6-30-1970

Phosphate removal from sewage using a combination of ferric chloride and a polymeric flocculant

Ravindra C. Patel
New Jersey Institute of Technology

Recommended Citation

Patel, Ravindra C., "Phosphate removal from sewage using a combination of ferric chloride and a polymeric flocculant" (1970). *Theses*. 2389.
https://digitalcommons.njit.edu/theses/2389

PHOSPHATE REMOVAL FROM SEWAGE USING A COMBINATION OF FERRIC CHLORIDE AND A POLYMERIC FLOCCULANT

BY

RAVINDRA C. PATEL

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

Newark, New Jersey
1970

APPROVAL OF THESIS

PHOSPHATE REMOVAL FROM SEWAGE USING A COMBINATION OF FERRIC CHLORIDE AND A POLYMERIC FLOCCULANT

BY

RAVINDRA C. PATEL

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED:

NEWARK, NEW JERSEY

JUNE, 1970

ABSTRACT

The present work is concerned with a newer technique and approach to the problem of phosphate removal from waste water. This includes the removal of phosphate from the sample of activated sludge, i.e., a sample from the aeration tank of the secondary sewage treatment. The phosphate is removed by using ferric chloride as a precipitating agent and a cationic polyelectrolyte (P.E.) as a flocculating agent. Results of this study showed that: (a) P.E. addition gives a significant improvement in phosphate removal over that obtained by ferric chloride alone. In some cases the phosphate removal increased from 92 to 96.5 per cent by the addition of a small amount of cationic P.E., (b) There is a general trend in phosphate removal that for a given amount of phosphate in the sewage sample one P.E. concentration gives a peak removal. Below and above this concentration the removal is lower then the peak. (c) The amount of phosphate left after the total treatment is approximately the same in all tests and amounts to 2.6 to 2.7 ppm. (d) A correlation between initial phosphate content and the amount of P.E. needed to obtain the peak removal is a straight line on log-log graph paper.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

I. INTRODUCTION

Like plant and animal organisms, lakes and streams have life spans. Lakes and reservoirs are not permanent features on the landscape. The life span of lakes is normally reckoned in millenniums or even eons of time.

A lake begins as a body of cold, clear water. It is relatively a barren body of water because it is not able to support much biological life. Streams from its drainage basin soon bring in silt, (which settles to the bottom) and nutrients, which encourage the rapid growth of plants and animals. As aquatic organisms increase and organic deposits pile up on the bottom, the lake gets smaller and shallower. The water gets warmer; plants take root in the bottom and gradually take over space. The lake after many years then becomes a marsh, bog and finally, dry land. This natural aging process is called eutrophication. But man in both his enterprise and short sighted nature has accelerated the rate of eutrophication.

As previously stated eutrophication is characterized by a build up of nutrients in the lake environment. Pollution by this over supply of nutrients has been traced to the wastewaters of cities and industries and also to agricultural run off. Over enrichment of lakes and streams had led to the over production of algae and other photosynthetic life upsetting the natural balance in food chain and interferring with many water uses.

For the most part, compounds of nitrogen and phosphorous have received the blame for these problems because of the important role they play in plant growth, although other nutrients may also be involved. In addition, certain compounds and phosphorous have been reported to cause some problems in water quality and treatment.

Among the phosphorous containing compounds, the inorganic phosphates are most significant. These occur largely in the orthophosphate (PO_4^{-3}) form, or as condensed phosphates such as metaphosphate (PO_3^-), triphosphate ($P_3O_{10}^{-5}$), or pyrophosphate ($P_2O_7^{-4}$). The latter are gradually hydrolized in aqueous solution and finally revert to the ortho form.

The water quality and treatment problems that may result from the presence of nitrogen and phosphorous compounds may be divided into two groups: direct and indirect. The direct problems include such items as toxicity (where the presence of the compounds may represent a health hazard) and interference by one or more of these compounds in a water treatment process. The indirect problems caused by these compounds center around their ability to stimulate the growth of aquatic plants which can impair water quality.

There are specific facets of the problems which are important and as follows:

1. Hindrance to coagulation and sedimentation,
2. Adverse effects on hardness removal,
3. Growth of algae and other aquatic plants.

These are described, briefly, below.

1. Hindrance to coagulation and sedimentation. The increased use of synthetic detergents in the U.S. has led to an increase in the concentrations of the builder components in sewage (principally pyro and triphosphate salts). From this, considerable developed in assessing the influence of these builder constituents (and their degradation products) on the coagulation process in water treatment. As a result a number of studies have been reported in which tests have been employed to indicate the effects of various phosphate compounds on turbidity or color removal by coagulation and flocculation. In

addition, certain basic studies have been recently described which indicate the fundamental influence of phosphate compounds on coagulation. In general, the presence of pyrophosphate or triphosphate salts has been shown to interfere with the efficiency of the coagulation-flocculation-sedimentation process.

2. Adverse effects on hardness removal. There are some indications that the presence of certain condensed phosphate compounds can adversely affect hardness removal. In laboratory studies, Malina and Tryaporn(16) have reported that condensed phosphates interfere with lime-soda ash softening at concentrations of 0-3 mg/l and greater. Certain condensed phosphates can inhibit calcium carbonate precipitation. Orthophosphate ions do not exhibit threshold inhibition behavior with respect to calcium carbonate precipitation. High orthophosphate concentrations can, however, cause precipitation of other compounds such as calcium phosphate or hydroxy apatite.(28) The inhibitory phosphate concentration is a function of the total calcium concentration and other solution conditions. Corsaro *et al*(5) have argued that the inhibition mechanisms involve electric double-layer stabilization of the collodial calcium carbonate.

3. <u>Growth of algae and other aquatic plants</u>. The fertilization of water supplies by plant nutrients such as nitrogen and phosphorous must be ranked high on the list of problems facing water utilities. The results of a questionnarie (compiled by AWWA* Task Group) show that many water suppliers have water quality problems that can be related to the growth of aquatic plants. With the increased amounts of nitrogen and phosphorous containing compounds being used for domestic, agricultural and industrial purposes, the pollution of water supplies by these nutrients probably will cause greater numbers of problems in the future unless steps are taken to limit the influx of plant nutrients to water supplies.

The presence of excessive amounts of plant nutrients results in a host of water quality problems in addition to those caused by aquatic plants. Some aquatic plants are primarily producers of organic matter which serves as food for other organisms. The stimulation of algal growth often results in increased numbers of other plants and animals such as bacteria, sponges, protozoa, rotifer, crustacea, fungi, mollusca, etc. which may cause other water quality problems. Aquatic plants which may be directly stimulated by nutrients may be

---

*American Water Works Association

divided into two groups, algae and higher plants. Although higher plants may cause water supply problems, both the free floating and the attached algae can cause serious problems in water supplies. Largely, the growth of algae is determined by amount of sunlight, carbon dioxide and inorganic nutrients available. Since the amounts of sunlight and carbon dioxide are relatively constant during any season for a water, the key to the growth of excessive algae is the availability of inorganic nutrients, the two most significant being the nitrogen and phosphorous.

Algae have been reported to cause tastes and odors, clogging of filters, color and turbidity, chlorine demand, growth in pipes, cooling towers and on reservoir walls, corrosion, variable pH and hardness, floating scum, blockage of intake screens; and toxicity problems in water supplies. Palmer(19), McKee and Wolf(15) and others (1, 13, 20-25, 31 and 36) have presented excellent reviews and specific examples of the problems caused by algae in water supplies. Palmer reported that the algae most frequently causing water supply problems belong to 27 genera with asterionella, melosire, synedra and anabaene among the ones most often associated in filter clogging and odor pollution. Many rivers and lakes are subject to occasional algal blooms which may arise suddenly and persist for periods of sufficient duration to be of serious concern. The more highly fertilized waters experience frequent algal problems. For any one water supply, one normally finds a succession of algal blooms each causing specific problems. Algal blooms may be defined as blossom of algae, sudden burst of algae growth or springing up of algae.

CHAPTER II

II. Background

Inasmuch as most of the phosphates used as builders do not form insoluble materials in the carriage water, they tend to pass through present day sewage treatment plants and therefore are of real concern to those interested in controlling fertilization of aquatic areas.

The higher concentration of phosphates in sewage and effluents makes it necessary that consideration be given to removal of phosphorous from many effluents which previously would have been considered innocuous.

Approaches to Phosphate Removal

Since most of the phosphorous compounds found in waste water are not removed by conventional treatment processes, advance wastewater renovation methods and modifications of existing processes have been applied to the problems of removal of these nutrients. These treatment processes may be classified as biological, chemical, or physical.

At present, a major difficulty in designing or planning for removal of phosphorous is the lack of reliable information on the levels which minimize or eliminate their adverse effects. Much investigative work remains to be done to establish critical concentration levels for specific locations and to evaluate the effects of trace elements on biostimulation.

Accordingly, an effective phosphorous removal process must have two essential steps.

1. The conversion of soluble phosphates into an insoluble, suspended form, and
2. The permanent removal of the suspended phosphate from the waste stream.

Following is a discussion of processes to remove phosphate from sewage:

a. Adsorption on activated alumina. Yee(35) reported that activated alumina selectively adsorbs orthophosphates, polyphosphates, tripolyphosphates, and sodium hexametaphosphates--the forms of phosphate most commonly associated with stream pollution. The most sufficient mode of operation is by downflow through a bed packed with solid alumina. More than 99 per cent removal is accomplished for removal of phosphates in 5 to 25 ppm concentration. These concentration levels are comparable to those in water streams and in secondary waste treatment plant effluents, respectively. In both cases, the process should be directly applicable, providing solids in the waste solution do not clog the packed bed alumina.

Activated alumina treatment for phosphate removal neither adds salts to the treated water nor changes its basicity. Where packed bed operation is possible, it sorbs both the polyphosphates with an efficiency greater than 99 per cent.

b. Biological treatment. Biological treatment processes which have been used to remove phosphorous include conventional biological treatment such as activated sludge and trickling filters, modified activated sludge and algae harvesting.

Here the principle is the conversion of soluble phosphorous compounds to organically bound forms in biological cell tissue.

It has been demonstrated by Sawyer(30) that phosphorus can be effectively removed from sewage by the activated sludge process, provided the biological oxidation demand to phosphorus ratio is properly adjusted. This method involves addition of carbonaceous matter to provide more material for microbial synthesis and consequently is not practical unless a source of such food is available locally such as certain industrial waste. The method, however, has the advantage of fixing excess nitrogen in the activated sludge produced as well as phosphorus.

c. Harvesting of algae from artificially lighted ponds. Algae cultures, because of algae's relatively low C/P* ration. have been studied quite extensively for nutrients such as phosphorus, present in sewage plant effluents. This process has an economic value since it has been reported(27) that the daily contribution per capita to municipal sewage will produce from 0.12 to 0.14 pounds of protein. The protein has a potential value of $80.00 to $100.00 per ton of dry algae in areas short of food. In the United States, such proteins would be hard to sell except perhaps as an animal food supplement.

To remove nutrients from water using algae as the nutrient consuming medium, algae have been grown in oxidation ponds. However, high rate studies using algae in

---

*Carbon to Phosphorous ratio

a process similar to the activated sewage process have also been investigated. Phosphorous removal occurs either through metabolism and subsequent incorporation of the phosphorous in the algae cell tissues or through precipitation as calcium phosphate. The precipitation occurs when the pH in the pond is raised because of the utilization of the carbon dioxide by the algae culture.

In oxidation ponds phosphorous can be removed from municipal sewages in warm climates or during the summertime in more northern areas. It is doubtful, if much can be done to produce effective phosphorous removal in northern climates where ponds will be ice covered in the wintertime.

In oxidation ponds design factors would involve a one-foot deep pond with a detention time of 12 days with supplemental artificial illumination over the entire pond to provide at least 200 foot candles at the pond surface and operating at approximately 60% of the time.

The least expensive and reliable method to harvest the algae is chemical flocculation and air drying on sand beds. In actual field work, algae harvesting employing alum dosages of 50mg/l with a three minute mixing and 15 minute settling time followed by air drying on sand beds at 6400 square feet per acre oxidation pond would be required. No allowance needs to be made for the disposal of the dried algae because it can probably be disposed of with the other solid wastes of the community at little additional cost.

Methods of removing phosphorous using algae in a process similar to the activated sludge treatment have been studied(2,3) in the laboratory and field pilot plants. In the laboratory where a 1,000 foot candle light source in the contact tank and an 800 foot candle light source on the algae growth tank provided sufficient light, orthophosphate was reduced from 9.7 mgP/l to 1.6 mgP/l. However in the field plant, the depth was too great, and the mean light intensity (100 foot candles) in the culture was not great enough to effect an appreciable pH rise and little phosphorous was removed. In order to produce sufficient light throughout the culture, optimum pond depth is less than one foot(18)

d. Ion exchange. The removal of phosphate ions PO_4^{-3} from sewage plant effluents by ion exchange requires the use of anion exchange resins. These resins are generally aliphatic amines.

Strong basic anion exchange resins were found to remove phosphates effectively from sewage plant effluents(8,9,17,). Or the phosphates were removed by 94.5 per cent from 2.8 to 0.16 mg P/l, in work by Eliassen(8). But since the anion exchange resin was employed on the chlorides were increased by 52 per cent from 179 to 370 mg Cl^-/l. Eliassen and Wyckoff(9) reported on some pilot plant runs in which phosphorus was reduced by 97 per cent, from 8.5 mg P/l to 0.25 mg P/l by resin Duolite A-102D.

Ion exchange resins may prove successful for removal of phosphates from sewage plant effluents provided:

(i) filtration of the secondary effluent for removal of any suspended particulate matter is economically feasible. That is, solids will not clog the bed after passage of relatively small volumes of waste.

(ii) the presence of residual COD does not foul the resin. To resolve this question, studies on the resin life with accelerated flow rates and repeated regeneration are required.

Disposal of the waste regenerant may provide some difficulty, and the practice so far is to neutralize these wastes to innocuous effluents. Other methods of removing phosphates such as chemical coagulation also involve the waste disposal of the coagulated and filtered solids.

One point in favor of ion exchange is that the concentration of phosphates to be removed is very low. In this low range of contaminants, ion exchange has traditionally been favored as a purification method.

e. Chemical methods. Rudolph(29) has reported on the removal phosphorus from sewage by coagulation with lime and has indicated it to be quite effective. Similar studies with sewage enriched with the complex phosphates, tripolyphosphate and tetrasodiumpyrophosphate, have shown them to be readily removed, also, without any appreciable increase in lime requirements. Ferric salts and aluminum sulfate have been proposed for coagulation of phosphates from sewage. Results of studies show that these coagulants are highly effective in removing all forms of phosphates. This ability of phosphate removal is attributed to any coagulant's ability to form insoluble phosphates at certain pH values.

