH)$_2$ dosage	100		
Polymer added	N-100		
Polymer dosage	1		
Flocs appeared	Yes		
Flocs settled	Yes		
F. pH	9,9		
F. COD*	37		

II.6 Comparison of various coagulant-flocculant combinations

Test 1

	Turbidity	pH	COD*	Colour	
Initial values :	1,4	8,5	45	0,02	
Coagulant :	Floccotan	$Ca(OH)_2$		$Al_2(SO_4)_3$	$FeCl_3$
Coagulant dosage :	100	400		180	160
Polymer added :	AP-273	AP-273		N-100	A-150
Polymer dosage :	0,5	0,5		0,5	0,5
F. pH :	7,3	11,1		5,3	5,2
FT (15 min.) :	0,18	0,04		0,41	0,27
F. COD* :	70	32		30	26
F. colour :	0,024	0,006		0,006	0,003
% Colour removal :	0	70		70	85

Test 2

	Turbidity	pH	COD*	Cl^-	TDS
Initial values :	1,5	7,9	59	585	1420
Bentonite dosage :	-	-		-	100
Coagulant :	$FeCl_3$	$Al_2(SO_4)_3$		$Ca(OH)_2$	$Al_2(SO_4)_3$
Coagulant dosages :	158	190		600	200
Polymer added :	A-150	N-100		AP-273	N-100
Polymer dosage :	0,5	0,5		0,5	0,5
F. pH :	5,6	5,5		11,5	5,37
FT (60 min.) :	0,18	1,25		0,75	0,47
F. COD* :	23	23		30	22
F. Cl^- :	685	590		575	580
F. TDS :	1520	1480		1550	1450

III Effect of small amounts of polyelectrolytes on the final COD, when dissolved in water

To estimate the increase of final COD which may have occurred because of the polymer added (if, for instance, a portion of the polymer remained in solution instead of binding onto the flocs), an amount equal to 1 mg/l of different polymers was diluted in distilled water and the COD increase was determined. The results are shown below:

Initial COD (mg/l) :	0	0	0
Polymer added :	N-100	A-150	AP-273
Polymer dosage (mg/l) :	1	1	1
Final COD (mg/l) :	Not detectable	Not detectable	1,2

The results show that the effect of high molecular weight polymers on the final COD is negligible at the small dosages usually applied - less than 5 mg/l - when employed in conjunction with inorganic coagulants.

APPENDIX G

MILNERTON MATURATION POND EFFLUENT - MAIN TESTS

A. INORGANIC COAGULANTS APPLIED ALONE

Characteristics of the raw effluent sample used:

Initial total COD : 51 mg/l
" filtered COD : 46 mg/l
" turbidity : 1,7 FTU
" pH : 7,7

A.I. ALUM TESTS

Test 1

$Al_2(SO_4)_3$ dosage : 50 mg/l
pH created when only 50 mg/l is added : 6,7

ml 1 N NaOH :	-	-	-	-	-	-	-	-	0,2	0,8
ml 1 N H_2SO_4:	3,8	3	2,85	2,6	2,45	2,3	1,6	0,8	-	-
F. pH :	3,19	3,87	4,03	4,41	5,04	5,26	5,99	6,4	7,1	7,9
FT (60 min.):	1,15	8	8,55	3,95	1,55	1,55	1,45	1,55	1,05	0,45
% Turbidity removal :	32	-370	-402	-132	8,8	8,8	14,7	8,8	38	73

Comment : No flocs were formed in the sample with final pH 3,19

Test 2

$Al_2(SO_4)_3$ dosage : 100 mg/l
pH created when only 100 mg/l is added : 6,51

ml 1 N H_2SO_4 :	2,6	2,3	2,1	1,9	1,5	-
F. pH :	4,6	5,01	5,24	5,47	5,76	6,51
FT (60 min.) :	1,35	1,15	1,05	0,95	0,75	0,61
% Turbidity removal :	20	32	38	44	56	64
F. COD :	31	27	32	31	32	38
% COD removal :	39	47	37	39	37	25

The final turbidity results of Test 2 are not presented graphically in Figure 4.11 and were not taken into consideration for the regression analysis.

Test 3

$Al_2(SO_4)_3$ dosage : 100 mg/l

ml 1 N H_2SO_4 :	4,5	2,6	1,95	1,75	1,55	2,3	3	-	-	-	-
ml 1 N NaOH :	-	-	-	-	-	-	-	-	0,6	1,3	2,2
F. pH :	3,17	4,57	5,61	5,7	5,9	5,04	4,23	6,7	6,9	7,4	8,65
F. COD :	46	31	32	31	31	33	40	34	35	40	42
% COD Removal :	10	39	37	39	39	35	21	33	31	21	17

Comment: No flocs were formed in the sample in which the final pH was equal to 3,17.

Test 4

$Al_2(SO_4)_3$ dosage : 100 mg/l

ml 1 N NaOH :	-	-	-	-	-	-	-	-	-	0,6	1,3	2,2
ml 1 N H_2SO_4 :	4,5	2,6	2,1	1,95	1,75	1,55	1,25	0,6	-	-	-	-
F. pH :	2,81	3,75	4,18	4,32	4,68	5,16	5,5	6,15	6,45	6,8	7,52	8,7
FT (60 min.) :	1,15	5,65	1,7	1,25	1,35	1,15	1,55	0,83	0,61	0,28	0,25	0,13
% Turbidity Removal :	32	-232	0	26	20	32	9	51	64	83	85	92

Comment: No flocs were formed in the sample in which the final pH was equal to 2,81.

Test 5

$Al_2(SO_4)_3$ dosage : 200 mg/l

pH created when only 200 mg/l is added : 5,78

ml 1 N H_2SO_4 :	0,7	0,4	0,2	-	-	-
ml 1 N Na :	-	-	-	-	0,5	1,5
F. pH :	5,26	5,51	5,62	5,78	6,12	6,45
F. COD :	22	24	23	21	26	29
% COD Removal :	57	53	55	59	49	43

Test 6

$Al_2(SO_4)_3$ dosage : 200 mg/1

ml 1 N H_2SO_4 :	5,1	2,4	1,1	0,7	0,5	0,15	-	-	-	-	-	-
ml 1 N NaOH :	-	-	-	-	-	-	-	1,5	2	2,5	4	5
F. pH :	2,69	3,91	4,45	4,6	4,72	5,12	5,34	6,5	6,85	7,15	8,74	9,1
F. COD :	43	35	30	25	27	25	28	31	32	33	35	35
% COD Removal :	15	31	41	51	47	51	45	39	37	35	31	31
FT (60 min.) :	1,05	5,05	2,75	2,95	3,95	3,45	3,45	0,55	0,52	0,55	0,18	0,23
% Turbidity Removal :	38	-197	-61	-73	-132	-102	-102	67	69	67	89	86

Comment: No flocs were formed in the sample in which the final pH was equal to 2,69.

Test 7

$Al_2(SO_4)_3$ dosage : 300 mg/1

pH created when only 300 mg/1 is added : 4,68

ml 1 N H_2SO_4 :	3,2	1	0,6	0,3	-	-	-	-	-	-
ml 1 N NaOH :	-	-	-	-	0,9	1,1	2,3	2,8	3,2	3,8
F. pH :	3,48	4,2	4,26	4,35	4,85	5,16	6,2	6,45	6,7	7
FT (60 min.) :	1,45	6,45	4,75	4,75	3,55	3,35	0,65	0,33	0,4	0,43
% Turbidity Removal :	14	-279	-179	-179	-108	-97	61	80	76	75
F. COD :	38	26	27	26	25	24	27	28	29	32
% COD Removal :	25	49	47	49	51	53	47	45	43	37

Comment: No flocs were formed in the sample in which the final pH was equal to 3,48.

Test 8

$Al_2(SO_4)_3$ dosage : 400 mg/l

pH created when only 400 mg/l is added : 4,55

ml 1 N H_2SO_4	:	5,8	2	0,85	0,45	0,2	-	-	-	-	-
ml 1 N NaOH	:	-	-	-	-	-	2,3	3	3,5	4,2	5,2
F. pH	:	2,7	4,14	4,27	4,29	4,32	5,08	5,78	6,1	6,36	6,9
FT (60 min.)	:	1,45	3,65	9,85	10,35	11,35	4,45	2,15	1,25	0,78	0,83
% Turbidity Removal	:	14	-114	-479	-508	-567	-161	-26	26	54	51
F. COD	:	46	25	27	27	30	20	23	23	25	27
% COD Removal	:	10	51	47	47	41	61	55	55	51	47

Comment: No flocs were formed in the sample in which the final pH was equal to 2,7.

Test 9

$Al_2(SO_4)_3$ dosage : 500 mg/l

pH created when only 500 mg/l is added : 4,13

ml 1 N H_2SO_4	:	6,2	2,5	1,5	0,6	-	-	-	-	-	-
ml 1 N NaOH	:	-	-	-	-	-	3,5	4	4,5	6,5	3
F. pH	:	2,56	3,84	4,03	4,09	4,13	4,82	5,43	5,92	6,8	4,52
FT (60 min.)	:	1,55	12,85	17	15	12,35	3,05	1,15	0,67	0,4	3,25
% Turbidity Removal	:	9	-655	-900	-782	-626	-79	32	60	76	-91
F. COD	:	44	37	32	27	25	25	18	24	20	23
% COD Removal	:	14	27	37	47	51	51	65	53	61	55

Comment: No flocs were formed in the sample in which the final pH was equal to 2,56.

All the results of Section A.I are presented graphically in Figures 4.8 and 4.11.