Some literature on solutility products of ferric phosphate are consistent (values reported for the solubility product of ferric phosphate vary over fourteen orders of magnitude) with the solubility and complex formation equilibria of the iron (III)-phosphate system have been investigated using both U.V. absorption data and redox potential measurements the ferro-feri cell(10).

Solubility and Complex Formation Equilibria

No.	Equilibrium	Log of Equibibrium Constant* @ 25 deg C
1	I. Solubility of Phosphate	
	$Fe^{+3} + PO_4^{-3} = FePO_4$ (s)	23
	II.Complex Formation with Orthophosphate	
2	$Fe^{+3} + HPO_4^{-} + FeH_2PO_4^{+2}$	1.8
3	$Fe^{+3} + HPO_4^{-2} + FeHPO_4^{+}$	8.3
4	$a\ Fe^{+3} + b\ H_nPO_4^{3-n} = Fe_a(H_nPO_4)_6^{3a-b(3-n)}$	Evidence
	III. Hydrolysis of Fe^{+3}	
5	$Fe^{+} + OH^{-} = FeOH^{+2}$	11.8
6	$FeOH^{+2} + OH^{-} = Fe(OH)_2^{+}$	9.3
7	$Fe^{+3} + 3OH^{-} + Fe(OH)_3$	36

---

*See next page for description.

*These equilibria constants given here are approximate. The contents of equilibria 1, 2, 3, and 4 are quoted from reference(10). The constants of the other equilibria were selected from J. Schwarzenbach G. and Siller L.G., "Stability Constants", Chem. Soc., London, 1958.

In order to evaluate the chemical reaction tendency of metal ions with phosphate, the affinities of these useful ions to an OH^- ion and phosphate ion should be compared. For example compare reactions 3 and 5 and 1 and 7 in the above (or previous) table. The equilibrium constants show that OH^- has a stronger affinity for Fe^{+3} with HPO_4^{-2} or PO_4^{-3}. However, the extent of chemical interaction of Fe^{+3} with HPO_4^{-2} or PO_4^{-3} depends on the ratio $(HPO_4^{-2})/(OH^-)$ or $(PO_4^{-3}/(OH^-)^3$ respectively. Thus, with decreasing pH phosphate will have an increasing tendency to enter into the coordination sheath of the ferric ion. On the other hand, the solubility of ferric phosphate increases at low pH values. It has been found that at pH 5.3 $FePO_4$ is least soluble.

An interesting and promising modification of the chemical coagulation process is the precipitation of the phosphorus with a coagulant such as alum or iron and the removal of the precipitate in a high rate multiple medium filter bed such as that recently developed for water treatment by Culp(6) and Priday(26).

f. Complementary biological and chemical treatment processes involving modifications and combinations with biological oxidation. 1. Levin Process. Levin showed that certain modifications can be introduced in the activated sludge process which would make possible a removal of phosphate beyond that expected under normal operations. According to Levin, when the aeration rate in conventional activated sludge is 3 to 5 times greater than normal, microorganisms take up far more phosphorus than they need. This luxury uptake permits the process to utilize 1.2 to 1.3 mg P/liter.

Considering the levels of phosphorus now present in Today's sewage, it does not appear that these modifications will be worthwhile.

2. Chemical coagulation combined with high rate activated sludge. The process combining the conventional activated sludge with chemical precipitation of phosphates has been studied by Stumm(34) and also Nesbit(7). Stumm demonstrated that by adding chemicals after a short period

of activated sludge aeration, 1-2 hours rather than 6-8 which is conventional, it is possible to reduce significantly the detention time of the biological aeration stage. He also demonstrated that phosphates were removed. The cost of the chemicals treatment would be compensated for by a reduction in the cost of biological treatment resulting from shortened detention times. The benefit from such a scheme, if it worked, would only be to new activated sludge plants.

Recent work by Eberhardt and Nesbitt(7) was carried out to follow up on Stumm's ideas. They investigated the combination of the so-called high rate activated sludge (HRAS) process with chemical coagulation.

HRAS employs short aeration periods and high organic loadings and high mixed liquor solids concentrations to produce, as required and without the aid of added flocculating aids, a degree of treatment ranging from intermediate to complete. This process is commonly used in Europe and Great Britain.

HRAS was selected because its great solids concentration would produce better bioflocculation, less organic sludge and possibly improve removal or settleability of the precipitated inorganic phosphates by means of the solids contact principle.

Selection of a metallic salt for phosphate removal by precipitation was based on biological, as well as chemical, considerations since the reaction would occur in the mixed liquor, a portion of which would be returned to the aeration tank. Previous investigations(11) have shown that lime, ferric sulfate or chloride and aluminum sulfate to be the most effective chemical agents.

g. Electrochemical treatment of sewage. A method for treating raw sewage by mixing it with sea water has been developed. In this process, one gallon of sewage is added to 4 gallons of sea water and the solution is passed into a detention cell having a one-half hour mean residence time. The sea water and the sewage are not mixed, but are pumped into the cell separately so that the sewage, having a lower density than sea water, will be on top.

At the cathode, chlorine is formed which increases the pH of the solution. The chlorine ties up H^+ atoms leaving an excess of OH^-. This causes $Ca_3(PO_4)_2$ and $(Mg\ NH_4\ PO_4)$ to precipitate out the calcium and magnesium being supplied by the sea water.

The anode at the bottom of the cell releases H_2 gas which rises to the surface, carrying both the precipitates and raw sewage to the surface where it can be skimmed off. The chlorine acts as a disinfectant, saving some chemical cost. This method can bring the total phosphate concentration down to 0.7 ppm. The material is then discharged to the sea.

There are several disadvantages to this method. There must be a supply of sea water available since electrochemical removal of phosphates uses untreated sewage (the phosphate salts condensing on the sewage and then they rise to the top) but does not work well on secondary effluent. The amount of raw water (4 gal/gal of sewage water) increases the size of the plant to an inordinarily large size.

There are several possible solutions to these problems. An artificial sea water could be produced. Salts might be added to the sewage to make a sea-sewage water which could be treated as described. If the phosphate removal followed a secondary treatment plant, the suspended phosphate precipitates might be removed by filtration.

The low electrical cost makes this seem to be an economical process. The problems unresolved are:

(i) The factor of five dilutions, a 100 million gallon/day plant would have to handle 500 million gallon/day total water volume.

(ii) The removal of unsettled phosphate precipitates.

(iii) The supply of a synthetic sea water for communities not on the ocean.

h. Chemical phosphorous removal using polyelectrolytes. These techniques involve the conversion of soluble phosphorous into an insoluble form by precipitation or adsorption. This can be accomplished by the addition of metallic salts to the waste water to form slightly soluble metal phosphate compounds or by increasing the pH of the waste water with lime or other strong basic materials to cause the formation of insoluble phosphate salts.

Precipitation of soluble phosphorous to the insoluble form, however, does not complete a phosphorous removal process. The resulting precipitates are extremely fine and well suspended. Without further treatment, this fine phosphorus precipitates resist removal by sedimentation.

The first step, the conversion of soluble phosphates to insoluble, suspended phosphates, is accomplished with the addition of small quantities of metallic salts. Ferrous, ferric and aluminun salts are all effective.

The second step is the removal of the insoluble phosphorus from suspension. Under normal conditions, only 10 to 15 per cent of these extremely fine solids can be removed by sedimentation. However, these suspended metallic phosphates can be flocculated with suitable organic polyelectrolytes. The completeness of flocculation or solids capture of these systems is excellent, and the settling rate of the flocculated material is rapid.

The colloidal suspension formed by the addition of a small quantity of ferrous chloride requires modification by the addition of a strong base before it can be readily flocculated with organic polyelectrolytes. The transient strong base alkalinity modifies the collodial properties of the system. It is not a pH associated phenomena.

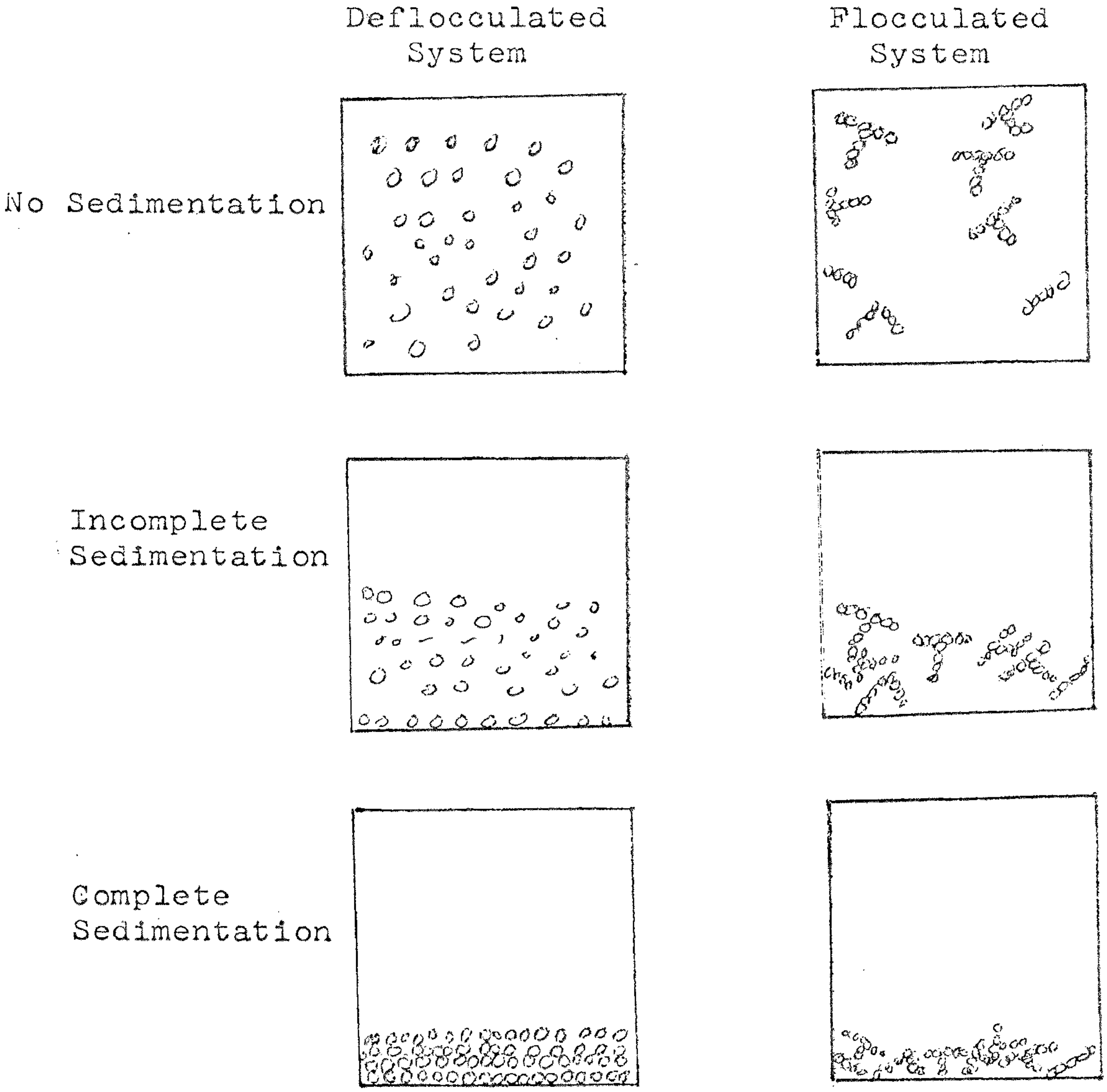
Flocculation and its mechanism is briefly described below:

Fine particles in a dispersion are often difficult to separate from the medium in which they are suspended. When the ultimate particles are in the low and fractional micron range of sizes, they settle too slowly for economic sedimentation, and they are often difficult to filter. If the size of the ultimate particle is of no concern, process conditions might be arranged for coarser precipitation or for crystal growth to sizes which can be handled. However, many materials cannot be so treated, nor is it always desirable to do so. "Instant" foods, pigments, whitings, clays, carbon blacks and mineral filters are prepared to a fine ultimate size to fulfill their function. The enlarged form is a temporary one. Other materials, e.g., coal slurries, mineral slimes, and turbid waters often difficult to handle in a fine state may be permanently enlarged. Flocculation techniques must take these needs into account.

A comparison of suspended and deflocculated systems is illustrated on next page. In the deflocculated system, the individual particles are dispersed in the fluid and they are

Figure II-1

COMPARISON OF FLOCCULATED AND DEFLOCCULATED SYSTEMS



separated and free to move independently of each other. Being small, they settle very slowly to a final dense sediment. When several particles are gathered together as flocculates, they settle much faster and the resulting sediment is less dense and is often mobile. They also filter more readily into a cake which is permeable and does not clog the filter.

Flocculation is basically a problem in colloid chemistry. If the conditions are right, flocculates will form. Gentle agitation assists in bringing particles into contact for the action to take place. Some dispersions are unstable and chemically ready to flocculate. Others need to have the dispersing agent on their surfaces neutralized or precipitated. In still other cases, the particulates need to be flocculated with a precipitate, as in the lime-alum clarification of water. Once the chemical conditions are satisfied to permit flocculation, the action proceeds.

Little needs to be said here about equipment for flocculation. When chemicals need to be added to fix the environment, the solutions may be continuously added to a stream through an eductor to give complete and instant mixing on a continuous basis. They can also be added to a dispersion in a tank with mild stirring.

Many waters are difficult to coagulate by the sample addition of aluminum or ferric salts. Activated silica and more recently certain materials called polyelectrolytes are added to stimulate floc formation. Activated silica is a negatively charged sol and acts to aid in flocculation of the positively charged metallic hydroxine sol formed by the metallic sol.

The polyelectrolytes when serving as coagulant aids undoubtedly out to reduce the stability of colloidal system and to facilitate their coagulation. The use of polyelectrolytes as coagulant aids has not been reduced to an exact science.

A number of companies have developed processes using polyelectrolytes. These are briefly described below:

(i) Dow Chemical Company has worked on an actual sewage treatment plant for several months. Dow Chemical Company's process uses a combination of ferrous or ferric chloride or alum and anionic polyelectrolyte. They have experimented with the phosphate removal only during the primary treatment of the incoming sewage. During this treatment, they have also used some calcium oxide or sodium hydroxide to get the strong base alkalinity. Total phosphorus removal ranged between 60 and 80 per cent with a mean of 72 per cent.

(ii) Calgon Corporation announced a process for treating sewage which uses highly effective polymeric water treatment chemicals in conjunction with granular activated carbon. The polymer chemicals are used to coagulate and settle the solids from raw sewage in the first step of the treatment process. This clarified water is then passed over large filter beds of granular activated carbon where the remaining suspended solids are filtered out and the dissolved organic contaminants adsorbed by the carbon. Calgon also in their announcement, said that this process improves chemical coagulation techniques for removal of phosphates. According to them, the improvements in phosphate removal which occur, from the application of the Calgon process, is dependent upon the degree to which the polymers improve the removal of suspended matter from the waste stream. Since waste areas vary in the amount of alum, iron salts or lime required for phosphate removal and also in the amount of suspended matter contained in the stream, the effectiveness of the Calgon process in the phosphate removal will vary from waste to waste. The only way of determining any improvement in phosphate and suspended solids removal, according to Calgon, is to run laboratory tests on the particular streams involved.

(iii) Eldib Engineering and Research, Inc. have made laboratory studies on removal of phosphate from sewage by activated sludge, followed by coagulation of sludge and precipitation of phosphates with cationic polyelectrolytes. The polyelectrolyte used was Purifloc C-31, a cationic polyelectrolyte made by Dow Chemical Company, Midland, Michigan. According to eldib, the cost of treatment for the polyelectrolyte alone is 20¢ per one thousand gallons.

Recently, Eldib Engineering and Research, Inc. made new studies to determine the effectiveness of polyelectrolytes in conjunction with alum to remove phosphates. The sewage samples were obtained from different treatment processes in the same plant. This study was conducted at a single concentration of alum and cationic polyelectrolyte. They have found some interesting and encouraging results. These results, however, are not available to the public.

j. Proposed scope of this thesis. A review of the literature shows many different methods of phosphate removal that have been tried. Data from these projects indicate that the most efficient method for phosphate removal still does not exist.

Rather than removing the phosphate from raw sewage in a primary treatment where some part of the condensed phosphates are still not hydrolized and to repeat the addition of chemicals in secondary treatment, the removal of phosphate from the activated sewage (aeration tank in secondary treatment) is cheaper and more logical to perform. Moreover, sometimes, the phosphate is added during the secondary aeration tank to help bacteria biodegrade organic compounds. Here, if unused phosphate is not removed, it will end up in water streams.

Based on the review of the literature, alum would be the best inorganic precipitating chemical. This was studied in combination with polyelectrolyte to remove phosphate and improve the phosphate removal by alum alone. The improvement was not sufficient. Ferric chloride is next best and performs approximately as well as alum when used alone, and no work has been done using a combination of ferric chloride and a cationic polymer. Actual experimental work carried out using a combination of ferric chloride and an organic polymer is described in the following section.

This thesis is concerned with a new technique and approach to the problem of phosphate removal, and involves the removal of phosphate from the sample of activated sewage, i.e., a sample from the aeration tank of the secondary treatment. The phosphate removal procedure uses ferric chloride as a precipitating chemical and a cationic polyelectrolyte as a flocculating agent. This approach is based on the same idea as it appeared in the Dow's process. However, no work has been done previously in exactly the same manner as the work conducted for this thesis.

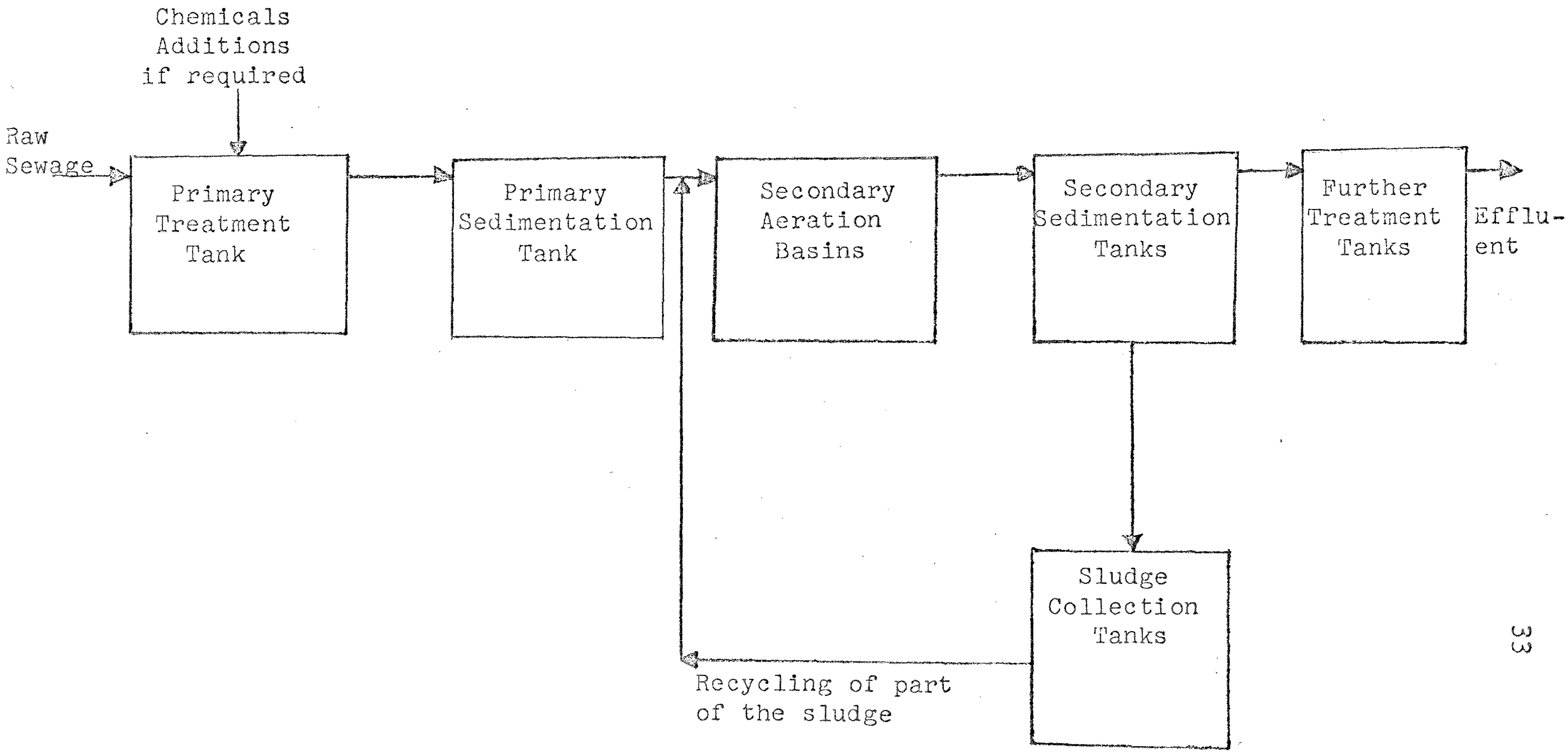
CHAPTER III

III. Sewage Sample Collection, Experimental Set-up and Analytical Procedure.

Sewage treatment plants have generally two main treatment steps--Primary and Secondary. Few advanced sewage plants have tertiary treatment also. A sketch of a sewage treatment plant is shown in figure III-1. Sewage, sometimes, is given a pre-treatment before primary treatment. In primary treatment suspended solids are separated, but soluble ingredients such as phosphates and nitrogen compounds pass through the primary treatment into the secondary treatment. These phosphates enter the sewage treatment plant through both industrial and domestic waste waters. In primary treatment the suspended solids capable of settling within a reasonable time are removed from sewage in sedimentation tanks. The settled material is left in the tank until a layer of sludge has been accumulated. In primary treatment chemicals are also added for the clarification of sewage. Modern chemical treatment consists of the removal of non-settleable solids from sewage by the application of coagulating agent which has the ability to bring the finely dispersed particles together to form a floc closely separated from the liquid by settling.

Figure III-1

SCHEMATIC FLOW DIAGRAM FOR TREATING RAW SEWAGE AND DIFFERENT STEPS INVOLVED IN PRIMARY AND SECONDARY TREATMENTS



Effluent from the sedimentation tanks are passed to the secondary treatment. The secondary treatment generally contains two steps; viz; aeration and settling. The effluent coming from the primary treatment is mixed with a sufficient amount of biologically active sludge to attain a rapid clarification. This sewage mixed with sludge (returned from digestion tank) is aerated to supply oxygen. This process of aeration is also known as activated sludge process. This process produces big flocs which settle out quickly, leaving a clear, relatively stable liquor. To produce rapid results the flocs must be kept in suspension by agitation and in contact with oxygen, otherwise the sludge becomes inactive or septic. A continuous supply of active sludge must be mixed with the incoming sewage, hence a portion of the settled sewage is returned to the raw sewage. From the aeration tank the sewage is brought into secondary sedimentation tank and clear effluent from this sedimentation tank, after settling is discharged as a final effluent or is passed to a tertiary treatment.

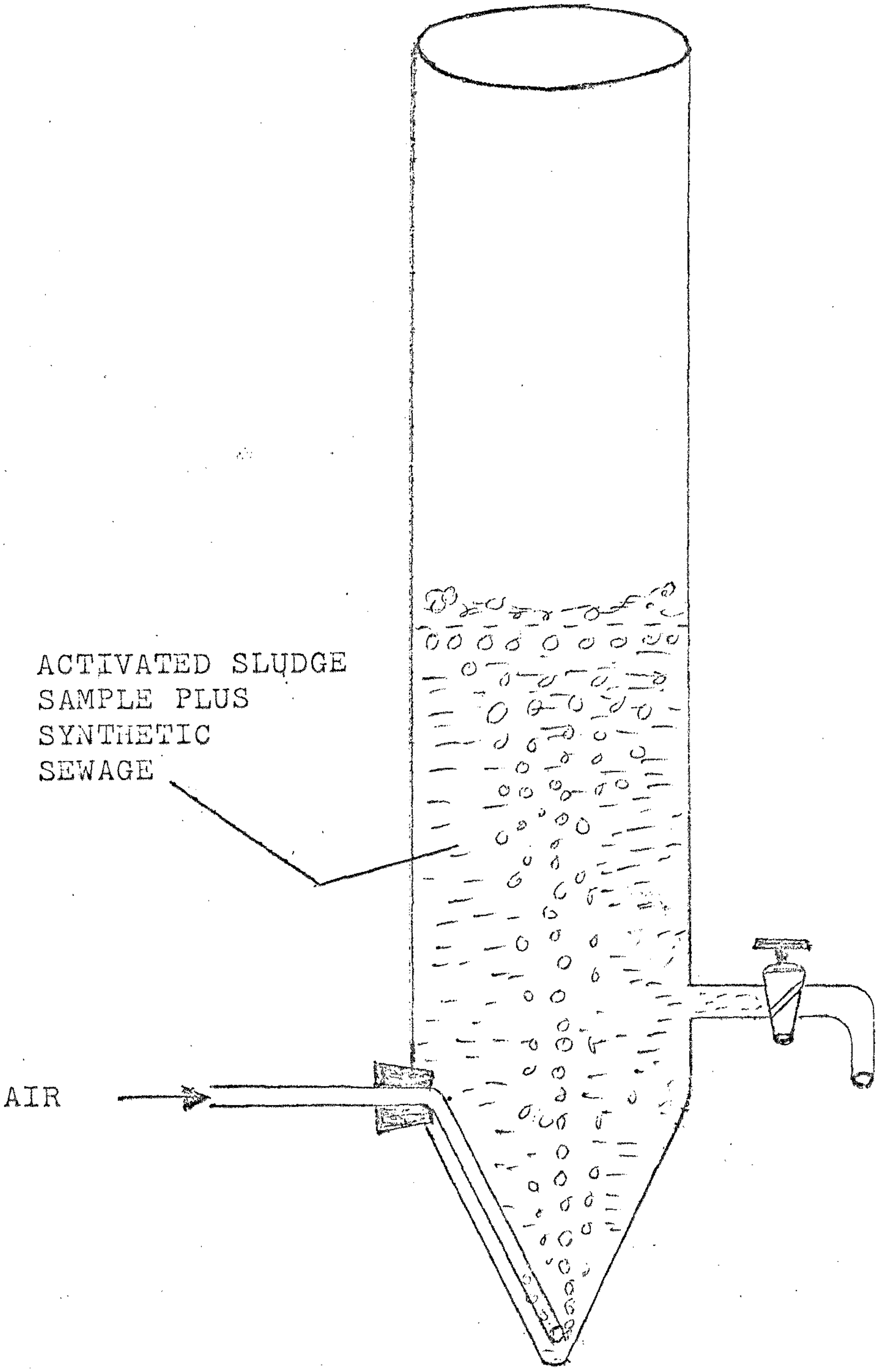
In primary stage, most of the phosphorus is removed in the primary sedimentation tank. Some of the remaining phosphorus is also removed in the secondary treatment. Here the phosphates oxidize into orthophosphates, which can be removed by precipitation with chemicals by settling in secondary sedimentation tank.

A. Sample collection, acclimation and chemical treatment. For the present work, a sample is collected from the secondary aeration tank. This is also known as activated sludge sample.

This sample was acclimated in the laboratory to stimulate the conditions through which it will go in the sewage treatment plant. Figure III-2 shows the unit used to acclimate the sample. The samples were acclimated for one week with a synthetic sewage containing 20 ppm of LAS and 80 ppm of sodium tripolyphosphate (80 ppm of sodium tripolyphosphate are equivalent to 285 pp, PO_4^{-3}). The activated sludge and synthetic sewage were placed in a specifically designed aeration chamber, aerated for 23 hours and allowed to settle for one hour. The supernatant liquid is withdrawn after this period of settling. The liquid remaining in the aeration chamber was brought back to volume with new nutrient, polyphosphate solution, LAS and the cycle repeated.

Figure III-2

A LABORATORY-SCALE UNIT FOR ACCLIMATION AND AERATION OF SEWAGE SAMPLE



At the end of the acclimation period, one liter of the contents of the aerated sewage was withdrawn while the aeration was in action. Three such sewage chambers were used, each containing a liter of sewage. 500 mls. of the withdrawn samples were poured in four different pots of a gangstirrer. A small sample of acclimated sludge is withdrawn before charging to the pots for the determination of initial concentration of phosphate ($PO_{\bar{4}}^{2}$) present by the analytical method shown in the following section. The pH of this was adjusted to 5.0 ± 0.1 and an equal amount of ferric chloride to that of phosphate present was added. These were agitated for one minute at 80 rpm and different amounts of cationic polyelectrolyte were added to these four beakers. The agitator was activated as follows:

2 minutes at 80 rpm
10 minutes at 30 rpm
5 minutes at 15 rpm

Following the rapid mixing steps, the flocculated solids were settled under dynamic (at 15 rpm agitation) conditions.