A.II FERRIC CHLORIDE TESTS

Test 1

$FeCl_3$ dosage : 50 mg/l

pH created when only 50 mg/l is added : 6,8

ml 1 N H_2SO_4	:	5,9	4	3	2,7	2,6	2,3	1,65	1,05	-	-	-
ml 1 N NaOH	-	-	-	-	-	-	-	-	-	0,1	0,7	0,6
F. pH	:	2,48	3,02	4,1	5,13	5,29	5,61	6,1	6,32	7,06	7,63	8,76
F.T. (60 min.)	:	0,24	1,35	0,43	0,54	0,38	0,59	0,56	0,52	0,51	0,51	0,34
% Turbidity Removal	:	86	20	74	68	77	65	67	69	70	70	80
F. COD	:	34	34	31	35	35	32	37	35	38	38	32
% COD Removal	:	33	33	39	31	31	37	27	31	25	25	37

Test 2

$FeCl_3$ dosage : 100 mg/l

pH created when only 100 mg/l is added : 6,44

ml 1 N H_2SO_4	:	10	5,1	3,3	2,6	2,3	2,1	1,9	1,1	0,5	-	2,2	-	-
ml 1 N NaOH	:	-	-	-	-	-	-	-	-	-	-	-	0,95	1,8
F. pH	:	2,11	2,53	2,99	3,5	3,75	4,96	5,29	6,1	6,3	6,44	4,3	7,1	8,26
F.T. (60 min.)	:	47	3,55	6,45	1,05	0,72	0,58	0,46	0,37	0,61	0,64	0,85	0,59	0,53
F. COD	:	38	34	27	22	23	25	25	29	29	30	20	34	36
% COD Removal	:	25	33	47	57	55	51	51	43	43	41	61	33	29

Test 3

$FeCl_3$ dosages : 200 mg/l

pH created when only 200 mg/l is added : 5,65

ml 1 N H_2SO_4 :	10	4	1,8	1,1	1,05	1	0,6	0,5	-	-	-	-	-
ml 1 N NaOH :	-	-	-	-	-	-	-	-	-	0,5	1	1,5	2,5
F. pH :	2,1	2,64	3,08	3,41	3,64	3,81	4,57	4,62	5,65	6,09	6,3	6,5	7
FT (60 min.) :	23	13	22	6,05	2,25	3,45	3,75	0,72	0,61	0,63	0,74	0,8	0,63
F. COD :	36	30	22	17	16	13	18	20	22	21	27	29	32
% COD Removal :	29	41	57	67	68	74	65	61	57	59	47	43	37

Test 4

$FeCl_3$ dosage : 300 mg/l

pH created when only 300 mg/l is added: 3,14

ml 1 N H_2SO_4 :	10	2,5	-	-	-	-	-	-	-	-	-	-	-
ml 1 N NaOH :	-	-	-	0,4	0,8	1,05	1,3	1,65	2,15	2,9	3,5	4,2	0,8
F. pH :	2,06	2,71	3,14	3,51	3,98	4,74	5,01	5,53	5,83	6,25	6,5	6,98	4
FT (60 min.) :	7,25	43	7,35	3,15	2,25	3,55	1,05	1,05	0,83	0,67	0,68	0,8	2,05
% Turbidity Removal :	-326	-2429	-332	-85	-32	-108	38	38	51	60	60	53	-20
F. COD :	39	28	18	19	13	16	17	18	21	25	35	28	20
% COD Removal :	23	45	64	62	74	68	66	64	59	51	31	45	61

Test 5

$FeCl_3$ dosage : 400 mg/l

pH created when only 400 mg/l is added : 2,74

ml 1 N H_2SO_4	:	10	2	-	-	-	-	-	-	-	-	-	-	-	-	-	-
ml 1 N NaOH	:	-	-	-	1,8	2,3	2,6	2,8	3,3	4	4,4	5,2	6	1,8	2,3	2,5	2,6
F. pH	:	2,04	2,59	2,74	3,33	3,84	4,33	5,1	5,45	5,97	6,3	6,6	7,2	3,4	3,85	4,17	4,34
F.T. (60 min.)	:	2,15	36	27	15	11,35	10,85	0,82	0,78	0,84	0,62	0,42	0,57	38	21	10	3,35
% Turbidity Removal	:	-26	-2017	-1488	-782	-567	-538	52	54	50	63	75	66	-2135/	-1135/	-488 /	-97
F. COD	:	43	24	18	22	20	-	15	16	18	22	23	27	17	17	15	14
% COD Removal	:	15	53	64	57	61	-	70	68	68	57	55	47	66	66	70	

Test 6

$FeCl_3$ dosage : 500 mg/l

pH created when only 500 mg/l is added : 2,7

ml 1 N NaOH	:	3,9	4,1	4,5
F. pH	:	3,91	4,23	4,92
F.T. (60 min.)	:	8,45	4,35	1,95
% Turbidity Removal	:	-397	-155	-14
F. COD	:	13	9	15
% COD Removal	:	74	82	70

All the results of Section A.II are presented graphically in Figures 4.9 and 4.12.

A.III LIME TESTS

Test 1

Initial Ca^{2+} concentration in raw effluent : 50 mg/l

$Ca(OH)_2$ dosage :	200	300	500	700	900	1000
F.pH :	10,21	10,79	11,28	11,8	12,01	12,1
FT (60 min.) :	0,33	0,38	0,11	0,37	0,34	0,35
F. COD :	40	32	26	22	21	21
F. Ca^{2+} :	-	-	-	160	180	-

The above results are presented graphically in Figure 4.10.

B. INORGANIC COAGULANTS APPLIED TOGETHER WITH ORGANIC POLYELECTROLYTES

Initial raw effluent's total COD : 45 mg/l

" " " turbidity : 1,5 FTU

B.I ALUM WITH SUPERFLOC N-100

Test 1

$Al_2(SO_4)_3$ dosage : 100 mg/l

ml 1 N H_2SO_4 :	1,6	1,6	1,6	1,6	1,6	1,6
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	6,37	6,16	6,15	6,05	6,08	5,98
FT (30 min.) :	1,25	1,05	0,72	0,55	0,41	0,37
F. COD :	34	32	31	30	30	30

Optimum polymer dosage : below 1 mg/l

Test 2

$Al_2(SO_4)_3$ dosage : 300 mg/l

ml 1 N NaOH :	1,1	1,1	1,1	1,1	1,1	1,1
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	5,66	5,65	5,62	5,64	5,62	5,61
FT (30 min.) :	1	0,79	0,66	0,51	0,48	0,41
F. COD :	29	27	26	25	24	24

Optimum polymer dosage : below 0,5 mg/l

Test 3

$Al_2(SO_4)_3$ dosage : 500 mg/l

ml 1 N NaOH :	4	4	4	4	4	4
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	5,55	5,57	5,58	5,61	5,6	5,6
FT (30 min.) :	0,56	0,44	0,51	0,45	0,31	0,45
F. COD :	24	24	23	22	22	20

Optimum polymer dosage : below 0,25 mg/l

B.II FERRIC CHLORIDE WITH SUPERFLOC A-150

Test 1

$FeCl_3$ dosage : 50 mg/l

ml 1 N H_2SO_4 :	3	3	3	3	3	3
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	4,06	4,38	3,97	3,93	3,92	3,79
FT (20 min.) :	0,95	0,71	1,05	0,95	0,66	0,85
F. COD :	42	42	36	36	33	31

Optimum polymer dosage : below 0,25 mg/l

Test 2

$FeCl_3$ dosage : 100 mg/l

ml 1 N H_2SO_4 :	2,1	2,1	2,1	2,1	2,1	2,1
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	4,26	4,42	4,35	4,24	4,2	4,26
FT (15 min.) :	1,35	1,45	1,05	0,85	0,85	0,83
F. COD :	29	25	22	23	23	23

Optimum polymer dosage : below 2 mg/l

Test 3

$FeCl_3$ dosage : 300 mg/l

ml 1 N H_2SO_4 :	0,8	0,8	0,8	0,8	0,8	0,8
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	3,87	3,79	3,72	3,7	3,66	3,69
FT (60 min.) :	0,55	0,81	1,35	1,95	2,65	3,15
F. COD	20	20	17	18	18	18

Optimum polymer dosage : below 2 mg/l

Test 4

$FeCl_3$ dosage : 500 mg/l

ml 1 N NaOH :	4,1	4,1	4,1	4,1	4,1	4,1
Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	4,01	3,98	3,85	3,87	3,89	3,9
FT (60 min.) :	0,85	1,65	2,35	2,75	4,85	6,65
F. COD :	19	17	15	16	16	16

Optimum polymer dosage : 2 mg/l

B.III LIME WITH SEPARAN AP-273

$Ca(OH)_2$ dosage : 900 mg/l

Polymer dosage :	5	2	1	0,5	0,25	0,1
F. pH :	12,08	12,07	12,06	12,1	12,12	12,15
FT (30 min.) :	0,08	0,22	0,15	0,18	0,19	0,2
F. COD :	31	26	26	26	26	26

Optimum polymer dosage : below 5 mg/l

APPENDIX H

MILNERTON HUMUS TANK EFFLUENT - PRELIMINARY TESTS

Test 1

	Turbidity	pH	Total COD	Filtered COD		Cl^-
Initial values :	5,5	7,3	83	78		500
ml 10% NaOH :	-	2,7	-	2,15	-	-
Bentonite dosage:	-	-	-	-	-	100
Coagulant :	$FeCl_3$	$FeCl_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Ca(OH)_2$	$Al_2(SO_4)_3$
Coagulant dosage:	190	600	220	600	600	220
Polymer added :	A-150	A-150	N-100	N-100	AP-273	N-100
Polymer dosage :	0,5	0,5	0,5	0,5	0,5	0,5
F. pH :	4,5	4,4	4,6	4,9	11,3	4,9
F. COD :	30	25	35	31	34	29
F. Cl^- :	630	860	500	490	500	490

Test 2

	Turbidity	pH	Total COD		Filtered COD	Colour	TDS	Cl^-
Initial values :	7,7	7,3	95		75	0,046	1450	625
ml 10% NaOH :	-	2,7	-	2,15	-	-		
Bentonite dosage :	-	-	-	-	-	100		
Coagulant :	$FeCl_3$	$FeCl_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Ca(OH)_2$	$Al_2(SO_4)_3$		
Coagulant dosage :	190	600	220	600	600	230		
Polymer added :	A-150	A-150	N-100	N-100	AP-273	N-100		
Polymer dosage :	0,5	0,5	0,5	0,5	0,5	0,5		
F. pH :	5,07	5,1	4,95	5,25	11,37	4,74		
F.T. (60 min.) :	0,14	0,13	1,25	0,35	0,49	0,95		
F. colour :	0,0015	0,001	0,008	0,004	0,011	0,006		
% Colour Removal:	97	98	83	91	76	87		
Final TDS :	1660	1990	1610	1810	1520	1560		

APPENDIX I

MILNERTON HUMUS TANK EFFLUENT - MAIN TESTS

A. FIRST SERIES OF TESTS

Characteristics of the raw effluent sample used:

Initial total COD : 133 mg/l
" filtered COD : 80 mg/l
" turbidity : 18 FTU
" pH : 7,56

A.I ALUM TESTS

Test 1

Initial total COD : 119 mg/l
$Al_2(SO_4)_3$ dosage : 100 mg/l
pH created when only 100 mg/l is added : 6,7

ml 1 N H_2SO_4 :	4	3,5	3	2,5	2,2	1,9	1,5	-
F. pH :	3,88	4,36	5,25	5,7	5,76	5,88	6,05	6,7
FT (30 min.) :	9,15	6,15	4,25	3,1	3,15	3,25	3,65	4,45
F. COD :	46	36	36	34	37	37	39	45

Test 2

Initial total COD : 119 mg/l
$Al_2(SO_4)_3$ dosage : 200 mg/l
pH created when only 200 mg/l is added : 6,19

ml 1 N H_2SO_4 :	3,5	2,5	2	1	-
F. pH :	4,04	4,33	4,54	5,75	6,19
FT (60 min.) :	10	2,65	2,05	2,05	0,95
F. COD :	39	33	32	35	36

Test 3

Initial total COD : 119 mg/l
$Al_2(SO_4)_3$ dosage : 300 mg/l
pH created when only 300 mg/l is added : 5,4

ml 1 N H_2SO_4 :	2	1	-	-	-
ml 1 N NaOH :	-	-	-	1,05	2
F. pH :	4,33	4,53	5,4	6,13	6,36
FT (60 min.) :	11,35	5,75	4,65	2,35	1,5
F. COD :	29	28	32	31	35

Test 4

Initial total COD : 119 mg/l

$Al_3(SO_4)_3$ dosage : 400 mg/l

pH created when only 400 mg/l is added : 4,43

ml 1 N H_2SO_4 :	2	1	-	-	-	-	-
ml 1 N NaOH :	-	-	-	1	2,3	3	4
F. pH :	4,22	4,31	4,43	4,86	5,8	6,15	6,52
FT (60 min.) :	5,35	4,75	4,55	4	1,45	1,15	0,95
F. COD :	35	32	31	31	30	31	35

Test 5

Initial total COD : 119 mg/l

$Al_2(SO_4)_3$ dosage : 500 mg/l

pH created when only 500 mg/l is added : 4,31

ml 1 N H_2SO_4 :	1,5	-	-	-	-
ml 1 N NaOH :	-	-	1	2	4
F. pH :	4,22	4,31	4,41	4,6	5,9
FT (60 min.) :	11,35	10,85	9,35	7,25	2,45
F. COD :	36	33	32	30	

All the test results of Section A.I are presented graphically in Figures 5.3 and 5.7.