After the solids have settled, supernatant solution (liguid) from each pot is pipetted out very carefully without disturbing the settled solids. These samples are analyzed quantitatively for the phosphate (PO_4^{-2}) that is still present in the waste water.

B. Analytical technique for measuring phosphate concentration in sewage after treatment with ferric chloride and an organic polyelectrolyte selection of method. The aminonaphtholsulfuric acid method is most useful for routine analysis in the range of 0.1 to 30 mg/l PO_4. The stannous chloride method is more sensitive and better suited but is more susceptible to interferences. Therefore, aminonaphtholsulfuric acid technique was used as the method determining quantitatively the concentration of the phosphate (as PO_4) in the treated effluent.

Principle

In a dilute phosphate solution, ammonium molybdate reacts in acid medium to form a hetropoly acid molybdophosphoric acid which is reduced to intensely colored complex molybdenum blue by the combination of aminonaphtholsulfuric acid and sulfite reducing agents.

Minimum Detectable Concentration

The minimum detectable concentration (that concentration which produces 1 per cent transmittance above the normal expected deviation in reading at zero concentration) with a spectrophotometer (690 m/u) using 10 cm cell is about 0.02 mg/l PO_4.

Apparatus

(a) Colorimetric equipment: Visual comparison in nessler tubes is not normally recommended because of the difficulty in meeting the time requirements to obtain accurate results. The following instrument, therefore, was used. Spectrophotometer, for use at approximately 690 m/u. The color system also obeys Beer's law at 650 m/u, with somewhat reduced sensitivity, in the event the instrument available cannot be operated at the optimum wavelength. A light path of 0.5 cm or longer yields satisfactory results.

(b) Glassware: Acid washed glassware. This may be of great importance, particularly when determining low concentrations of phosphate. Phosphate contamination is common owing to the formation of thin films or adsorption on iron oxide films on glassware. Commercial detergents containing phosphate should be avoided. Glassware should be cleaned with hot dilute HCl and rinsed well with distilled water.

Reagents

(a) Phenolphthalein indicate solution. This was prepared by disolving 5 gms of phenolphthalein in 500 mls 95 per cent ethyl alcohol and diluting this by 500 mls distilled water. Then 0.02N NaOH was added until a faint pink color appeared.

(b) Dissolve 5 g phenolphthalein in 500 ml 95 per cent ethyl alcohol or isopropyl alcohol and add 500 ml distilled water. Then add 0.02N NaOH until a faint pink color appears.

Strong adic solution: Slowly add 300 ml conc H_2SO_4 to about 600 ml distilled water. When cool add 4.0 ml conc HNO_3 and dilute to 1 liter.

Ammonium molybdate reagent: Dissolve 31.4 g $(NH_4)_6MO_7O_{24}.4H_2O$ in about 300 ml distilled water. Cautiously add 252 ml conc H_2SO_4 to 400 ml distilled water. Cool, add 3.4 ml conc HNO_3, add the molybdate solution and dilute to 1 liter.

Aminonaphtholsulfonic acid reagent: Weigh out separately 0.75 g 1-amino-2-naphthol-4-sulfonic acid (use only a powder which is pale pink in color); 42 g anhydrous sodium sulfite,

Na_2SO_3; and 70 g anhydrous sodium metabisulfite (also called pyrosulfite) $Na_2S_2O_5$. Thoroughly grind the sulfonic acid with a small portion of the $Na_2S_2O_5$ powder in a clean, dry mortar. Dissolve the remaining salts in about 900 ml distilled water; dissolve the finely ground sulfonic acid in this mixture and dilute to 1 liter. Store in a brown glass-stoppered bottle at a temperature not exceeding 30°C. This solution will become slightly discolored with time; however, if not contaminated, it will give satisfactory results for most work for four months or more. For the most precise work, discard the solution when tests made with standards show a deviation from calibration of 2 per cent of concentration.

Stock phosphate solution: Dissolve in distilled water 0.7165 g anhydrous potassium dihydrogen phosphate, KH_2PO_4 and dilute to 1,000 ml with distilled water; 1.00 ml equals 50.0 mg PO_4.

Procedure

Before the samples are analyzed, they are checked to see whether precipitation has occurred after they have been collected. Filter the required amount of sample or centrifuge it. If the pH of the sample is less than 4, dilute 50.0 ml to 100 ml in a volumetric flask with distilled water and mix thoroughly. Use this diluted sample in the following steps. If the pH is greater than 10, add 1 drop of phenolphthalein indicator to 50.0 ml of sample and discharge the red color with strong-acid solution before diluting to 100 ml. (Such dilution is also useful when concentrations greater than 30 mg/l are present. When dilutions are made, the correct interpretation of "ml sample" in calculations must be made. For example, when 50.0 ml of original sample has been diluted to 100 ml for pH adjustment, the "ml sample" in the calculation is 25, not 50, although 50.0 ml of diluted sample is still used in the following steps.

Pipet 50.0 mls of filtered or clear sample containing not more than 1.5 mg (30 mg/l PO_4) into a clean, dry 125 mls erlenmeyer flask. Add 2.0 ml sulfonic acid reagent and mix again. Because the rate and intensity of color development are dependent on temperature, the reagents, standards and samples should be at the same temperature (20°-30°C.)

After exactly five minutes, measure the color photometrically, adjusting the instrument to 100 per cent transmittance with a proper blank. Interference from color, turbidity not removed by filtration,and chromate is greatly reduced or eliminated by preparing the blank from the sample in exactly the same manner, except that strong acid solution is used in place of the molybdate solution. Distilled water treated in the same manner with the strong-acid and sulfonic solution can be used where such interferences are absent. One distilled-eater blank can be used for a number interference-free samples.

Obtain the weight of orthophosphate in the sample taken by referring its photometric reading (per cent transmittance) to a standard curve.

A standard curve is constructed by using transmittance reading obtained with standard phosphate samples. These standard phosphate samples were prepared using potassium dihydrogen phosphate. Many different standard samples having different concentrations were prepared. The standard curve thus prepared has phosphate as x-axis and per cent transmittance as y-axis. The curve prepared using above information should be a straight on semi-logarithmic graph apper. (The line may not quite pass through the 100 per cent transmittance point at zero PO_4 concentration, but the reading is usually between 98 and 100 per cent, depending on the instrument used). This curve is Figure IV-10. By referring to this curve, the amount of orthophosphate in an unknown sample can be obtained.

Each test was repeated to confirm the results obtained.

CHAPTER IV

IV. Results and Discussion

Normal domestic waste water contains several different forms of phosphates. These consist of the particulate organic phosphates tied up in organic matter, orthophosphates and the polyphosphates. By the time they reach the aeration chamber of secondary treatment, almost all polyphosphates are hydrolized into orthophosphates.

For the present work, four different sewage samples were obtained from Bergen County Sewage Authority, and acclimated as described earlier on page 24. In this report, the removal of the orthophosphates by chemical treatment is studied. During the experiments, the initial phosphate content in each sewage sample had natural variation and the polyelectrolyte concentration was a variable in the different tests, however, the same ferric chloride concentration was used in all tests.

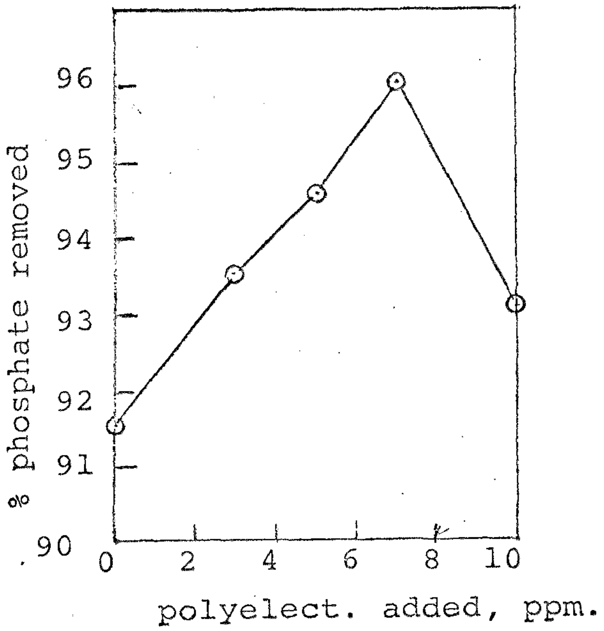
Each sewage sample was treated with several different concentrations of polyelectrolyte. These different concentrations of polyelectrolyte were used to determine the effect of polyelectrolyte addition on the phosphate removal efficiency and to find an optimum level of the polyelectrolyte. Tables IV-1 to IV-4 show the results of these tests at different initial phosphate concentrations and at different levels of polyelectrolyte concentration. These results are also shown as Figures IV-1 to IV-4.

The significance of these results will now be discussed.

Discussion

1. As can be seen from Figures IV-1 to 4 a peak (maximum) removal of phosphate was obtained in each test and the general shape of the curve is as shown below. These figures showed that when initial phosphate content was low in the sample, low amount of polyelectrolyte was needed to obtain the peak removal. (However, the peak was different for different tests in both height and displacement).

Fig. IV-2 (reduced scale)



2. At 72 g/l of initial phosphate concentration peak removal was 96.5 per cent and concentration of polyelectrolyte required was 11 g/l; while at 56 g/l of initial phosphate concentration, peak removal of phosphate, 95.5 per cent, was obtained using 4 ppm of polyelectrolyte.

Fig. IV-1
(reduced scale)
initial phos.- 56ppm.

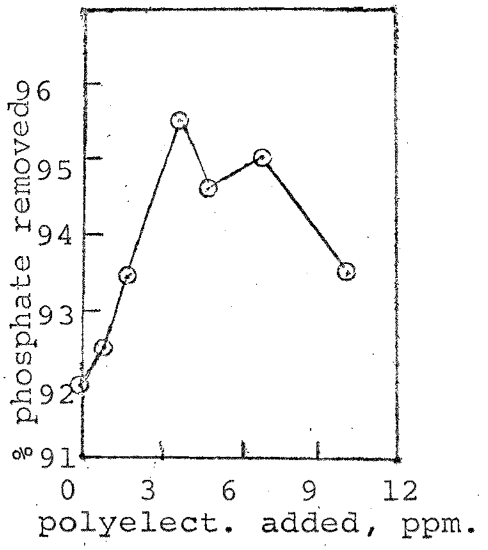
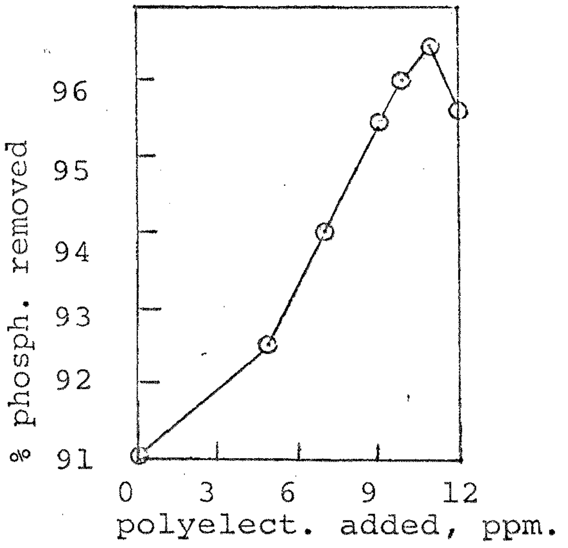


Fig. IV-4
(reduced scale)
initial phos.- 72ppm.



3. Ferric chloride alone in these tests, could, remove 91 to 92 per cent of the phosphate present. The removal of phosphate by ferric chloride is related to its coagulative power. A number of investigations(14, 4) support the view that certain iron adsorption of phosphates on iron hydroxide is mainly responsible for coagulative phosphate removal. Other investigations(10, 33) have concluded that predominantely chemical forces (ferric phosphate precipitation of isomorphis replacement) are the main causes of the phosphate elimination.

4. An increase in per cent phosphate removal was obtained when polyelectrolyte was added in addition to ferric chloride, see Figures IV-1 to IV-4 or the above reduced figures. In these figures "0" on the scale referred to only ferric chloride addition (same for all tests). A flocculating ability of polyelectrolyte was responsible for this increase in per cent phosphate removal. Flocculation is basically a problem in colloid chemistry. If the conditions are right, flocculates will form. Gentle agitation assists in bringing particles into contact for the action to take place. Some dispersions are unstable and chemically ready to flocculate. Polyelectrolytes are added to stimulate floc

formation.

5. Figure IV-5 (reduced below) shows that as the phosphate concentration in the sample increases, the per cent phosphate removal goes down at a constant level of ferric chloride usage. This can be explained by Figure IV-6 (also reduced below). This figure is a result of study done by Stumm(32) (Dept. of Water Resources and Sanitary Eng.; Harvard University, Cambridge, Mass.). It is apparent from this that at a ratio of Fe/P=2+, the phosphate removal is at peak and below or above this ratio the removal is lower than the removal obtained at Fe/P=2+.

Fig. IV-5
(reduced scale)

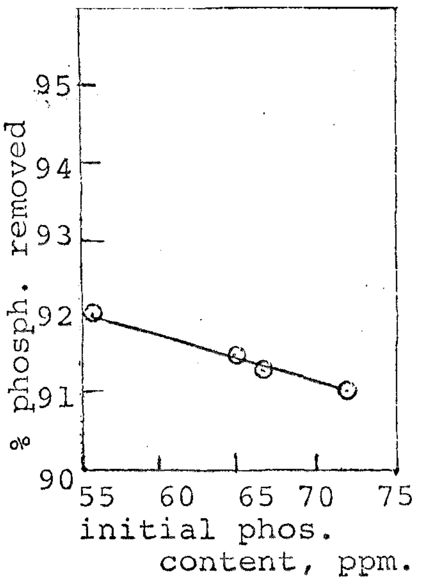
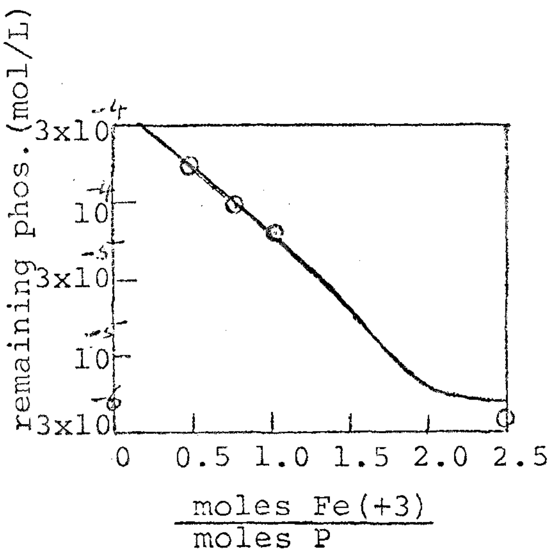


Fig. IV-6 (reduced scale)



6. On the other hand figure IV-7 shows that with the increase in the phosphate concentration in the sample, the per cent phosphate removal increases. However, the polyelectrolyte concentration was not kept constant but was also increased. Hence, this figure has two variables (not counting ferric chloride concentration which was held constant) viz; polyelectrolyte concentration and initial phosphate content, i.e., by fixing concentrations of polyelectrolyte and initial phosphate content, per cent phosphate can be determined.