A.II FERRIC CHLORIDE TESTS

Test 1

Initial total COD : 133 mg/l

$FeCl_3$ dosage : 100 mg/l

pH created when only 100 mg/l is added : 6,55

ml 1 N H_2SO_4 :	3,3	2,3	2,1	1,9	1,1	-	3	2,5	2,75
F. pH :	3,8	5,53	5,64	5,73	6,1	6,55	4,22	5,34	5,16
FT (30 min.) :	6,65	2,25	2,25	2,25	2,05	1,65	3,55	2,55	0,95
F. COD :	35	33	33	29	41	43	32	29	28

Test 2

Initial total COD : 133 mg/l

$FeCl_3$ dosage : 200 mg/l

pH created when only 200 mg/l is added : 5,82

ml 1 N H_2SO_4 :	1,8	1,5	1	-
F. pH :	3,63	4,02	4,9	5,82
FT (40 min.) :	8,15	3,45	1,75	1,35
F. COD :	22	23	24	25

Test 3

Initial total COD : 133 mg/l

$FeCl_3$ dosage : 300 mg/l

pH created when only 300 mg/l is added : 3,79

ml 1 N NaOH :	-	0,4	0,8	1,2	1,6	2,2
F. pH :	3,79	4,49	5,05	5,45	5,7	6
FT (40 min.):	1,75	1,15	0,73	0,55	1,25	1,85
F. COD :	19	16	21	24	25	29

Test 4

Initial total COD : 119 mg/l

$FeCl_3$ dosage : 400 mg/l

pH created when only 400 mg/l is added : 2,9

ml 1 N NaOH :	-	1	2	3	4
F. pH :	2,9	3,2	4,47	5,67	6,2
FT (30 min.):	51	16	1,55	4,45	4,25
F. COD :	27	24	20	28	36

Test 5

Initial total COD : 119 mg/l

$FeCl_3$ dosage : 500 mg/l

ml 1 N NaOH :	2	2,5	3,1	4
F. pH :	2,9	3,05	3,36	4,55
FT (40 min.):	8,55	6,35	2,7	0,95
F. COD :	25	-	23	19

All the test results of Section A.II are presented graphically in Figures 5.4 and 5.8.

A.III LIME TEST

Initial total COD : 133 mg/l

Lime dosage :	500	1000	1500	2000	2500	3000
F. pH :	10,95	12	12,3	12,46	12,57	12,62
FT (20 min.):	0,57	0,42	0,21	0,13	0,08	0,13
F. COD :	31	29	27	26	25	25

The above test results are presented graphically in Figure 5.5.

B. SECOND SERIES OF TESTS

Characteristics of the raw effluent sample used:

Initial total COD : 105 mg/l
" filtered COD : 75 mg/l
" turbidity : 18,5 FTU
" pH : 7,3

Test 1

$Al_2(SO_4)_3$ dosage : 100 mg/l
pH created when only 100 mg/l is added : 6,45

ml 1 N H_2SO_4:	1,85	1,7	1,5	1,2	0,6	
F. pH :	4,86	5,04	5,35	5,68	6,1	6,45
FT (60 min.):	3,65	2,65	1,65	0,77	0,53	0,42
F. COD :	31	32	30	31	31	33

These test results are presented graphically in Figures 5.6 and 5.9

APPENDIX J

ATHLONE MATURATION POND EFFLUENT - PRELIMINARY TESTS.(1)

I. INORGANIC COAGULANTS

I.1 Alum tests

Test 1

	Turbidity	pH	Total COD	Filtered COD*	
Initial values :	14	7,2	295	117	
$Al_2(SO_4)_3$ dosage:	100	200	300	400	1000
FT (30 min). :	5,05	1,95	3,35	7,05	34
F. pH :	6,7	6,1	5,4	4,62	4,22
F. COD* :	75	57	52	52	52

The final turbidity results are presented graphically in Figure 6.2, while the final COD results are presented in Figure 6.3.

I.1.1 Alum with bentonite

Test 1

	Turbidity	pH	Total COD	Filtered COD*
Initial values :	14	7,2	295	117
Bentonite dosage:	100			
$Al_2(SO_4)_3$ dosage :	200			
F. pH :	6,3			
FT (60 min.) :	0,95			
F. COD* :	56			

I.2 Ferric chloride tests

Test 1

	Turbidity	pH		Total COD		Filtered COD*
Initial values :	14	7,2		295		115
$FeCl_3$ dosage :	100	200	300	400	600	1000
F. pH :	6,6	6	4,7	3,12	2,65	2,3
FT (30 min.) :	12	1,45	2,95	48	16	2,15
F. COD* :	94	60	57	-	-	-

The final turbidity results are presented graphically in Figure 6.4. After adding 600 and 1000 mg/l $FeCl_3$, a yellow hue appeared in solution.

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(1) The F.COD* tests results obtained after alum, lime, and polymer treatments may be considered accurate, while those obtained after ferric chloride coagulation may be considered as approximate - see Section 3.6-(1).

I. 2.1 Ferric chloride with bentonite

Test 1

	Turbidity	pH	Total COD	Filtered COD*
Initial values :	14	7,2	295	117
Bentonite dosage :	100			
$FeCl_3$ dosage :	200			
F. pH :	6,2			
FT (30 min.) :	0,8			
F. COD* :	57			

I.3 Caustic Soda and Lime Tests

Test 1

	Turbidity	pH	Total COD		Filtered COD*
Initial values :	14	7,2	295		117
$Ca(OH)_2$ dosage :	100	200	300	400	1000
F. pH :	9	9,5	9,85	10,4	12,05
FT (60 min.) :	17	20	42	25	0,85
F. COD* :	122	117	107	106	62

The above test results are presented graphically in Figure 6.5.

Test 2

	Turbidity	pH	Total COD	Filtered COD*
Initial values :	14	7,2	295	117

This test consisted of adding 1 N NaOH solution to the effluent under continuous stirring until the pH reached 12. A voluminous precipitate was formed. The final COD was found equal to 100 mg/l.

Test 3

	Turbidity		pH	Total COD		Filtered COD*	Colour
Initial values :	15		7,1	212		115	0,207
$Ca(OH)_2$ dosage :	500	600	700	800	900	1000	
F. pH :	10,95	11,4	11,72	11,92	12,1	12,21	
F. COD* :	117	73	63	63	57	52	
F. Colour :	-	0,102	0,072	0,062	0,048	0,048	
% Colour removal :	-	51	65	70	77	77	

Test 4

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	14	7,1	240	117	0,141

$Ca(OH)_2$ dosage :	500	1000	1500	2000	2500
F. pH :	11,1	12,15	12,5	12,62	12,7
FT (40 min.) :	7,75	0,5	0,22	0,15	0,15
F. COD* :	90	51	47	46	43
F. Colour :	-	0,026	-	-	0,02
% Colour Removal:	-	81	-	-	86

Note: In this test lime was added as 5% lime milk.

I.3.1 Lime with bentonite

Test 1

	Turbidity	pH	Total COD	Filtered COD*
Initial values :	14	7,1	240	117

Bentonite dosage:	100
$Ca(OH)_2$ dosage :	1000
F. pH :	12,1
FT (60 min.) :	0,1
F. COD* :	54

II. ORGANIC POLYELECTROLYTES EMPLOYED WITH OR WITHOUT INORGANIC COAGULANTS

II.1 Organic polyelectrolytes applied alone

Test 1

	Turbidity	pH	Total COD	Filtered COD*
Initial values :	18,5	7,1	206	132

Polymer added :	C-521	N-607	444-K	AP-273	N-100	MG-200	A-150
Dosage (up to..):	500	300	50	20	40	30	20
Flocs formed :	Yes	Yes	Yes	No	No	No	No
Flocs settled :	No	No	No	-	-	-	-

Test 2

	Total COD	Filtered COD*	Colour
Initial values :	212	115	0,207
Floccotan dosage :	150		
C-521 dosage :	5		
F. COD* :	79		
% COD Renoval :	62		
F. Colour :	0,031		
% Colour Removal :	85		

Test 3

Calcium chloride was added to the effluent in dosages up to 200mg/l in order to reduce the charge of the suspended particles by Ca^{2+} adsorption. This charge reduction would aid the anionic polymers, which would be added afterwards, to flocculate the coagulated suspended matter. However, the addition of anionic polyelectrolytes proved to be completely ineffective in bringing about flocculation.