Fig. IV-7
(reduced scale)

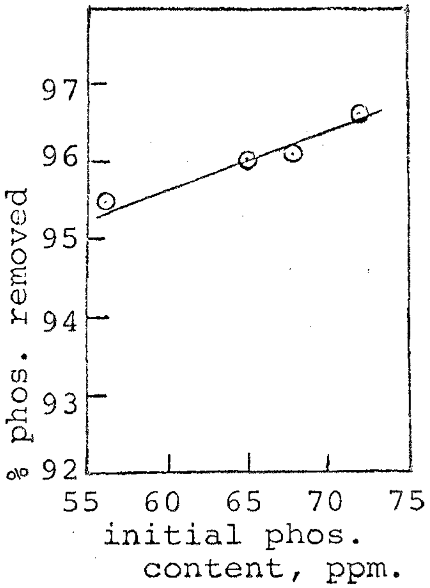
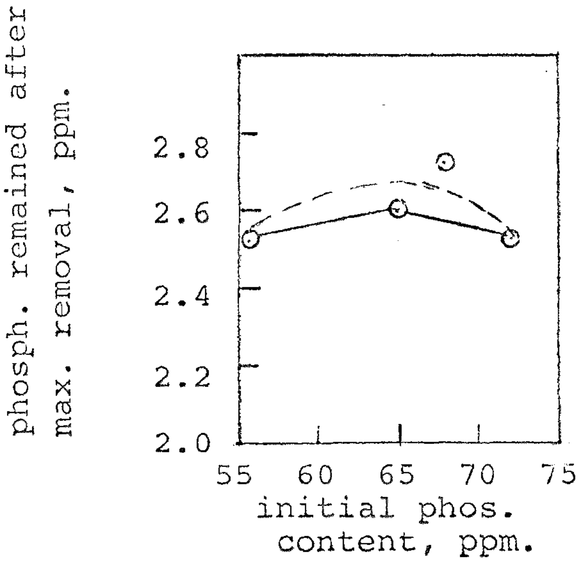
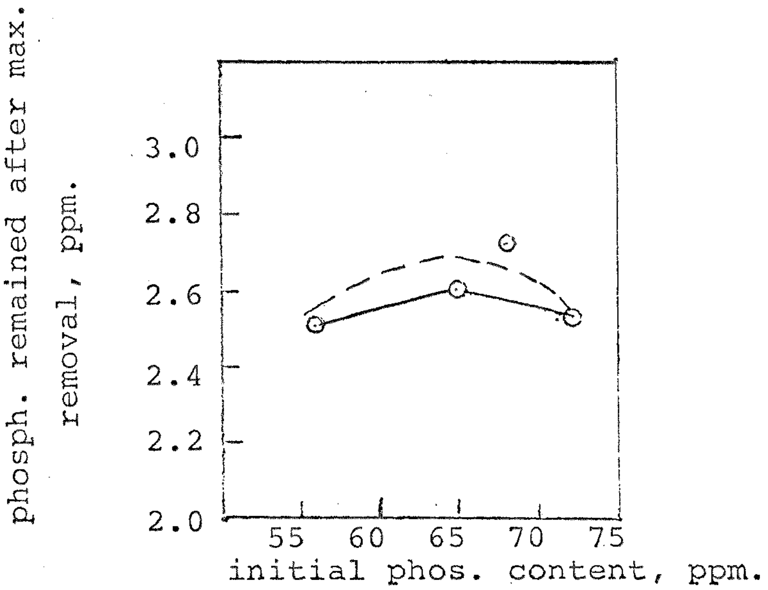


Fig. IV-8
(reduced scale)



7. Figure IV-8 is a relationship between the phosphate content before and after treatment in the sample. The phosphate content remain after the treatment in most of the tests varied from 2.5 to 2.6 ppm which can be assumed to be approximately the same. This indicated that even though the per cent removal is different, the final concentration of phosphate after treatment reaches a minimum and approximately constant level. Since phosphates at even very low (about 0.1 ppm) concentrations are capable of supporting aquatic life growth, it is evident that polyelectrolyte does help reduce water pollution caused by phosphates but further treatment may be needed to reduce phosphate concentration to an ideal 0.1 ppm value.

Fig. IV-8 (reduced scale)



8. Figures IV-1 to IV-4 showed that there could be a correlation between initial phosphate concentration and polyelectrolyte concentration such that a curve constructed using this correlation will give peak phosphate removal. Several trials were made and a straight-line curve was obtained on log-log graph paper, which is Figure IV-9 (see below). Equation of this curve, therefore, is:

$$y = (x^m)\ (c) \quad \text{or} \quad x = (y/c)^{1/m}$$

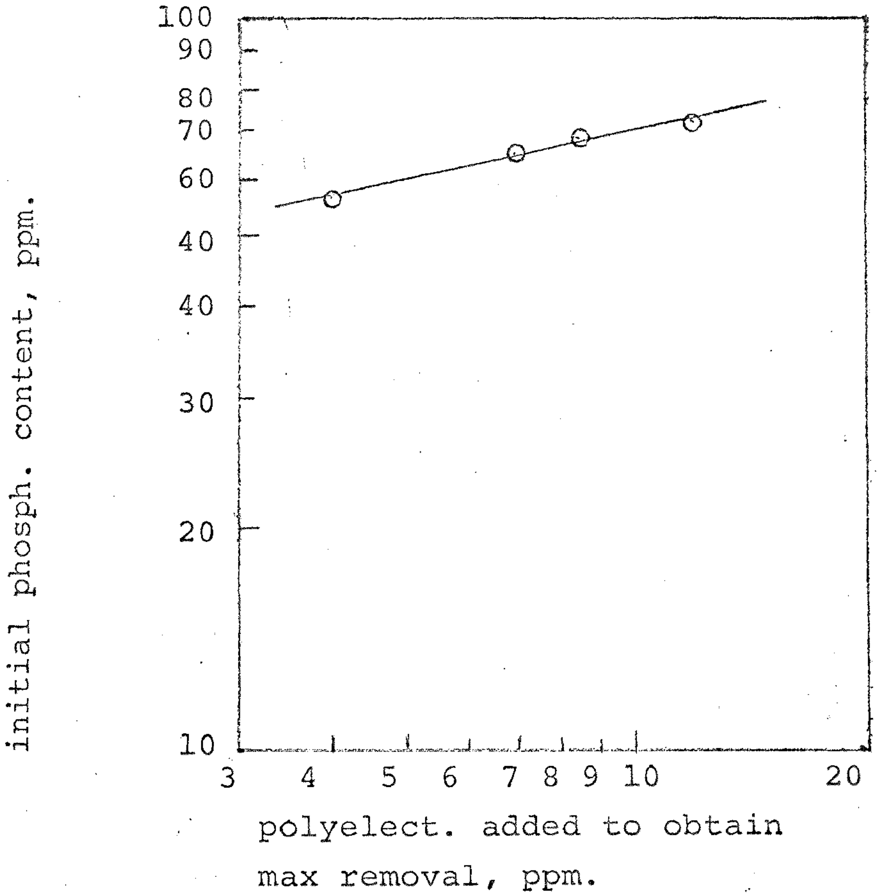
where y = initial concentration of phosphate present in sample, in ppm. x = (to be found), ppm of polyelectrolyte to be added to obtain peak phosphate removal

c = constant = 39.6 and m = slope of curve - 0.251

<u>For example</u> , assume that the initial phosphate concentration is 60 ppm. which is "y" in our case. Using the above equation polyelectrolyte concentration is calculated to be $x = 5.2$. For comparison by using the Figure IV-9 it can be found that polyelectrolyte concentration required is about 5 ppm.

Fig. IV-9 (reduced scale)--see next page

Fig. IV-9 (reduced scale)



Conclusions

1. Use of polyelectrolyte and ferric chloride has given a significant improvement in per cent phosphate removal over that obtained by ferric chloride alone. In some cases phosphate removal has increased from 92 to 96.5 per cent by the addition of a small amount (11 ppm) of cationic polymer.

2. There is a general trend in these tests that for a given phosphate content in sewage sample a level (or sometimes a range of concentrations) of polyelectrolyte will give the maximum or a peak removal. Below this concentration or below this range of concentrations the phosphate removal is low, probably, because of insufficient amount of chemicals.

3. The results show that there is a definite correlation between initial phosphate concentration and a polyelectrolyte concentration required to get maximum phosphate removal. This relationship is shown as Figure IV-8.

4. Highest per cent phosphate removal (96.5 per cent) was obtained at 72 ppm initial phosphate concentration and by using ferric chloride and 11 ppm of polyelectrolyte. At 65 to 68 ppm initial phosphate concentration, the removal was 96 per cent and at 56 ppm initial phosphate presence the removal

was 95.5 per cent, however, the polyelectrolyte requirement was only 4 ppm.

5. At a constant level of ferric chloride addition phosphate removal increases as the initial phosphate concentration goes down. Therefore, it appears that there is a point of initial concentration of phosphate where ferric chloride alone can remove the same amount of phosphate as ferric chloride plus polyelectrolyte can.

6. A curve constructed using initial phosphate concentration in the sample as X-axis and per cent phosphate removal on Y-axis, shows that the per cent removal varies directly with the initial phosphate content. However, the variation in per cent removal is small compared to the change in initial phosphate concentration. From this curve it can be predicted that the lowest phosphate removal should not go below 92 per cent.

7. A per cent phosphate removal cannot be determined from a given polyelectrolyte concentration outside of the four cases studied in this thesis because a separate curve is needed for a given phosphate content. However, one can determine from

Figure IV-9 an amount of polyelectrolyte needed to obtain the peak removal Figure IV-8 can be used to determine approximate content of remaining phosphate. By subtracting that amount from initial phosphate content one can determine approximate peak per cent phosphate removal.

8. Therefore, from these figures and knowing the initial phosphate content one can determine two things--

(a) How much polyelectrolyte is needed to get maximum (or peak) per cent phosphate removal

and

(b) the maximum per cent that can be obtained.

9. A Preliminary and quick cost estimate of the per cent phosphate removal showed that it is cheaper to remove first 90 to 92 per cent of phosphate than to remove the remaining 8 to 9 per cent by ferric chloride alone. However, the usage of ferric chloride alone is more expensive to remove the last 8 to 9 per cent of phosphate than the usage of a combination of ferric chloride and polyelectrolyte (see Appendix C).

TABLE IV-1

Phosphate Removal Efficiency of $FeCl_3$ plus Polymer From a Sample Containing 56 ppm of Phosphate Concentration

$FeCl_3$ Added	Polymer Added	% Phosphate Removal
200 ppm	0 ppm	92.0
200 ppm	1	92.5
200 ppm	2	93.5
200 ppm	4	95.5
200 ppm	5	94.5
200 ppm	7	95.0
200 ppm	10	93.5

TABLE IV-2

Phosphate Removal Efficiency of $FeCl_3$ plus Polymer From a Sample Containing 65 ppm of Phosphate Concentration

$FeCl_3$ Added	Polymer Added	% Phosphate Removed
200 ppm	0	91.5
200 ppm	3	93.5
200 ppm	5	94.5
200 ppm	7	96.0
200 ppm	10	93.0

TABLE IV-3

Phosphate Removal Efficiency of $FeCl_3$ plus Polymer From a Sample Containing 68 ppm of Phosphate Concentration

$FeCl_3$ Added	Polymer Added	% Phosphate Removal
200 ppm	0	91.2
200 ppm	1	93.0
200 ppm	2	93.0
200 ppm	4	92.5
200 ppm	5	93.5
200 ppm	8.5	96.0
200 ppm	10	94.0

TABLE IV-4

Phosphate Removal Efficiency of $FeCl_3$ plus Polymer From a Sample Containing 72 ppm of Phosphate Concentration

$FeCl_3$ Added	Polymer Added	% Phosphate Removal
200 ppm	0	91.0
200 ppm	5	92.5
200 ppm	7	94.0
200 ppm	10	96.0
200 ppm	11	96.5
200 ppm	12	95.5

APPENDIX

APPENDIX A

Actual Results Obtained Per Cent Transmittance

(1) Initial phosphate concentration in the supernant liquid of the untreated sewage 56 ppm.

Sample No.	$FeCl_3$+ Added ppm	Polyelectrolyte conc. ppm	% Trans.	PO_4^{-3} conc. in ppm	% PO^{-3} Removed
Initially	0	0	76*	5.5*	--
1	200	0	80	4.5	92
2	200	1	81.5	4.2	92.5
3	200	2	83.5	3.6	93.5
4	200	4	88	2.5	95.5
5	200	5	85.5	3.1	94.5
6	200	7	86.5	2.8	95.0
7	200	10	88	3.6	93.5

+ $FeCl_3$ added in the form of $FeCl_3$, $6H_2O$

* The sample diluted ten times.

(2) Initially phosphate concentration in the supernant liquid of the untreated sewage - 65 ppm.

Initially	0	0	73*	6.5*	--
1	200	0	76.5	5.5	91.5
2	200	3	81.5	4.2	93.5
3	200	5	83.5	3.6	94.5
4	200	7	87.5	2.6	96.0
5	200	10	79.5	4.6	93.0

+ $FeCl_3$ added in the form of $FeCl_3$, $6H_2O$.

* The sample diluted ten times.

(3) Initially phosphate concentration in the supernant liquid of the sample before the chemical treatment is 68 ppm.

Sample No.	$FeCl_3^+$ Added ppm	Polyelectrolyte conc. ppm	% Trans.	PO_4^{-3} conc. in ppm	% PO^{-3} Removed
Initially	0	0	72*	6.8*	--
1	200	0	74.5	6.2	91.2
2	200	1	79.0	4.8	93.0
3	200	2	79.0	4.8	93.0
4	200	4	78.0	5.1	92.5
5	200	5	80.5	4.4	93.5
6	200	8.5	87.0	2.7	96.0
7	200	10	82.0	4.1	94.0
8	200				

+ $FeCl_3$ added in the form of $FeCl_3$, $6H_2O$.

* The Sample diluted tem times.

(4) Initially phosphate concentration in the supernant liquid of the sample before the chemical treatment is 72 ppm.