Test 4

	Turbidity	pH	Total COD	Filtered COD		Colour
Initial values :	15	7,1	212	115		0,207
Floccotan dosage :	100	200	300	400	500	400
Flocs formed :	Yes	Yes	Yes	Yes	Yes	Yes
Flocs settled :	No	No	No	No	No	No
Polymer added :	444-K	C-100	AP-273	444-K	N-100	C-521
Polymer dosage :	2	2	1	2	1	50
Flocs settled :	No	Yes	Yes	Yes	Yes	No
FT (15 min.) :	6,55	0,83	0,39	0,7	0,52	13
F. COD* :	97	91	90	97	130	92
F. Colour :	0,145	0,064	0,059	0,055	0,049	0,05
% Colour Removal :	30	69	71	73	76	76

II.2 Bentonite with organic polyelectrolytes

Test 1

	Turbidity	pH		Total COD		Filtered COD*			Colour	
Initial Values :	18,5	7,1		206		132			0,173	
Bentonite dosage :	95	95	95	95	95	95	95	95	95	95
Polymer added :	C-521	N-607	C-521	N-607	444-K	N-100	MG-200	AP-273	A-150	444-K
Polymer dosage :	50	20	10	10	4	0,5	1	5	0,5	5
F.T. (15 min) :	3,65	3,55	3,75	2,65	5,85	4,55	4,95	-	6,15	5,25
Flocs appeared :	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	Yes	Yes
Flocs settled :	Slowly	Slowly	Slowly	Slowly	Slowly	Yes	Yes	-	Yes	Slowly
F. COD* :	103	105	112	108	115	120	120	-	125	111
F. Colour :	0,089	0,104	0,118	0,107	0,125	0,138	0,139	-	0,151	0,118
% Colour Removal :	48	40	32	38	28	20	19	-	13	32

Test 2

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18,5	7,1	206	132	0,173

Bentonite dosage:	190	470
Polymer added :	C-521	C-521
Polymer dosage :	30	50
F. pH :	7,3	7,4
FT (15 min.) :	1,65	1,05
F. COD* :	85	77
% COD Removal :	59	62
F. Colour :	0,0815	0,0665
% Colour Removal:	53	61

Test 3

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	14	7,1	240	117	0,141

Bentonite dosage:	200	200	100
Polymer added :	N-100	AP-273	N-100
Polymer dosage :	3	1	1,5
FT (10 min.) :	2,25	5,35	4,25
F. pH :	7,5	7,45	7,7
F. COD* :	100	107	101
F. Colour :	-	0,132	-
% Colour Removal:	-	6	-

Test 4

	Total COD	Filtered COD*	Colour
Initial values :	212	115	0,207

Bentonite dosage:	100
444-K dosage :	20
F. COD* :	61

Test 5

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18	7,45	206	140	0,182
Bentonite dosage:	200	250	100		
Polymer added :	C-521	C-521	N-100		
Polymer dosage :	30	50	3		
F. pH :	7,25	7,35	7,45		
FT (15 min.) :	5,1	3,45	7,5		
F COD* :	102	92	123		
F. Colour :	0,101	0,08	0,155		
% Colour Removal:	45	56	15		

II.3 Alum with organic polyelectrolytes

Test 1

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18,5	7,1	206	132	0,173
Alum dosage :	200	200	200	200	
Polymer added :	C-521	AP-273	N-100	A-150	
Polymer dosage :	50	1	0,5	2	
F. pH :	6,6	6,6	6,6	6,55	
FT (10 min.) :	1,55	1,05	1,25	0,5	
F. COD* :	62	63	63	60	
F. Colour :	0,032	0,032	0,0305	0,0285	
% Colour Removal:	81	81	82	83	

Test 2

	Total COD	Filtered COD*	Colour
Initial values :	212	115	0,207
$Al_2(SO_4)_3$ dosage:	400		
444-K dosage :	15		
F. COD* :	48		
F. Colour :	0,017		
% Colour Removal:	92		

II.4 Ferric chloride with organic polyelectrolytes

Test 1

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18,5	7,1	206	132	0,173

pH adjusted at :	5,1	5,1	5,1	5,2	5,3	5
$FeCl_3$ dosage :	100	200	300	400	600	1000
Polymer added :	N-607	C-521	AP-273	444-K	A-150	N-100
Polymer dosage :	50	10	0,5	1	0,5	0,5
Flocs settled :	No	Yes	Yes	Yes	Yes	Yes
FT (10 min.) :	-	1,65	0,5	0,43	0,3	0,15
F. Colour :	-	0,03	0,0115	0,018	0,01	0,0085
% Colour Removal:	-	83	93	90	94	95

Test 2

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18,5	7,1	206	132	0,173

$FeCl_3$ dosage :	200	200	200
Polymer added :	444-K	A-150	N-100
Polymer dosage :	2	0,5	0,5
F. pH :	6,5	6,55	6,5
FT (10 min.) :	3,65	1,35	1,65
F. Colour :	0,044	0,032	0,035
% Colour Removal	75	81	80

II.5 Alum and ferric chloride with organic polyelectrolytes

Test 1

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18,5	7,1	206	132	0,173

Coagulant :	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$FeCl_3$
Coagulant dosage :	400	400	200
Polymer added :	N-100	C-521	A-150
Polymer dosage :	0,5	50	0,25
F. pH :	5,1	5,05	5,3
FT (15 min.) :	1,45	2,05	2,55
F. COD* :	47	51	-
F. Colour :	0,04	0,046	0,038
% Colour Removal:	77	73	78

II.6 Bentonite with alum or ferric chloride and organic polyelectrolytes

Test 1

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	18,5	7,1	206	132	0,173

Bentonite dosage:	95	95
Coagulant :	$Al_2(SO_4)_3$	$FeCl_3$
Coagulant dosage :	60	50
Polymer added :	N-100	A-150
Polymer dosage :	0,5	0,25
F. pH :	6,8	6,85
FT (15 min.) :	3,25	3,95
F. COD* :	86	92
F. Colour :	0,0815	0,1015
% Colour Removal :	53	41

II.7 Lime with organic polyelectrolytes

Test 1

	Total COD	Filtered COD*	Colour
Initial values :	240	47	0,141

Lime dosage :	2500
AP-273 dosage :	2
F. pH :	12,7
FT (5 min.) :	0,42
F. COD* :	46
F. Colour :	0,020
% Colour Removal:	86

Note: In a similar test it was observed that, if AP-273 was added before the lime addition, it was not effective as flocculant at all.

Test 2

	Turbidity	pH	Total COD	Filtered COD*	Colour
Initial values :	15	7,1	212	115	0,207

$Ca(OH)_2$ dosage :	500	600	700	800	900	1000
AP-273 dosage :	0,2	0,2	0,2	0,2	0,2	0,2
FT (30 min.) :	8,45	3,45	1,55	1,35	0,76	0,84
F. pH :	10,95	11,4	11,72	11,92	12,1	12,21
F. COD* :	117	73	63	63	57	52
F. Colour :	0,207	0,102	0,072	0,062	0,048	0,048
% Colour Removal:	0	51	65	70	77	77

II.8 Bentonite with lime and organic polyelectrolytes

Test 1

	Turbidity	pH	Total COD	Filtered COD*
Initial values :	14	7,1	240	117

Bentonite dosage:	200	1000
$Ca(OH)_2$ dosage :	1000	1000
AP-273 dosage :	1	1
FT (15 min.) :	0,63	0,36
F. pH :	12,1	12,1
F. COD* :	59	57

II.9 Comparison of effects of various inorganic coagulant and organic polyelectrolyte combinations with or without bentonite.

Test 1

		Turbidity		pH		Total COD			Filtered COD	Colour	TS		TDS
Initial values	:	18		7,45		206			140	0,182	795		780
		TSS		TVS	Fe^{3+}		Na^{+}	Ca^{2+}	Mg^{2+}	Cl^{-}	SO_4^{2-}		
		55		165	$\sim$0		260	30	20	215	100		
Bentonite dosage	:	-	-	-	-	-	100	100	200	250	-100	-	-
Coagulant	:	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Al_2(SO_4)_3$	$Ca(OH)_2$	$Ca(OH)_2$	$Al_2(SO_4)_3$	$FeCl_3$	-	-	-	$FeCl_3$	Floccotan
Coagulant dosage	:	400	300	200	1000	700	60	50	-	-	-	300	200
Polymer added	:	N-100	N-100	N-100	AP-273	AP-273	N-100	A-150	C-521	C-521	N-100	A-150	AP-273
Polymer dosage	:	1	1	0,5	1	1	1	0,5	30	50	3	0,5	1
F.T. (15 min.)	:	2,7	2,15	1,75	2,05	0,73	8,75	4,65	4,93	3,45	7,35	0,39	0,84
F. pH	:	5	6,05	6,5	11,85	11,7	6,95	6,85	7,25	7,35	7,45	5,72	7,2
F. COD*	:	65	70	75	74	80	111	106	102	92	123	74	100
F. Colour	:	9035	0,03	0,032	0,036	904	0,121	0,104	0,101	0,08	0,155	0,011	0,047
% Colour Removal	:	81	83	82	80	78	33	43	45	56	15	94	74
Final TDS	:	935	895	790	1000	795	-	-	-	820	-	890	850
F. Fe^{3+}	:	-	-	-	-	-	-	$\sim$1	-	-	-	1	-
F. Cl^{-}	:	-	-	-	-	-	-	210	-	-	-	290	-
F. SO_4^{2-}	:	380	345	265	-	-	150	-	-	-	-	-	-
F. Ca^{2+}	:	-	-	-	115	70	-	-	-	-	-	-	-
F. Mg^{2+}	:	-	-	-	0	0	-	-	-	-	-	-	-

APPENDIX K

ATHLONE MATURATION POND EFFLUENT - MAIN TESTS

A. FIRST SERIES OF TESTS

Characteristics of raw effluent sample used:

Initial total COD : 140 mg/l
" filtered COD : 117 mg/l
" turbidity : 6,5 FTU
" pH : 7,47

A.I Alum tests

Test 1

Initial total COD : 140 mg/l
$Al_2(SO_4)_3$ dosage : 100 mg/l
pH created when only 100 mg/l is added : 6,6

ml 1 N H_2SO_4 :	4	3	1	-	-	-	3,5
ml 1 N NaOH :	-	-	-	-	1	3	-
F. pH :	4,26	5,06	6,3	6,6	7,05	9	4,61
FT (30 min.) :	13	8,45	3,45	4,55	6,55	2,25	11,35
F. COD :	82	53	58	65	83	77	63

Test 2

Initial total COD : 140 mg/l
$Al_2(SO_4)_3$ dosage : 200 mg/l
pH created when only 200 mg/l is added : 6,07

ml 1 N H_2SO_4 :	3	1,2	-	-	-	-
ml 1 N NaOH :	-	-	-	1	2	4
F. pH :	4,57	5,4	6,07	6,45	6,8	8,5
FT (60 min.) :	13,5	3,05	1,95	1,45	1,45	0,82
F. COD :	60	48	50	53	58	69

Test 3

Initial total COD : 140 mg/l
$Al_2(SO_4)_3$ dosage : 300 mg/l
pH created when only 300 mg/l is added : 5,1

ml 1 N H_2SO_4 :	3	-	-	-	-	-
ml 1 N NaOH :	-	-	1	2	3	4
F. pH :	4,4	5,1	5,8	6,18	6,6	7,1
FT (60 min.) :	18	4,45	1,95	1,35	1,15	0,73
F. COD :	64	46	48	53	57	63

Test 4

Initial total COD : 140 mg/l
$Al_2(SO_4)_3$ dosage : 400 mg/l
pH created when only 400 mg/l is added : 4,5

ml 1 N H_2SO_4 :	3	-	-	-	-	-
ml 1 N NaOH :	-	-	1	3	4	5
F. pH :	4,23	4,5	4,85	6,45	6,7	7,05
FT (60 min.) :	18	8,55	5,05	1,15	0,75	0,69
F. COD :	62	50	42	47	51	54