Initially	0	0	70*	7.2*	--
1	200	0	73	6.5	91.0
2	200	5	77	5.4	92.5

Sample No.	$FeCl_3$+ Added ppm	Polyelectrolyte conc. ppm	% Trans.	PO_4^{-3} conc. in ppm	% PO^{-3} Removed
3	200	7	81	4.3	94.0
4	200	10	86.5	2.9	96.0
5	200	11	88	2.5	96.5
6	200	12	85	3.2	95.5

+ $FeCl_3$ added in the form of $FeCl_3$, $6H_2O$.

* The sample diluted ten times.

(5) Master table showing all the Results in Terms of % Phosphate Removed at Different Concentration of Polyelectrolytes

Initial PO_4^{-3} conc. in ppm	0	1	2	3	4	5	7	10	11
56	92	92.5	93.5	--	95.5	94.5	95	93.5	--
65	91.5	--	--	93.5	--	94.5	96.0	93.0	--
68	91.2	93.0	93.0	--	92.5	93.5	96.0*	94.0	--
72	91.0	9.5**	--	--	--	92.5	94.0	96.0	96.5

* 8.5 ppm polyelectrolyte concn.

** 12.0 ppm polyelectrolyte concn.

APPENDIX B

Calculation Procedures

(a) To calculate % phosphate removal

$$\% \text{ phosphate removed } \frac{a-b}{a} \times 100$$

Phosphate concentration in ppm in the sample before chemical treatment

Where a = phosphate concentration in ppm in the sample before chemical treatment

b = phosphate concentration in the sample after chemical treatment

e.g., in the first case, initial PO_4^{-3} concn. = a = 56 ppm after the treatment the phosphate concentration is = b = 4.5

$$\text{Therefore } \% \text{ phosphate removed} = \frac{56-4.5}{56} \times 100$$

$$+ 92\%$$

See Tables 1 to 4 for these results.

(b) To determine the correlation between initial concentration and polyelectrolyte concentration required to obtain the maximum phosphate removal.

We know the following:

Initial PO_4^{-3} Concn.	PPM of Polyelectrolyte Required for Maximum PO_4^{-3} Removal
56	4
65	7
68	8.5
72	11

Assume that our equation for log-log curve would fit which is $y = cx^m$

where y = initial phosphate concn in the sample

x = polyelectrolyte ppm required to obtain the maximum

m = slope of the curve

c = constant of the equation

To evaluate the constants m to c, we need two equations

$$56 = c(4)^m$$

$$72 = c(11)^m$$

$$\therefore \frac{56}{4^m} = c$$

$$\text{to } \frac{72}{4^m} = c$$

$$\text{or } \frac{56}{4^m} = \frac{72}{11^m}$$

$$\text{or } 1.285 = (2.754)^m$$

$$\therefore m = 0.251$$

$$56 = c(4)^{0.251}$$

$$\therefore c = 39.6$$

Using these values, we can calculate the amounts of polyelectrolytes needed to obtain maximum removal from the samples having 65 and 68 initial PO_4^{-3} concn.

$y = x^{m}c$ or $x = (y/c)^{1/m}$

$\therefore 65 = x^{0.251}(39.6)$

or $x^{0.251} = 65/39.6$

or $x = (65/39.6)^{1/0.251}$

$\therefore x = 7.2$

and

$68 = x^{0.251}(39.6)$

$\therefore x = 8.65$

These numbers approximately match those obtained by the experiment.

.Log-log curve equation should fit for the correlation between the initial phosphate concentration and a polyelectrolyte concentration needed to attain maximum phosphate removal.

APPENDIX C

(a) Economics. The following table shows the costs to remove phosphate per one million gallons of sewage. The cost to remove phosphate using an inorganic coagulant alone is compared with that to remove phosphate using a combination of inorganic coagulant and polyelectrolyte. It shows that it is cheaper to remove first 90 to 92 per cent of phosphate then to remove the remaining 8 to 9 per cent. This removal, although expensive, is obtained by the addition of high cost organic flocculant. At 72 ppm initial concentration, the inorganic material added was just enough to tie up all the PO_4^{-3} ions, and the removal was 91 per cent. However, at 56 ppm initial concentration of phosphate, the $FeCl_3$ addition was 25 per cent more than required, but the improvement in per cent removal obtained was only 1 per cent (i.e.; from 91 to 92 per cent removal). On this basis, it can be projected that to remove another 4 to 5 per cent more phosphate, $FeCl_3$ requirements would be twice as much. Hence the cost of the removal would then be twice as much. On the other hand, less than 30 per cent increase in cost using polyelectrolyte will improve the removal by 5.5 per cent, see Table 5 of Appendix A (at 72 ppm initial phosphate concentration the $FeCl_3$ alone removed 91 per cent and $FeCl_3$ plus 11 ppm of polyelectrolyte removed 96.5 per cent).

Summary of Costs to Remove Phosphate (72 ppm PO_4^{-3} Initially)

Chemicals Used in a system	Costs of Chemicals in $			Per cent increase in cost to get 96.5% removal	Per cent Phosphate Removal	Projected Cost of Removal of 96.5% Phosphate by $FeCl_3$ alone
	$FeCl_3$	Polyelectrolytes	Total			
$FeCl_3$ alone	82.20	---	82.20	--	91	$164.40
$FeCl_3$+ polyelectrolyte	82.20	27.00	109.20	30%	96.5	---

(b) Calculations on Cost of Phosphate Removal

0.2 grams/liter of $FeCl_3$ required

$\therefore \frac{0.2 \text{ grams } FeCl_3}{\text{liter}} \times \frac{3.72 \text{ liters}}{\text{gals}}$

or $\frac{0.744 \text{ gms}}{\text{gals}}$ $FeCl_3$ required

or $\frac{7.44 \times 10^5 \text{gms}}{1 \text{ million gals}}$ $FeCl_3$ required

$= \frac{1644 \text{ lbs}}{\text{MM gals}}$ $FeCl_3$ required

at $0.05/lb. price of $FeCl_3$ the total cost to treat one million gallons of sewage = $82.20

i.e., 91 per cent of 72 ppm or 64.5 ppm phosphate was removed at a cost of $82.20. or $\frac{\$82.20}{64.5} = \$1.27$ required to remove 1 gal of PO_4^{-3} from 1 MM gals of sewage.

Polyelectrolyte required = 11 ppm

$$= \frac{0.011 \text{ gm}}{1000 \text{ ml}} \times \frac{1000 \text{ mls}}{1 \text{ liter}} \times \frac{3.712 \text{ liter}}{1 \text{ gal}} \times 10^6 \text{ gals} \times \frac{1 \text{ lb}}{454 \text{ gm}}$$

$$= \frac{90 \text{ lbs polyelectrolyte}}{10^6 \text{ gals sludge}}$$

at a price of \$0.30/lbs of dilute solution cost of polyelectrolyte to remove 69.5 ppm (96.5 per cent of 72 ppm) = \$27/10^6 gals sludge.

or $\frac{\$82.2 + \$27}{69.5}$ = \$1.57 required to treat 10^6 gals of sludge and to remove equivalent amount of one gal of phosphate

To obtain the same removal (96.5 per cent) by $FeCl_3$ alone would cost 2 x \$82.2 = \$164.4 (theoretically projected cost from its removal rate) or $\frac{\$164.4}{69.5}$ = \$2.37 would require if 96.5 per cent removal is to be obtained by ferric chloride alone.

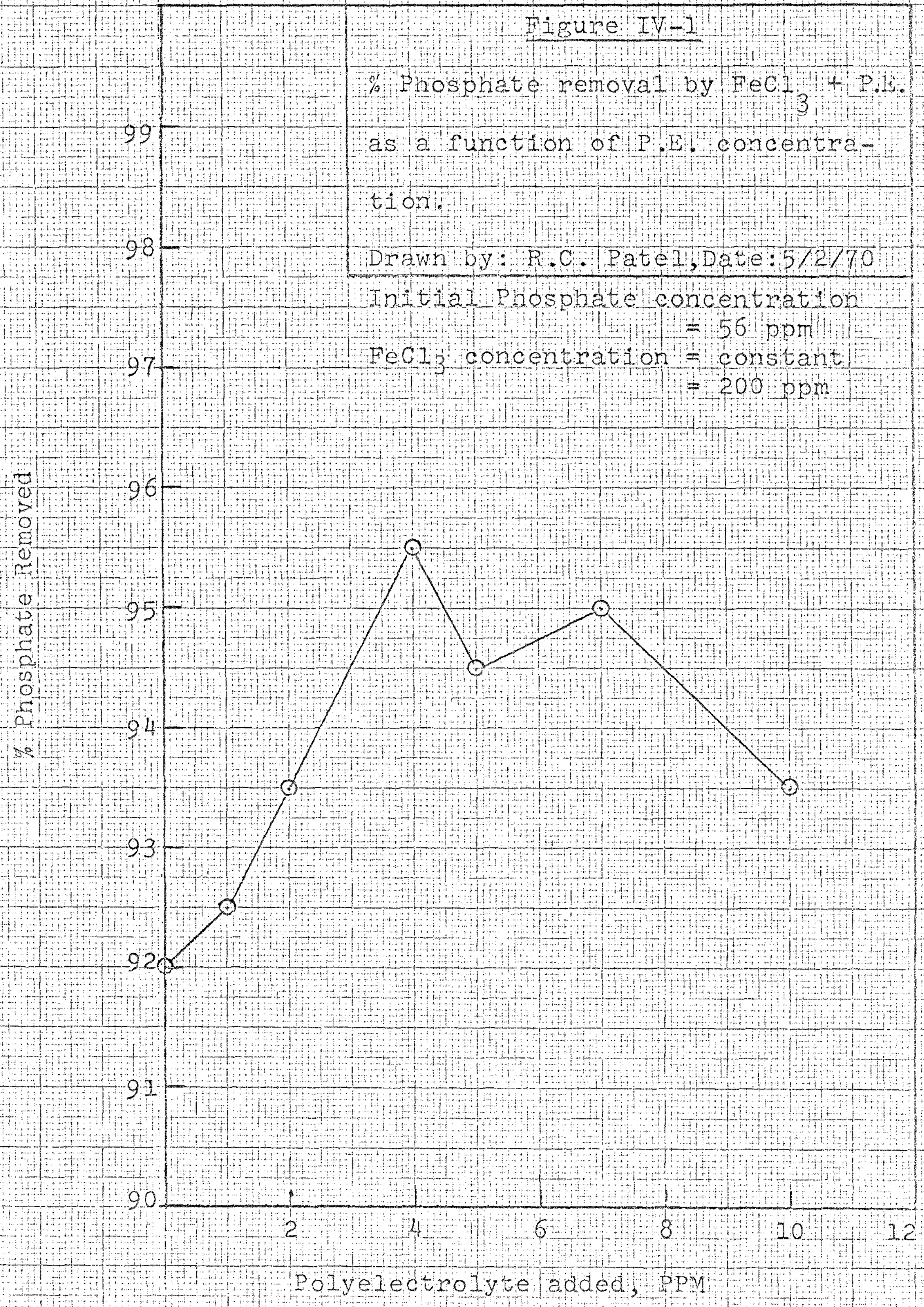


Figure IV-1

% Phosphate removal by $FeCl_3$ + P.E. as a function of P.E. concentration.

Drawn by: R.C. Patel, Date: 5/2/70

Initial Phosphate concentration = 56 ppm

$FeCl_3$ concentration = constant = 200 ppm

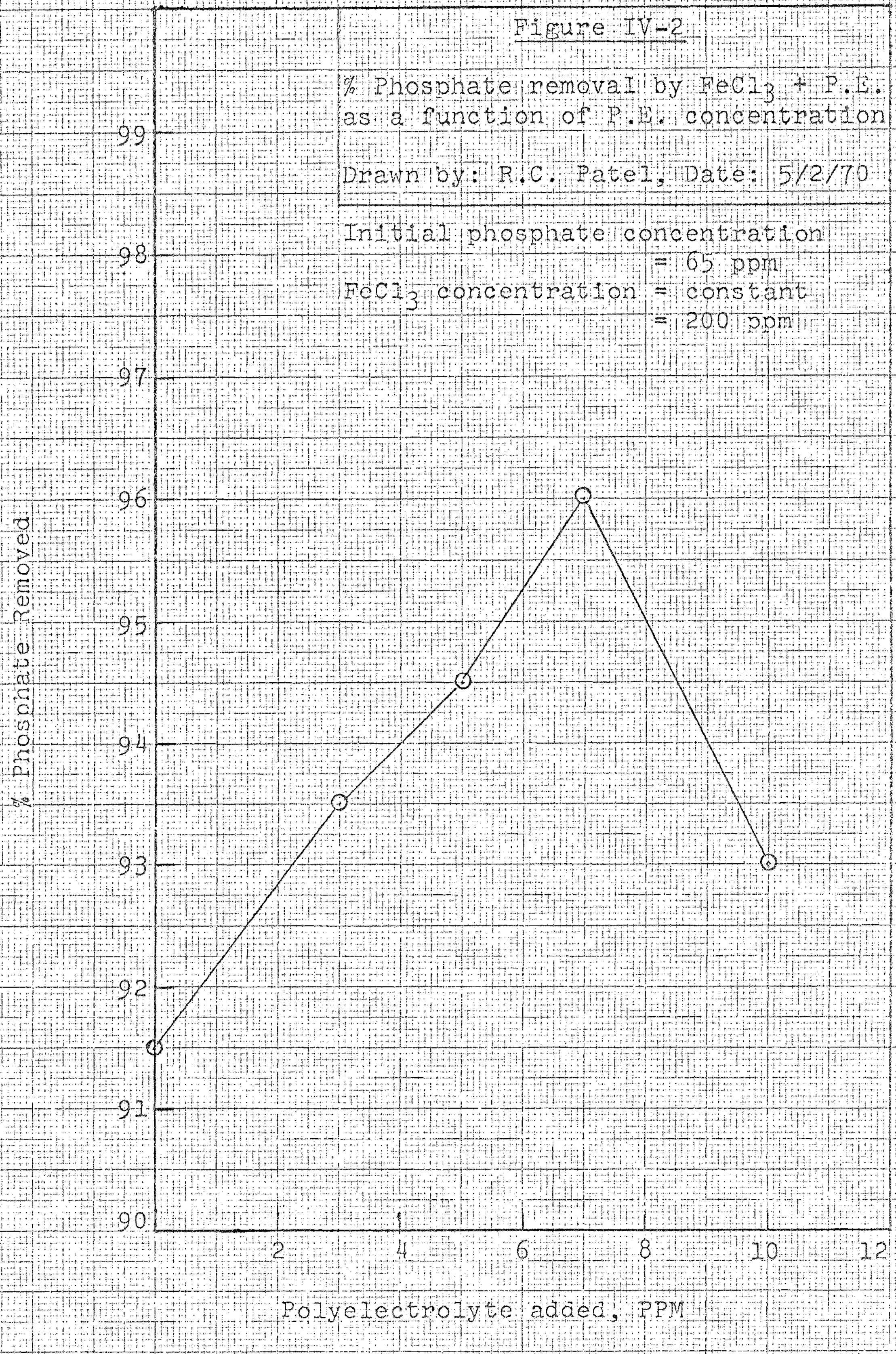


Figure IV-2
% Phosphate removal by $FeCl_3$ + P.E. as a function of P.E. concentration
Drawn by: R.C. Patel, Date: 5/2/70
Initial phosphate concentration = 65 ppm
$FeCl_3$ concentration = constant = 200 ppm
% Phosphate Removed
99
98
97
96
95
94
93
92
91
90
2
4
6
8
10
12
Polyelectrolyte added, PPM

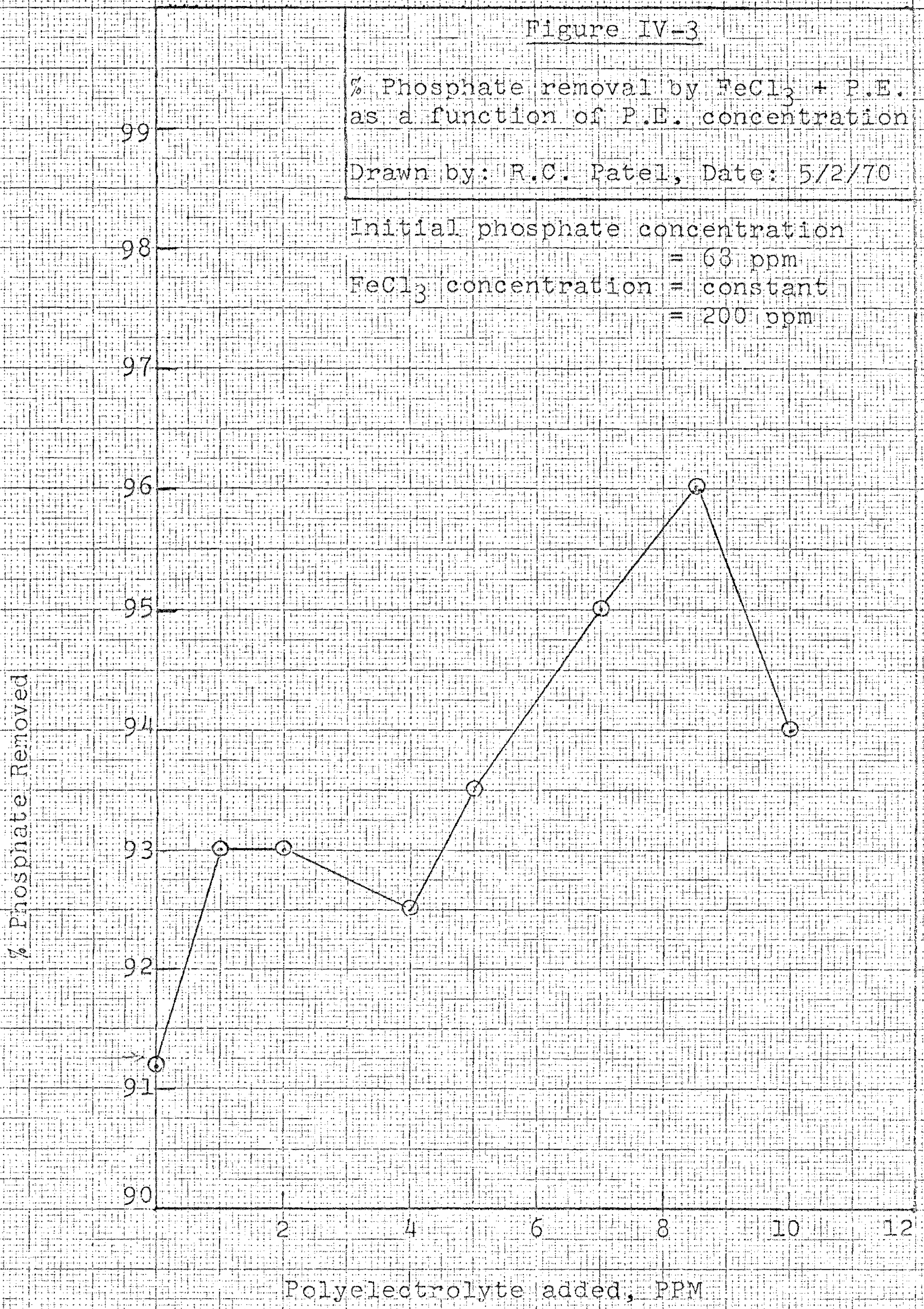


Figure IV-3

% Phosphate removal by $FeCl_3$ + P.E. as a function of P.E. concentration

Drawn by: R.C. Patel, Date: 5/2/70

Initial phosphate concentration
= 63 ppm
$FeCl_3$ concentration = constant
= 200 ppm

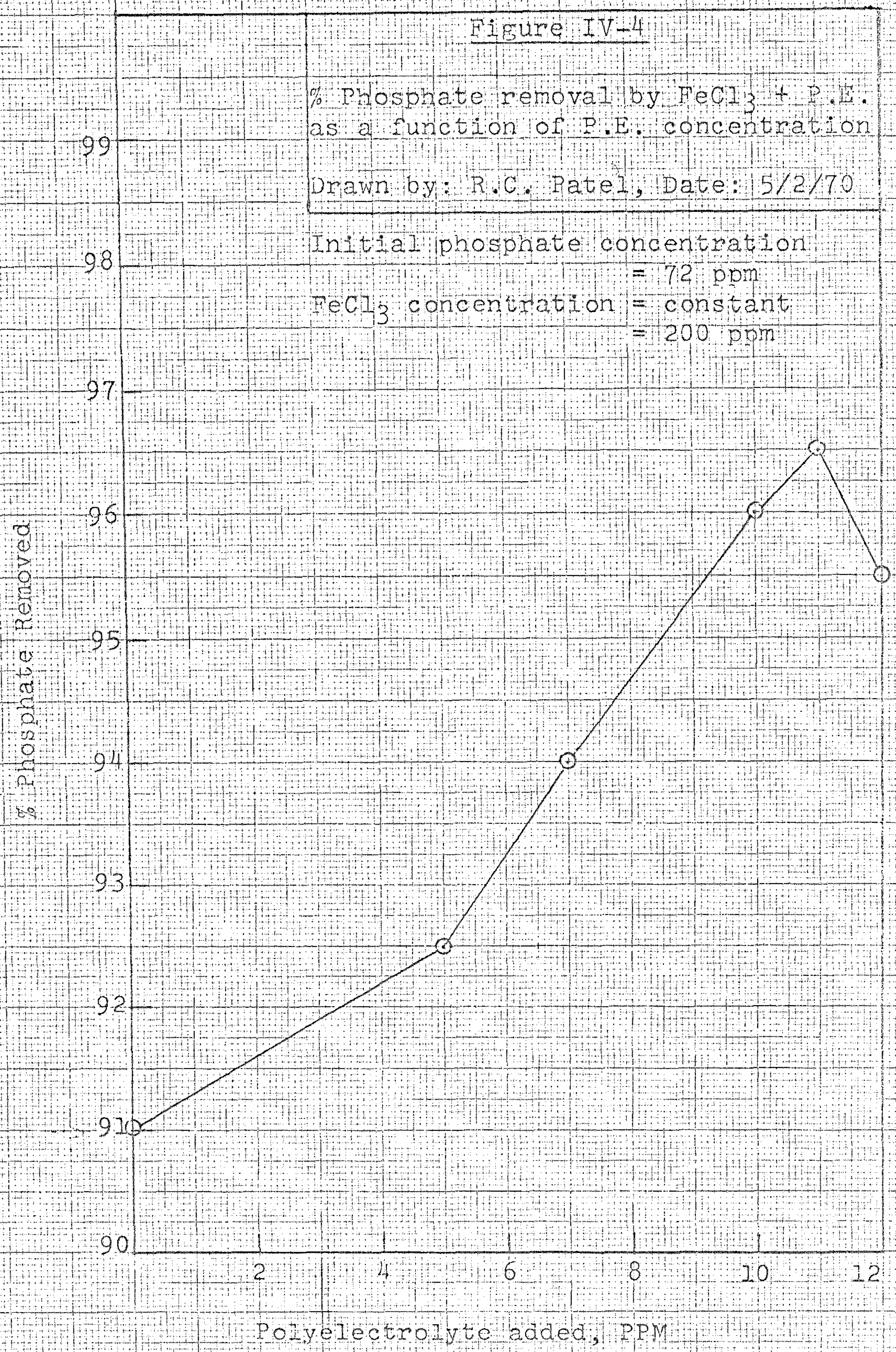


Figure IV-4

% Phosphate removal by $FeCl_3$ + P.E. as a function of P.E. concentration

Drawn by: R.C. Patel, Date: 5/2/70

Initial phosphate concentration
= 72 ppm
$FeCl_3$ concentration = constant
= 200 ppm

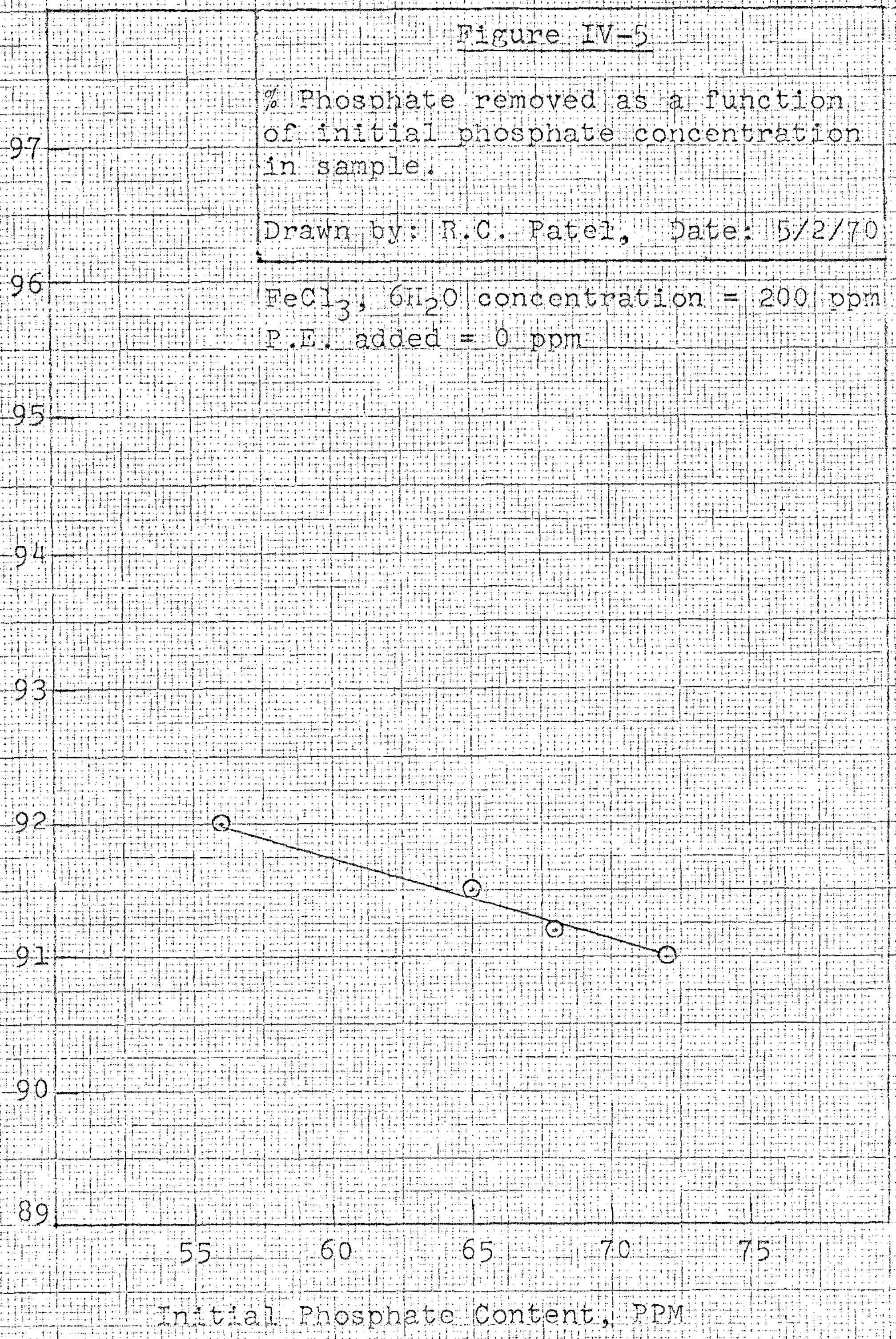


Figure IV-5

% Phosphate removed as a function of initial phosphate concentration in sample.