Test 5

Initial total COD : 140 mg/l
$Al_2(SO_4)_3$ dosage : 500 mg/l
pH created when only 500 mg/l is added : 4,39

ml 1 N H_2SO_4 :	3	1	-	-	-	-	-	-	-	-	4
ml 1 N NaOH :	-	-	-	3	3,1	4	5	7	8	10	-
F. pH :	4,22	4,31	4,39	5,23	5,45	5,78	6,1	6,85	7,6	8,8	4
FT (60 min.) :	16	8,35	8,45	3,45	2,65	2,05	1,25	0,43	0,38	0,27	7,15
F. COD :	64	53	46	46	42	46	47	52	52	58	78

Test 6

Initial total COD : 140 mg/l

$Al_2(SO_4)_3$ dosage : 600 mg/l

pH created when only 600 mg/l is added : 4,38

ml 1 N H_2SO_4 :	3	-	-	-	-	-	-
ml 1 N NaOH :	-	-	1	3	4	4,1	5
F. pH :	4,24	4,38	4,44	4,65	5	5,18	5,8
FT (60 min.) :	11,5	9,65	7,35	6,05	4,15	2,35	2,75
F. COD :	68	50	47	46	43	42	44

Test 7

Initial total COD : 128 mg/l

$Al_2(SO_4)_3$ dosage : 700 mg/l

ml 1 N NaOH :	5
F. pH :	4,97
FT (60 min.) :	2,85
F. COD :	42

Test 8

Initial total COD : 128 mg/l

$Al_2(SO_4)_3$ dosage : 800 mg/l

ml 1 N NaOH :	6	6,5
F. pH :	4,63	4,85
FT (60 min.) :	2,05	2,65
F. COD :	41	42

The test results reported in Section A.I are presented graphically in Figures 6.6 and 6.9.

A.II FERRIC CHLORIDE TESTS

Test 1

Initial total COD : 130 mg/l

$FeCl_3$ dosage : 100 mg/l

pH created when only 100 mg/l is added : 6,6

ml 1 N H_2SO_4 :	4	3,4	3,1	2,9	2,6	2	-	-
ml 1 N NaOH :	-	-	-	-	-	-	-	1
F. pH :	3,46	3,71	4,11	4,93	5,3	5,73	6,6	7,4
FT (30 min.) :	13,5	11	3,15	1,65	1,55	4,05	7,65	3,05
F. COD :	57	48	41	39	44	47	66	73

Test 2

Initial total COD : 130 mg/l

$FeCl_3$ dosage : 200 mg/l

pH created when only 200 mg/l is added : 5,8

ml 1 N H_2SO_4 :	2,4	2,1	1,8	1,4	1,2	1	0,5	-	-
ml 1 N NaOH :	-	-	-	-	-	-	-	-	1,7
F. pH :	3,25	3,16	3,62	3,77	4,56	4,9	5,53	5,8	6,5
FT (40 min.) :	31	47	6,35	2,85	1,05	1,65	1,15	1,35	4,15
F. COD :	44	44	36	33	36	34	34	41	54

Test 3

Initial total COD : 130 mg/l

$FeCl_3$ dosage : 300 mg/l

pH created when only 300 mg/l is added : 3,8

ml 1 N H_2SO_4 :	3,1	2	-	-	-	-	-	-
ml 1 N NaOH :	-	-	-	0,5	0,3	1	2	3
F. pH :	2,9	2,99	3,8	4,62	4,23	5,28	6,07	6,35
FT (60 min.) :	72	97	10	0,95	1,65	0,75	0,5	0,95
F. COD :	54	46	34	33	34	32	40	47

Test 4

Initial total COD : 130 mg/l

$FeCl_3$ dosage : 400 mg/l

ml 1 N NaOH :	1,5	2	2,3	3	4,5
F. pH :	3,72	4,32	4,93	5,52	6,4
FT (60 min.) :	17	6,15	1,45	0,73	0,3
F. COD :	33	28	31	35	38

Test 5

Initial total COD : 130 mg/l

$FeCl_3$ dosage : 500 mg/l

ml 1 N NaOH :	3	3,2	3,5	4,2	5,5	3,9
F. pH :	3,48	3,83	4,16	4,95	6,08	4,65
FT (60 min.) :	16	23	4,95	4,55	0,95	1,45
F. COD :	31	33	26	29	34	32

Test 6

Initial total COD : 134 mg/l

$FeCl_3$ dosage : 600 mg/l

ml 1 N NaOH :	3,5	4	4,5	5	5,5	6	6,5	7	9	5,9
F. pH :	3,1	3,22	3,51	3,91	4,65	5,42	5,86	5,96	6,73	5,39
FT (60 min.) :	46	39	25	11	4,65	0,47	-	0,77	0,4	0,76
F. COD :	38	47	38	30	34	-	33	-	66	-

Test 7

Initial total COD : 134 mg/l

$FeCl_3$ dosage : 700 mg/l

ml 1 N NaOH :	6	6,5	6,8	7	7,5
F. pH :	3,77	3,97	4,37	4,9	5,13
FT (60 min.) :	16	7,55	2,35	1,65	1,05
F. COD :	29	30	27	28	30

Test 8

Initial total COD : 134 mg/l

$FeCl_3$ dosage : 800 mg/l

ml 1 N NaOH :	7	8	8,5	9
F. pH :	3,17	4,07	4,31	4,86
FT (60 min.) :	47	18	3,55	2,45
F. COD :	32	25	28	29

The test results of Section A.II are presented graphically in Figures 6.7 and 6.10.

A.III Lime tests

Test 1

Initial total COD : 140 mg/l

Initial Ca^{2+} concentration : 38 mg/l

Lime dosage :	500	1000	1500	2000	3000
F. pH :	11,2	12,1	12,4	12,5	12,6
FT (25 min.) :	8,05	0,73	(unreliable)		
F. COD :	89	61	48	39	32

The above results are presented graphically in Figure 6.8.

B. SECOND SERIES OF TESTS

Characteristics of raw effluent sample used:

Initial total COD : 138 mg/l
" filtered COD : 113 mg/l
" turbidity : 7,5 FTU
" pH : 7,5

Coagulant: $FeCl_3$

(Continued)

Test 1

Initial total COD : 138 mg/l

$FeCl_3$ dosage : 500 mg/l

pH created when only 500 mg/l is added : 2,67

ml 1 N H_2SO_4 :	1,5	-	-	-	-	-	-	-	-	-	-	-
ml 1 N NaOH :	-	-	2,5	2,9	3,2	3,6	4,2	5,2	5,9	6,9	7,5	9
F. pH :	2,56	2,67	3,41	3,8	4,27	5,02	5,36	5,98	6,3	6,55	6,95	8
FT (40 min.) :	78	52	9,05	3,05	2	1,55	0,59	0,39	0,48	1,25	1,7	2,85
F. COD :	48	46	37	34	30	34	35	43	37	45	59	66

Test 2

Initial total COD : 127 mg/l

$FeCl_3$ dosage : 600 mg/l

pH created when only 600 mg/l is added : 2,49

ml 1 N NaOH :	-	2,2	4,1	4,5	4,8	5,2	5,8	6,7	7,8	8,8	10	10
F. pH :	2,49	2,75	3,49	3,98	4,4	4,85	5,56	6,1	6,5	6,83	7,37	7,86
FT (40 min.) :	18	48	10	3,25	1,85	1,65	0,55	0,37	1,15	2,05	2,95	3,25
F. COD :	-	42	32	30	27	33	28	31	35	44	54	63

The test results of Section B are presented graphically in Figures 6.11 and 6.15.

C. THIRD SERIES OF TESTS

Characteristics of raw effluent sample used:

Initial total COD : 184 mg/l Initial pH : 7,65

" filtered COD : 150 mg/l

" turbidity : 15 FTU

Coagulant : $FeCl_3$

Test 1

Initial total COD : 174 mg/l

$FeCl_3$ dosage : 200 mg/l

pH created when only 200 mg/l is added : 6,1

ml 1 N H_2SO_4 :	4,4	2,4	1,7	1,4	1	0,7	2,1	1,9	-	-	-	-
ml 1 NaOH :	-	-	-	-	-	-	-	-	-	1	1,7	2,6
F. pH :	3	3,6	4,83	5,1	5,58	5,75	4	4,35	6,1	6,3	6,5	6,58
FT (30 min.) :	11,5	9,35	2,65	2,45	2,2	2,45	3,15	2,55	2,45	5,05	5,05	5,85
F. COD :	80	51	42	44	48	48	47	45	55	65	73	69

Test 2

Initial total COD : 184 mg/l

$FeCl_3$ dosage : 300 mg/l

pH created when only 300 mg/l is added : 4,63

ml 1 N H_2SO_4 :	3,3	0,9	0,4	-	-	-	-	-	-	-	-	-
ml 1 N NaOH :	-	-	-	-	0,2	0,6	1	1,6	2,2	3	3,5	4
F. pH :	2,74	3,32	3,95	4,63	5,04	5,38	5,7	5,96	6,2	6,58	6,67	6,82
FT (40 min.) :	47	3,05	2,05	1,65	1,65	1,65	0,29	0,43	0,55	1,25	1,65	1,35
F. COD :	58	49	41	42	43	44	43	49	47	57	59	61

Test 3

Initial total COD : 184 mg/l

$FeCl_3$ dosage : 400 mg/l

pH created when only 400 mg/l is added : 3,18

ml 1 N H_2SO_4 :	2,3	-	-	-	-	-	-	-	-	-	-	-
ml 1 N NaOH :	-	-	0,8	1,4	1,6	2	2,5	3	3,6	4,5	5,5	1,2
F. pH :	2,8	3,18	3,63	4,53	4,68	5,33	5,55	5,83	6,06	6,03	6,7	4
FT (30 min.) :	82	33	13	3,95	4,15	3,15	0,41	0,32	0,33	0,77	1,15	4,95
F. COD :	61	48	42	39	37	40	50	41	44	49	56	41

The test results of Section C are presented graphically in Figures 6.12 and 6.16.

D. FOURTH SERIES OF TESTS

Characteristics of raw effluent sample used:

Initial total COD : 115 mg/l
" filtered COD : 90 mg/l
" tubidity : 12,5 FTU
" pH : 7,5

D.I Coagulant : $FeCl_3$

Test 1

$FeCl_3$ dosage : 100 mg/l

pH created when only 100 mg/l is added : 6,6

ml 1 N H_2SO_4 :	4,9	3,7	3,4	3,1	3	2,8	2	-	-	-	-	-
ml 1 N NaOH :	-	-	-	-	-	-	-	-	0,4	1	1,6	3,6
F. pH :	3,37	3,05	3,83	4,39	5,12	5,16	5,87	6,6	6,82	7,03	7,62	9,15
FT (30 min.) :	9,45	14	4,35	3,25	3,95	4,25	6,65	4,65	3,65	3,55	1,85	1,65
F. COD :	52	56	43	42	45	45	57	63	72	72	72	71

The results of Section D.I are presented graphically in Figures 6.13 and 6.17.

D.II Coagulant : Lime

Lime dosage	:	200	300	400	500	700	900	1000	1200	1600
F. pH	:	9,53	9,93	10,67	11,1	11,65	11,95	12,1	12,1	12,1
FT (40 min.)	:	16,85	14,85	18,85	4,35	0,95	1,05	0,63	0,53	-
F. COD	:	89	83	80	64	50	45	45	45	42

The results of Section D.II are presented graphically in Figure 6.14.

APPENDIX L

RESULTS OF STATISTICAL ANALYSES

L.1 Elaboration of the final COD test results presented in Appendix G

The results reported in Tables L.1 and L.2 are the results of the regression analysis done on the final COD test values reported in Appendix G. The general form of the regression curve is $y = bo + b_1 \; x \; b_2 \; x^2 + b_3 \; x^3$.

Incorporation of results in the sense explained in Section 3.5 is denoted by +.

TABLE L.1

Coagulant : Alum

Alum dosage (mg/l):	100		200 + 300		400 + 500	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
	3	49	3	48,2	3,5	44,9
	4	37	4	31	4	31,1
	4,5	33,7	4,5	26,6	4,5	23,7
	5	32	5	24,4	5	21
	5,5	31,7	5,5	24,2	5,5	21,3
	6	32,6	6	25,6	6	23
	6,5	34,5	6,5	28,5	6,5	24,2
	7	37	7	32,4		
b_o :	143,9		187,2		462	
b_1 :	-49,5		-73,2		-231	
b_2 :	6,78		10,2		39,8	
b_3 :	-0,26		-0,41		-2,25	
Correlation coefficient :	0,8		0,89		0,83	
Standard error (mg/l) :	3,06		1,99		2,83	

The regression analysis results reported in Table L.1 have meaning only in the pH range betweem 3,5 and 7. Below pH 3,5 flocs were not formed - see Appendix G, Section A.I, and Figure 2.3-(a) - and consequently, a slight COD removal occurred. The slight COD removal that was detected was due to settling of a portion of the particulate matter of the effluent during the test performance period, as well as to the death- due to low pH - and subsequent removal by settling of the small metazoa living in the effluent. Above approximately pH 7 the final COD values presented in Figures 4.8 and 4.9 tend to go parallel to the horizontal axis. The experimental points corresponding to final pH values below pH 3,5 and above pH 7 were not considered for the regression analysis.

TABLE L.2

Coagulant : Ferric chloride

FeCl$_3$ dosage (mg/l):	50		100		200+300+400+500	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
					2	37,7
	2,5	34	2,5	34,3	2,5	28
	3	33,3	3	27,2	3	21,3
	3,5	32,9	3,5	23	3,5	17,2
	4	32,5	4	21,4	4	15,3
	4,5	32,9	4,5	21,6	4,5	15,2
	5	33,3	5	23,2	5	16,6
	5,5	34	5,5	25,6	5,5	19,1
	6	35	6	28,4	6	22,3
	6,5	36,4	6,5	31	6,5	25,9
	7	38	7	33	7	29,4
b_o :	42		132		113,7	
b_1 :	-4,62		-65,1		-55,4	
b_2 :	0,58		12,15		9,69	
b_3 :	-		-0,69		-0,5	
Correlation coefficient :	0,76		0,97		0,83	
Standard error (mg/l) :	1,6		1,23		3,33	

The results reported in Tables L.1 and L.2 are presented graphically in Figures 4.13 and 4.14 respectively.

The regression analysis results reported in Table L.2 have meaning only for pH values between pH 2 and 7. Below pH experimental points were not available to establish the relationship, and above pH 7 the points were rejected for similar reasons to those previously mentioned in the case of alum. According to Figure 2.3-(b), precipitation of ferric hydroxide may occur as low as approximately pH 1,5. The experimental points corresponding to final pH below 2,5 and above 7 were not considered for the regression analysis.

L.2 Elaboration of the final turbidity test resulults presented in Appendix G

The statistical evaluation deals with test results obtained after 60 minutes settling. If the final turbidity after 60 minutes settling is denoted as FRT and the final pH as FpH, linear regression of the log (FRT) on the log (FpH) values may be considered. This was in fact done using the Wang calculator, System 2200, in a similar manner to the one employed when regression analysis of the final COD test results was done. However, the resulting regression line from regression of log (FRT) on log (FpH) did not pass through the experimental points, but formed an angle with the zone of scatter. This occurred in spite of the fact that the experimental points lay closer to the vertical line than to the horizontal, which meant that there was a strong dependence of log (FRT) on log (FpH) - see Figures 4.15, 4.16. This anomaly was due to the specific problems arising when linear regression in a log-log scale is considered. To overcome this problem linear regression of log (FpH) on log (FRT) was considered instead. The fit of the regression line in relation to the zone of scatter was satisfactory in this case. The general expression of the straight line is $y = b_o + b_1 x$, where y is log (FpH) and x is log (FRT). The results of the regression analysis are presented in Tables L.3 and L.4 for alum and ferric chloride coagulations, respectively.

The regression analyses results reported in Tables L.3 and L.4 have meaning only within the pH ranges between 3,5 and 9 for alum, and between 2,5 and 9 for ferric coagulations. The reason the lower limit was set is explained in Section 4.3.3 of Chapter 4. The higher limit was set because no experimental points were available above pH 9.

TABLE L.3

Coagulant : Alum

FRT :	10	5,01	3,16	2	1,26	0,93	0,63
Log (FRT) :	1	0,7	0,5	0,3	0,1	-0,03	-0,2
Log (FpH) :	0,595	0,648	0,683	0,717	0,752	0,775	0,805
FpH :	3,93	4,44	4,8	5,21	5,65	5,95	6,38

The parameters b_o and b_1 have the following values:

$b_o = 0{,}769$ $\qquad$ $b_o = -0{,}17$

The correlation coefficient is equal to 0,908.

TABLE L.4

Coagulant : Ferric chloride

FRT :	10	5,01	3,16	2	1,26	0,93	0,63
Log (FRT) :	1	0,7	0,5	0,3	0,1	-0,03	-0,2
Log (FpH) :	0,534	0,589	0,626	0,663	0,699	0,723	0,754
FpH :	3,42	3,88	4,22	4,6	5	5,28	5,67

The parameters b_o, b_1 and the correlation coefficient have the following values:

$b_o = 0{,}718$ $\qquad$ $b_1 = -0{,}183$

Correlation coefficient = 0,795.

The values of the calculated correlation coefficients well exceed the critical values given in the statistical tables under the assumption that there is no correlation between the variables and that the observations were drawn by chance alone at the 1 per cent level of significance. This means that with 1 per cent probability of being wrong a relationship does exist.

L.3 Elaboration of the final COD test results presented in Appendix I

The results reported in Tables L.5 and L.6 are the results of regression analyses done on the final COD test results reported in Appendix I. The general form of the regression curve is:

$y = b_o + b_1 x + b_2 x^2 + b_3 x^3$.

Incorporation of results in the sense explained in Section 3.5 is denoted by +.

TABLE L.5

Coagulant : Alum

Coagulant dosage: (mg/l)	100		200		300+400+500	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
	3,5	56	3,5	45,8	3,5	46,6
	4	42,9	4	38	4	36,4
	4,5	35,8	4,5	33	4,5	30,8
	5	33,5	5	30,9	5	28,9
	5,5	34,7	5,5	31,6	5,5	29,6
	6	38,3	6	35,2	6	31,8
	6,5	42,9	6,5	41,6	6,5	34,3
	7	47,7	7	50,8	7	36,2
b_0 :	421		180		344	
b_1 :	-195,6		-58,2		-162	
b_2 :	31,8		5,67		27	
b_3 :	-1,65		-		-1,46	
Correlation coefficient :	0,957		0,817		0,668	
Standard error (mg/l) :	1,68		2,23		1,94	

TABLE L.6

Coagulant : Ferric chloride

Coagulant dosage: (mg/l)	100		200		300+400+500	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
			2	42,4	2	39,7
	2,5	73,2	2,5	35	2,5	31,5
	3	54,5	3	29,3	3	25,3
	3,5	41,3	3,5	25,2	3,5	21
	4	32,9	4	22,7	4	18,5
	4,5	28,7	4,5	21,9	4,5	18,1
	5	28,3	5	22,7	5	19,8
	5,5	31	5,5	25,2	5,5	23,6
	6	36,1	6	29,6	6	29,7
	6,5	43,3	6,5	35,2	6,5	38
	7	51,8	7	42,6	7	48,6

		100	200	300+400+500
(Continued)				
b_0	:	267,9	88,6	88,5
b_1	:	-117,4	-29,66	-30,7
b_2	:	17,7	3,29	2,97
b_3	:	-0,768	-	0,087
Correlation coefficient	:	0,91	0,81	0,977
Standard error (mg/l)	:	2,75	2,65	1,1

The regression analyses results reported in Tables L.5 and L.6 are presented graphically in Figures 5.10 and 5.11 respectively.

The regression analysis results reported in Table L.5 have meaning only between pH 3,5 and 7, while those of Table L.6 only between pH 2 and 7. The reasons are similar to those given in Section L.1.

L.4 Elaboration of the final turbidity test results presented in Appendix I, Section A.I

Employing the method described in Section L.2 the following regression analysis results were obtained:

TABLE L.7

Coagulant : Alum

FRT	:	10	7,94	2,51	0,63	0,158
Lot (FRT)	:	1	0,9	0,4	-0,2	-0,8
Log (FpH)	:	0,629	0,643	0,715	0,801	0,887
FpH	:	4,25	4,39	5,19	6,32	7,71

The parameters b_0 and b_1 as well as the forrelation coefficient have the following values:

$b_0 = 0{,}772$ $b_1 = -0{,}143$

Correlation coefficient : 0,85

The results reported in Table L.7 have meaning only between pH 3,5 and 7. Below pH 3,5 stable colloids did not appear, while above pH 7 no experimental data were available.

L.5 Elaboration of the final COD test results presented in Appendix K

The regression analyses results reported in Tables L.8 and L.9 below are the results of the regression analyses done on the final COD values reported in Section A.I (Table L.8), and A.II and B (Table L.9) of Appendix K. The results reported in Section A.II of Appendix K were considered together with those reported in Section B of the same Appendix, because the initial quality of the bulk sample used to perform the tests reported in Section A.II was similar to that of the bulk sample used for the tests reported in Section B. The final COD results reported in Section B were plotted together with the final COD results reported in Section A.II. These are presented graphically in Figure 6.7.

Table L.8

Coagulant : Alum

Alum dosage (mg/l):	100		200+300		400+500+600+700+800	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
	4	93,6	4	83,5	4	74,3
	4,5	69,7	4,5	60,9	4,5	49,6
	5	54,6	5	49,5	5	40,4
	5,5	48,2	5,5	46,6	5,5	41,3
	6	50,2	6	49,4	6	47
	6,5	61,6	6,5	55,2	6,5	52,1
	7	81,5	7	61,3		
b_o :	599		995		1480	
b_1 :	-196		-456		-749	
b_2 :	17,5		71,6		128	
b_3 :	-		-3,64		-7,2	
Correlation coefficient :	0,991		0,978		0,92	
Standard error (mg/l) :	2,12		1,5		3,86	

TABLE L.9

Coagulant : Ferric chloride

$FeCl_3$ dosage (mg/l):	100		200+300+400+500		600+700+800	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
	2	148,9		63,8	2	62
	2,5	106,3	2,5	52,6	2,5	49,5
	3	75,5	3	43,7	3	40,1
	3,5	54,8	3,5	37,1	3,5	33,5
	4	42,9	4	32,9	4	29,7
	4,5	38,2	4,5	31	4,5	28,2
	5	39,4	5	31,6	5	28,9
	5,5	45	5,5	33,9	5,5	31,7
	6	53,6	6	38,7	6	36,2
	6,5	63,7	6,5	45,7	6,5	42,2
	7	73,8	7	54,8	7	49,6
b_o :	463,7		133,8		147,9	
b_1 :	-225		-45		-58,7	
b_2 :	37,6		5,1		8,49	
b_3 :	-1,9		-0,044		-0,3	
Correlation coefficient :	0,994		0,872		0,856	
Standard error (mg/l) :	1,38		3,69		5,87	

The regression analysis results reported in Table L.8 have meaning only in the pH range between 3,5 and 7 for similar reasons to those explained in Section L.1. The experimental points corresponding to final pHs below 3,5 and above 7 were not considered for the regression analysis. A regression analysis was also done on the final COD results presented in Section C and D.I of Appendix K. The results are presented in Tables L.10 and L.11 respectively.

TABLE L.10

Coagulant : Ferric chloride

$FeCl_3$ dosage: (mg/l):	200		300		400	
	Final pH	Final COD	Final pH	Final COD	Final pH	Final COD
			2	72,2		
	2,5	105	2,5	61,6	2,5	66,7
	3	78	3	53,3	3	54,3
	3,5	58,8	3,5	45	3,5	45,5
	4	46,8	4	42,9	4	39,8
	4,5	41,3	4,5	40,9	4,5	37,1
	5	41,5	5	41	5	37,2
	5,5	46,7	5,5	43,4	5,5	39,9
	6	56	6	48	6	44,8
	6,5	68,9	6,5	55,1	6,5	51,7
	7	84,4	7	64,4	7	60,4
b_o :	388		133		189	
b_1 :	-169		-38		-71,4	
b_2 :	25,1		3,7		9,82	
b_3 :	-1,01		0,049		-0,319	
Correlation coefficient :	0,976		0,97		0,974	
Standard error (mg/l) :	3,23		2,01		2,01	

TABLE L.11

Coagulant : Ferric chloride

Coagulant dosage : 100 mg/l

Final pH :	2,5	3	3,5	4	4,5	5	5,5	6	6,5	7
Final COD :	74	58,3	47,8	42,61	41,8	44,4	49,7	56,7	64,4	72,1

The parameters are: $b_o = 282$, $b_1 = -133$, $b_2 = 23$, $b_3 = -1,19$. The correlation coefficient is equal to 0,988 and the standard error to 2,1 mg/l.

The regression curves whose parameters are reported in Tables 1.(, L.10 and L.11 have meaning only between pH 2 and 7 for similar reasons to those explained in Section L.1. The experimental points corresponding to final pH below 2,5 and above 7 were not considered for the regression analyses.

The results reported in Table L.8, L.9, L.10 and L.11 are presented graphically in Figures 6.19, 6.19, 6.20 and 6.21, respectively.

L.6 Elaboration of the final turbidity test results presented in Sections A.I and A.II of Appendix K

Employing the method described in Section L.2 the following regression analysis results were obtained.

TABLE L.12

Coagulant : Alum

FRT :	10	5,01	3,16	2	1,26	0,93	0,63
Log (FRT) :	1	0,7	0,5	0,3	0,1	-0,03	-0,2
Log (FpH) :	0,638	0,69	0,726	0,761	0,796	0,819	0,849
FpH :	4,34	4,9	5,32	5,77	6,25	6,59	7,06

The parameters are: b_o = 0,814, b_1 = -0,175.

The correlation coefficient is equal to 0,929.

TABLE L.13

Coagulant : Ferric chloride

FRT :	10	5,01	3,16	2,1	1,26	0,93	0,63
Log (FRT) :	1	0,7	0,5	0,3	0,1	-0m03	-0,2
Log (FpH) :	0,594	0,633	0,66	0,686	0,712	0,729	0,752
FpH :	3,93	4,29	4,57	4,85	5,15	5,35	5,65

The parameters are: b_o = 0,725, b_1 = -0,137.

The correlation coefficient is equal to 0,946.

The regression lines whose parameters are reported in Tables L.12 and L.13 have meaning between pH 3,5 and 9 the former and between pH 2,5 and 7,5 the latter. The reasons are similar to those explained in Section L.2.

L.7 Elaboration of the remaining turbidity regression analysis results presented in Sections L.2, L.4, and L.6 of the present Appendix

Considering the parameters b_o and b_1 reported in Tables L.3, L.4, L.7, L.12 and L.13 and reporting them together Table L.14 is made:

TABLE L.14

Effluent	MMP		MHT	AMP	
Coagulant	Al	Fe(III)	Al	Al	Fe(III)
b_o	0,769	0,718	0,772	0,814	0,725
b_1	-0,17	-0,183	-0,143	-0,175	-0,131

It may be observed that the b_o values for the alum are higher than those for ferric coagulations. Calculating the mean b_o value separately for alum and ferric coagulations the following values are obtained:

$\bar{b}_o$ (Al) : 0,785 $\bar{b}_o$ (Fe(III)) : 0,721

No clear pattern emerges from comparison of the b_1 values. The mean b_1 value for both alum and ferric coagulations is equal to 0,160. Attributing this value to both Al and Fe(III) coagulations the following general relationships may be obtained:

Al : $\log(FpH) = 0,785 - 0,160 \log(FRT)$ (1)

Fe(III) : $\log(FpH) = 0,721 - 0,160 \log(FRT)$ (2)

Solving both (1) and (2) for log(FRT) the following equations are obtained:

Al : $\log(FRT) = 4,82 - 6,25 \log(FpH)$ (3)

Fe(III) : $\log(FRT) = 4,51 - 6,25 \log(FpH)$ (4)

These equations are represented graphically in Figure 7.16. They may be considered as approximately relating the remaining turbidity after coagulation to the final pH. Each may be considered valid within the following pH range:

Equation (3) : $3,5 \leq pH \leq 9$

Equation (4) : $2,5 \leq pH \leq 9$.

APPENDIX M

COST ESTIMATION OF CHEMICALS REQUIRED TO PRODUCE OPTIMUM COAGULATION

The cost of the chemicals used for the treatment of each effluent was estimated separately for alum, ferric chloride, and lime coagulations. This was based on 1000 litres of effluent and on the following prices (1975 prices):

Chemical	Cost
$Al_2(SO_4)_3.16H_2O$	R 61/ton
$Al_2(SO_4)_3$	R112,3/ton (or 11,2 cents/kg)
$FeCl_3.6H_2O$	R240/ton
$FeCl_3$	R400/ton (or 40 cents/kg)
$Ca(OH)_2$, as CaO	5 cents/kg
H_2SO_4 (98%)	5,5 cents/kg
NaOH(100%)	36 cents/kg
Polymer	R1/kg (approximate average)

The cost of carbon dioxide was calculated from the cost of coke required to produce it. This was done in the following way:

Coke contains approximately 80 per cent carbon. The price of coke is R30 per ton (1975), or 3 cents/kg. From 1 tone of coke 1 x 0,8 tons of carbon, or 2,93 tons of carbon dioxide, are produced. The approximate price of carbon diozide is thus, R30/2,93 tons. If this price is doubled to include amortization as well as maintenance and labour costs, the approximate cost of the carbon dioxide produced in this way would be R60/2,93 tons = 2 cents/kg.

The cost of the chemicals required for optimum coagulation is presented in Sections A, B and C below, separately for each cogulant. It is expressed in cents per 1000 litres of raw effluent and does not include any cost for polymers. The difference, however, would be very small in the latter case (the overall average increase would be about 0,1 cent per 1000 litres for each milligram of polymer).

In the case of lime coagulation the costs with and without the required carbon dioxide to bring the pH of the treated effluents down to the initial level before coagulation are reported. The amount of carbon dioxide required in each case was calculated from the difference in concentration of the Ca^{2+} ions determined before and after coagulation. This amount is equal to the stoichiometrically required to precipitate an amount of Ca^{2+} ions equal to the determined difference in concentration.

A. MILNERTON MATURATION POND EFFLUENT

1. Coagulant : Alum

$Al_2(SO_4)_3$ dosage	:	100	200	300	400	500
Final COD	:	32	24	24	21	21
ml 1 N NaOH	:	-	-	1,1	2,3	4
ml 1 N H_2SO_4	:	2,3	0,7	-	-	-
Cost	:	1,7	2,4	4,9	7,7	11,3

2. Coagulant : Ferric chloride

$FeCl_3$ dosage	:	50	100	200	300	400	500
Final COD	:	32	21	15	15	15	15
ml 1 N NaOH	:	-	-	-	0,8	2,6	4,1
ml 1 N H_2SO_4	:	3	2,2	1	-	-	-
Cost	:	2,8	4,5	8,2	13,5	19,7	25,9

3. Coagulant : Lime

Initial (Ca^{2+}) : 50 mg/l

$Ca(OH)_2$ dosage	:	200	300	500	700	900	1000
Final (Ca^{2+})	:	-	85	120	160	180	265
Final COD	:	40	32	26	22	21	21
Cost without CO_2	:	1	1,5	2,5	3,5	4,5	5
Cost with CO_2	:	-	1,5	2,6	3,7	4,7	5,4

The above results of Section A are presented graphically in Figure 7.10.

B. MILNERTON HUMUS TANK EFFLUENT

1. Coagulant : Ferric chloride

$FeCl_3$ dosage	:	100	200	300	400	500
Final COD	:	29	22	18	18	18
ml 1 N NaOH	:	-	-	-	2	4
ml 1 N H_2SO_4	:	3	1,5	-	-	-
Cost	:	4,8	8,4	1 2	18,1	25,7

2. Coagulant : Alum

$Al_2(SO_4)_3$ dosage	:	100	200	300	400	500
Final COD	:	33	31	29	29	29
ml 1 N NaOH	:	-	-	-	1	2
ml 1 N H_2SO_4	:	3	1,5	-	-	-
Cost	:	1,9	2,6	3,3	5,9	8,4

3. Coagulation : Lime

Initial (Ca^{2+}) : 55 mg/l

$Ca(OH)_2$ dosage	:	500	1000	1500	2000	2500	3000
Final COD	:	31	29	27	26	25	25
Final (Ca^{2+})	:	120	265	400	450	-	-
Cost without CO_2	:	2,5	5	7,5	10	12,5	15
Cost with CO_2	:	2,6	5,4	8,2	10,8		

The above results of Section B are presented graphically in Figure 7.11.

C. ATHLONE MATURATION POND EFFLUENT

1. Coagulant Alum

$Al_2(SO_4)_3$ dosage	:	100	200	300	400	500	600	700	800
Final COD	:	48	47	47	40	40	40	40	40
ml I N NaOH	:	-	-	-	1	3,1	4,1	5	6
ml 1 N H_2SO_4	:	3	1,2	-	-	-	-	-	-
Cost	:	1,9	2,5	3,3	5,9	10,0	12,6	15,0	17,6

2. Coagulant Ferric chloride

$FeCl_3$ dosage	:	100	200	300	400	500	600	700	800
Final COD	:	38	31	31	31	31	28	28	28
ml 1 N NaOH	:	-	-	0,3	2	3,5	5	6,5	8
ml 1 N H_2SO_4	:	3,1	1,3	-	-	-	-	-	-
Cost	:	4,8	8,3	12,4	18,1	25,0	31,2	37,3	43,5

3. Coagulant : Lime

Initial (Ca^{2+}) : 38 mg/l

$Ca(OH)_2$ dosage	:	500	1000	1500	2000	3000
Final COD	:	89	81	48	39	32
Final (Ca^{2+})	:	-	265	-	450	-
Cost without CO_2	:	2,5	5	7,5	10	15
Cost with CO_2	:	-	5,5	-	10,9	-

All the above results of Section C are presented graphically in Figure 7.12.

APPENDIX N

ERROR ANALYSIS

An examination of the results which were presented graphically in Chapters 4, 5 and 6 shows that a certain degree of experimental error was involved. Random variations in experimental results, if caused by errors inherent in the experimental and analytical systems, were impossible to eliminate. It is therefore important to be aware not only of where these errors can arise, but also of their approximate magnitudes, so that an estimate can be made of the degree of scatter attributable to them. The sources of possible error are outlined below:

N.1 CHEMICAL OXYGEN DEMAND

The possible sources of variation inherent in the experimental system and analytical technique, which could have affected COD removal, are listed and discussed below:

A. Errors inherent in the jar test procedure

(a) Temperature:

The tests were performed at room temperature, but random variations in temperature have affected the rate of reactions. However, the variation due to this error is not considered high.

(b) Period of Stirring:

Variations in the duration of stirring (due to a certain time lag in between additions) inherent in the method of coagulant addition employed,may have effected the results. The variation of the final COD results due to this effect is not, however, considered high, because the destabilization step remained practically unaffected by prolonged stirring.

(c) Stirring Speed:

The accuracy of the speed of the stirrer was ± 2 per cent of maximum speed, according to the manufacturer of the jar tester. This variation had a negligible effect on the final COD, because it hardly affected the destabilization mechanism.

(d) Sample Volume:

A variation in the final volume of the water in the jars was introduced after the coagulant addition. This was due to the different coagulant solution volumes added in each jar. The variation of the final COD due to this factor could have been as high as 5 per cent in some cases, but in most cases was lower.

(e) pH

The pH was measured by means of a Corning, Model 12, electronic pH meter. According to its manufacturer the precision of this instrument is ± 0,0002 pH and the accuracy ± 0,01 pH if the expanded scale is used in both cases. The variation of the final COD results due to this variation in pH is not considered high.

B. Errors Inherent in the Analytical Method

For the determination of COD the standard reflux method under controlled conditions was employed. From COD determinations conducted using standard solution of potassium acid phthalate it was found that at the 50 mg/l COD level the accuracy of the reflux method was 8 per cent (±4 mg/l), while at the 25 mg/l COD level it was decreased to 10 per cent (±2,5 mg/l). The precision of the analysis at the 50 mg/l COD level was found to be 4 per cent (±2 mg/l), while at the 15 mg/l COD level it was decreased to 10 per cent (±1,5 mg/l).

During the preliminary tests, in which the COD was mainly determined by means of the autoanalyzer, the precision of the COD determination (according to the manufacturer of the autoanalyzer) was 3,1 per cent at the 120 mg/l COD level (at 95 per cent level of significance) and 0,92 per cent at the 50 mg/l COD level.

If the standard errors of the estimates reported in Sections L.1, L.3 and L.5 of Appendix L are considered and reported together, Table N.1 may be made.

TABLE N.1

Standard Error of Final COD Estimate

Effluent :	MMP		MHT		AMP	
Coagulant :	$Al_2(SO_4)_3$	$FeCl_3$	$Al_2(SO_4)_3$	$FeCl_3$	$Al_2(SO_4)_3$	$FeCl_3$
Standard Error, mg/l:	3,06	1,6	1,68	2,75	2,12	1,38
	1,99	1,23	2,23	2,65	1,5	3,69
	2,83	3,33	1,94	1,1	3,86	5,87

The mean value of the standard errors reported in Table N.1 may be considered as a representative value of the overall precision associated with the COD determination (that is with both the experimental and analytical systems). The mean standard error is equal to 2,5 mg/l.

If the precision of the standard reflux analytical method for COD determination (mentioned under N.1-B above) is considered and compared with the mean standard error, it is readily observed that the mean standard error is higher than the precision of the analytical method. The difference is attributed to the following sources of error:

(i) Those mentioned under N.1-A.

(ii) Inaccurate pH reading.
This occurred when the required time period for the needle of the pH meter to settle to a certain reading was not quite allowed for.

(iii) Prolonged storage of raw effluent's bulk samples.
This resulted in deterioration of the raw effluent quality which exceeded the acceptable limit. This deterioration, although had a negligible effect on the minimum residual COD after coagulation - see Section 6.3.4 -, might have had an effect on intermediate final COD values. The effect of the prolonged storage had been anticipated and was tried to be minimized during the course of the experiments by performing those tests of a certain series which required material from the same bulk sample to be used during the same day and as fast as possible. To achieve this, a coagulation test was performed while the samples from the previous test were being analyzed for COD.

The above-mentioned mean standard error combined with the accuracy of the standard reflux method employed for COD analysis - see Section N.1-B - suggest that the maximum deviation between two reported final COD values could be as high as 10 mg/l ((2,5+2,5)x2=10) at the 25 mg/l COD level, and as high as 13 mg/l at the 50 mg/l COD level. In this sense, each of the contours shown in Figures 4.13, 4.14, 5.10, 5.11, 6.18, 6.19, 6.20 and 6.21 does not correspond exclusively to the reported in it final COD value, but may correspond to a zone as wide as ±5mg/l from the reported value at the level of 25 mg/l final COD, and to a zone as wide as ±6,5 mg/l from the reported value at the level of 50 mg/l final COD.

N.2 TURBIDITY

The sources of error responsible for variations in the turbidity results are outlined below:

A. Errors inherent in the analytical technique employed for the turbidity determination.

The turbidity was always measured by means of a Hach turbidimeter, model 2100A, whose accuracy and precision were 2 per cent at all levels.

B. Errors inherent in the pH determination.

The pH determination was subject to variations as mentioned under N.1-A-(d). The source of error mentioned under (ii), page N-3, has probably affected the correlation between final turbidity and final pH.

C. Errors inherent in the method of sampling of the supernatant.

Occasionally, small unsettled flocs were collected during sampling which resulted in slightly increased final turbidity values.

The standard error of the estimates obtained from the regression analyses - Sections L.2, L.4 and L.6 of Appendix L - does not correspond and has no relation to the final turbidity itself but only to the loagarithm of the final turbidity. This occurred because of the logarithmic scale used. Consequently, the standard error figures which were obtained cannot be related to the turbidity itself and, in this sense, have no meaning. This is the reason why these figures have not been reported.

N.3 COLOUR

The method used for colour determination employed a Beckman, Model 1211, colorimeter. The precision of this method is 0,2 per cent, according to the manufacturer of the instrument. No accuracy data are provided, presumably because of the fact that no method free of error exists to measure colour.

N.4 CONCENTRATION OF IONS IN SOLUTION

The concentration of the metal ions in solution was measured by means of a spectrophotometer whose precision was 1 per cent, according to its manufacturer. The concentration of anions in solution was measured by means of an autoanalyzer. For Cl^- ion determination the precision was

2,3 per cent at the 10 mg/l level. For this determination the Micromedic Pipette was employed to dilute the samples to the appropriate Cl^- level for subsequent determination of this level via the autoanalyzer. The coefficient of variation of the Pipette was 0,1 per cent.

N.5 RESIDUE

The accuracy and precision of the methods employed for the determination of the total solids, total dissolved solids, total suspended solids and total volatile solids levels are mentioned in Standard Methods, (28), where the reader is referred to.

CONVERSION TABLE FOR TURBIDITY UNITS*

	Turbidity unit:	Kieselgur Units (SiO_2)	Absolute Units A.E.	Formazin Turbidity Units E.B.C.	Formazin Turbidity Units A.S.B.C.	Jackson Turbidity Units	Helm Units ($BaSO_4$)	Mastic Units	Langrohr Units reciprocal
1	Kieselgur Units according to German Standards method (1 mg SiO_2 per litre dist. H_2O = 1 ppm)	1	*0,000445*	*0,1*	*6,9*	*1*	*4*	*8*	*0,000465*
1	Absolute Units A.E. (Zeiss–Pulfrich Turbidity Unit)	*2250*	1	*225*	*15 500*	*2250*	*9000*	*18000*	*1,05*
1	Formazin Turbidity Units E.B.C.	*10*	*0,00445*	1	*69*	*10*	*40*	*80*	*0,00465*
1	Formazin Turbidity Units A.S.B.C.	*0,145*	*0,000065*	*0,0145*	1	*0,145*	*0,58*	*1,16*	*0,0000675*
1	Jackson Turbidity Units	*1*	*0,000445*	*0,1*	*6,9*	1	*4*	*8*	*0,000465*
1	Helm-Units ($BaSO_4$–Suspension)	*0,25*	*0,00011*	*0,025*	*1,72*	*0,25*	1	*2*	*0,000116*
1	Mastic-Units (1 drop mastic solution per 50 ml dist. H_2O; 50 drops ~ 1 ml)	*0,125*	*0,000056*	*0,0125*	*0,86*	*0,125*	*0,5*	1	*0,0000582*
1	Langrohr Units according to German Standards method, reciprocal (cm light path at 25 mm dia.)	*2150*	*0,956*	*215*	*14835*	*2150*	*8600*	*17200*	1

* SIGRIST - PHOTOMETER AG.