Drawn by: R.C. Patel, Date: 5/2/70

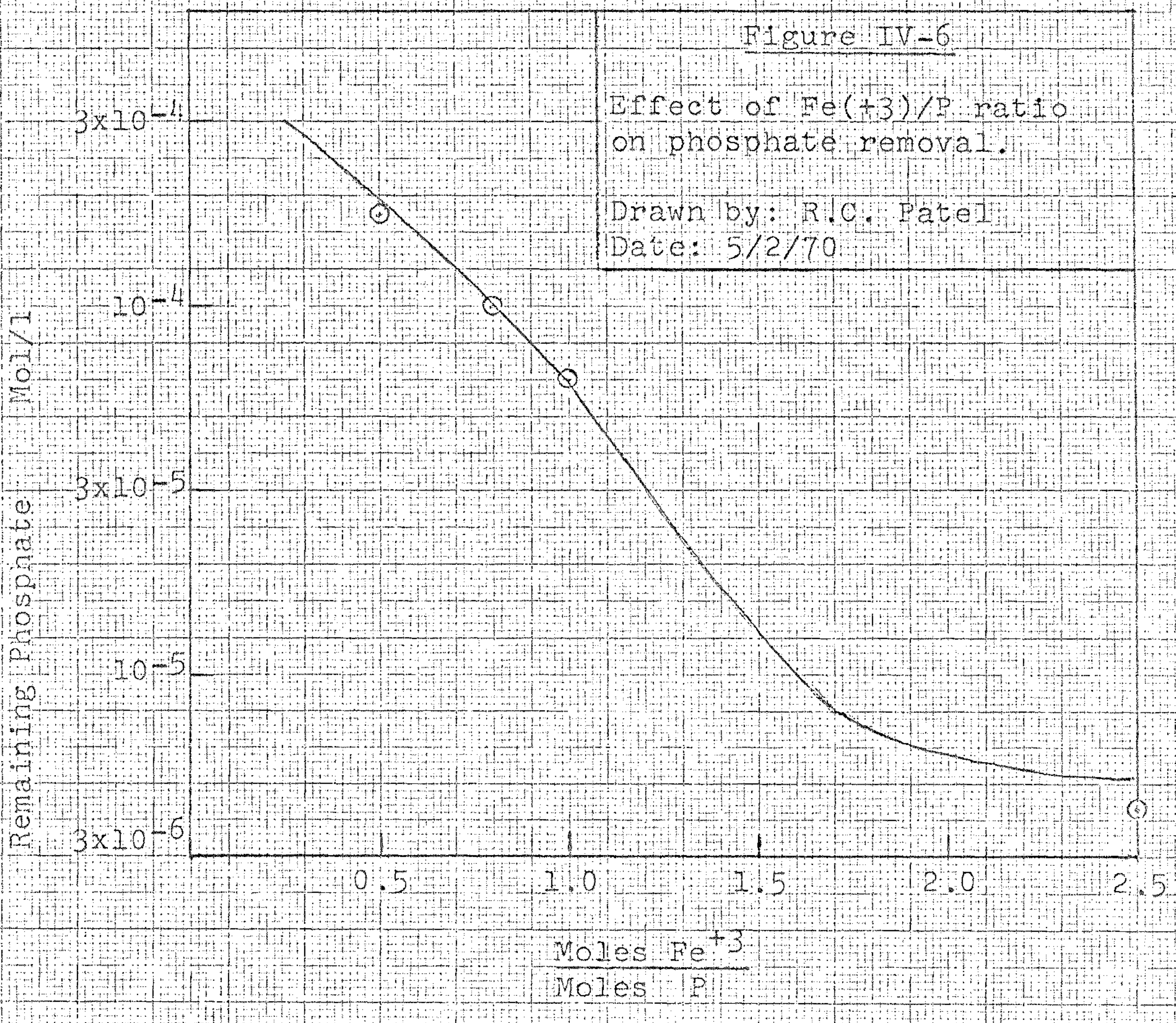


Figure IV-6

Effect of Fe(+3)/P ratio on phosphate removal.

Drawn by: R.C. Patel
Date: 5/2/70

SOURCE: Stumm, W., Harvard University, Cambridge, Mass., U.S. P.H.S. Research Grant, WP98

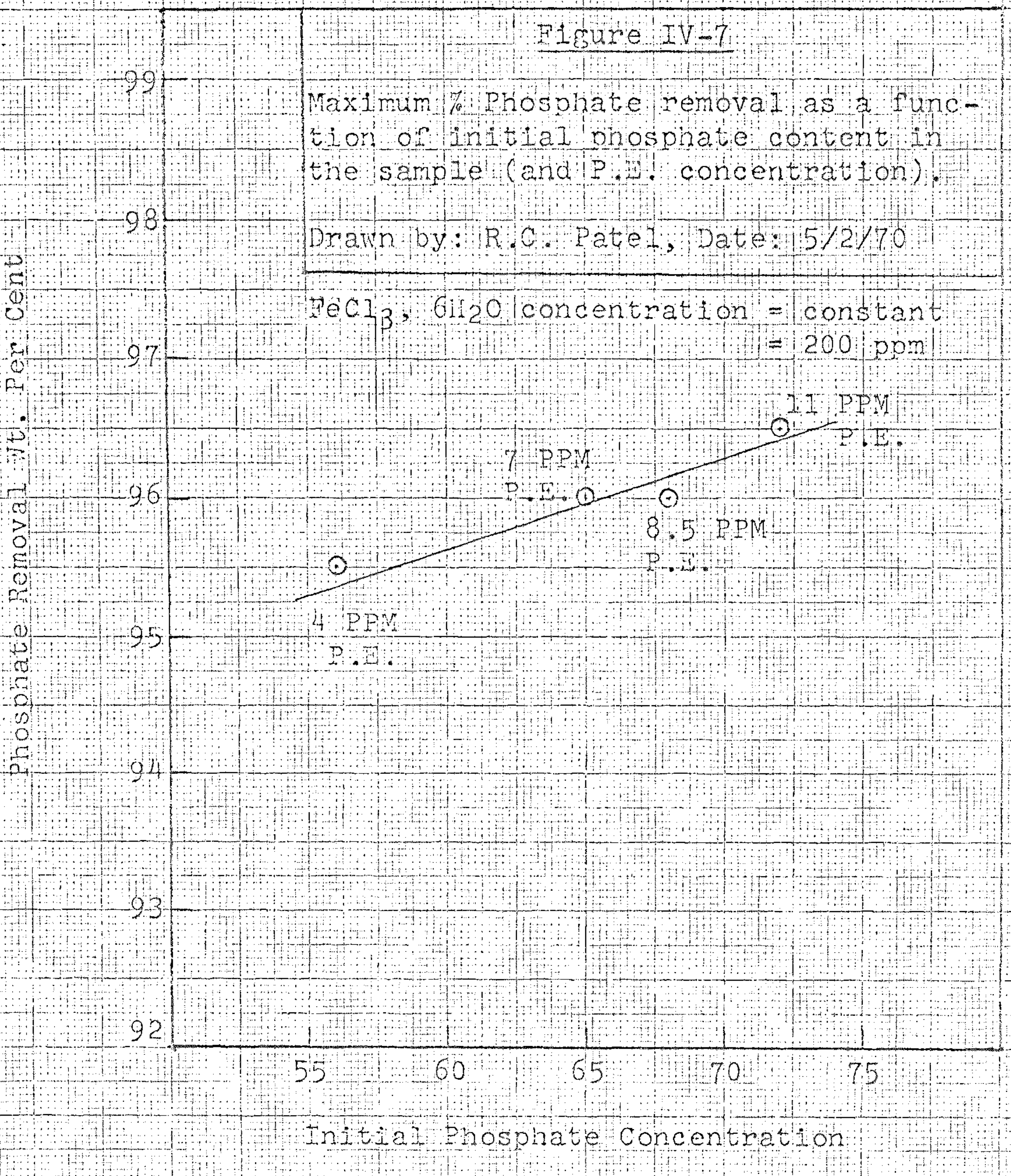


Figure IV-7

Maximum % Phosphate removal as a function of initial phosphate content in the sample (and P.E. concentration).

Drawn by: R.C. Patel, Date: 5/2/70

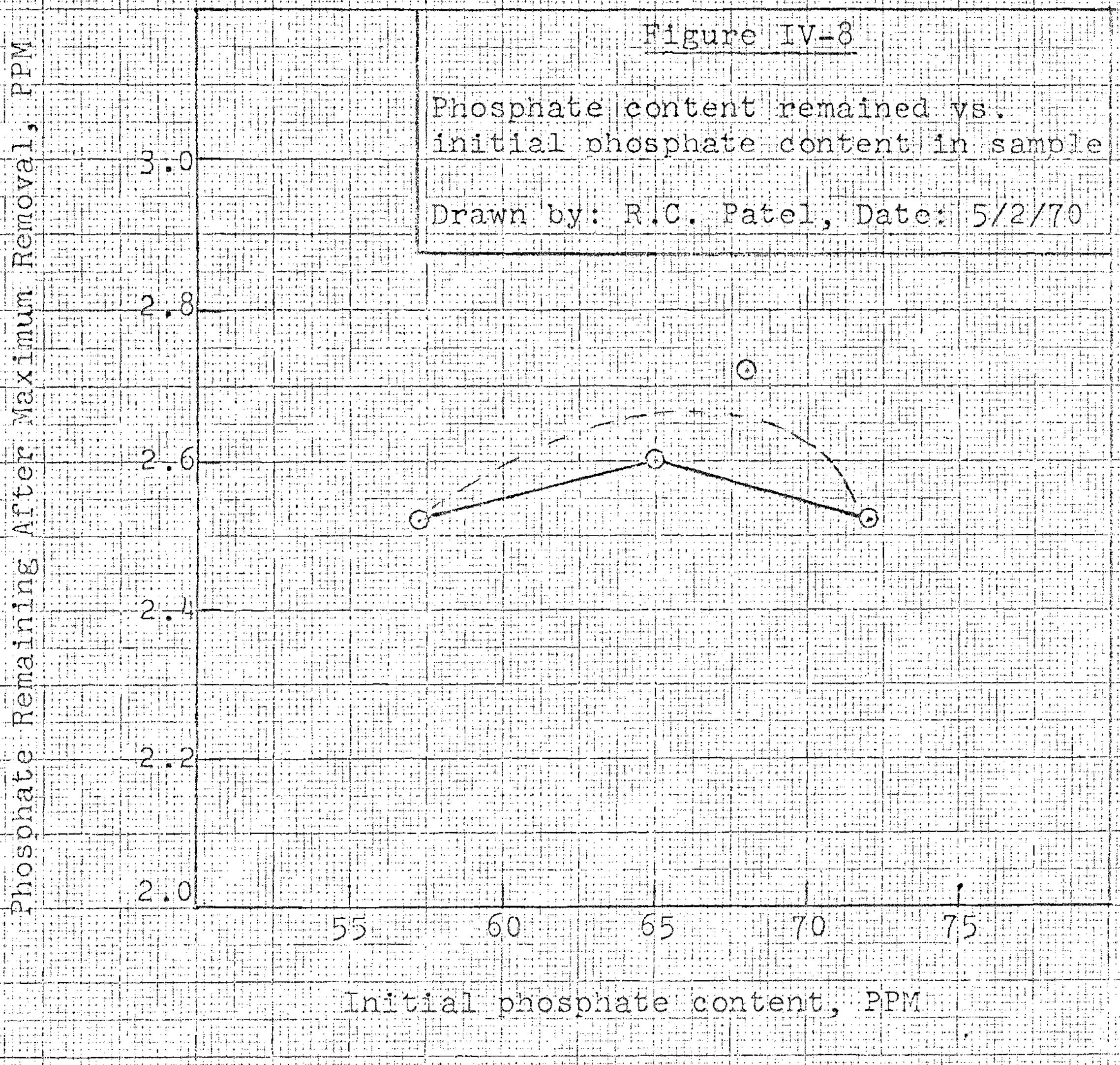


Figure IV-8

Phosphate content remained vs. initial phosphate content in sample

Drawn by: R.C. Patel, Date: 5/2/70

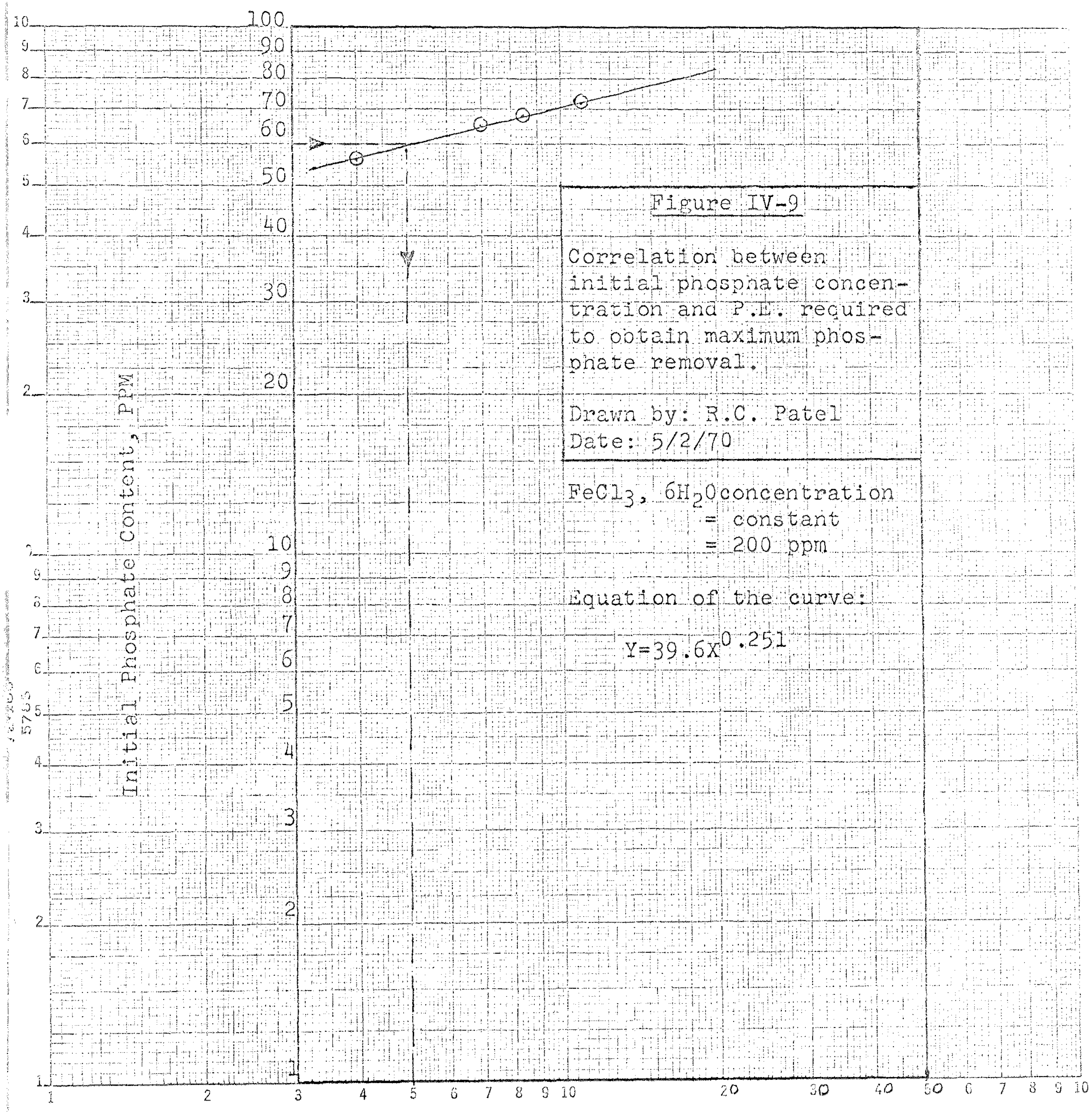


Figure IV-9

Correlation between initial phosphate concentration and P.E. required to obtain maximum phosphate removal.

Drawn by: R.C. Patel
Date: 5/2/70

$FeCl_3, 6H_2O$ concentration
= constant
= 200 ppm

Equation of the curve:

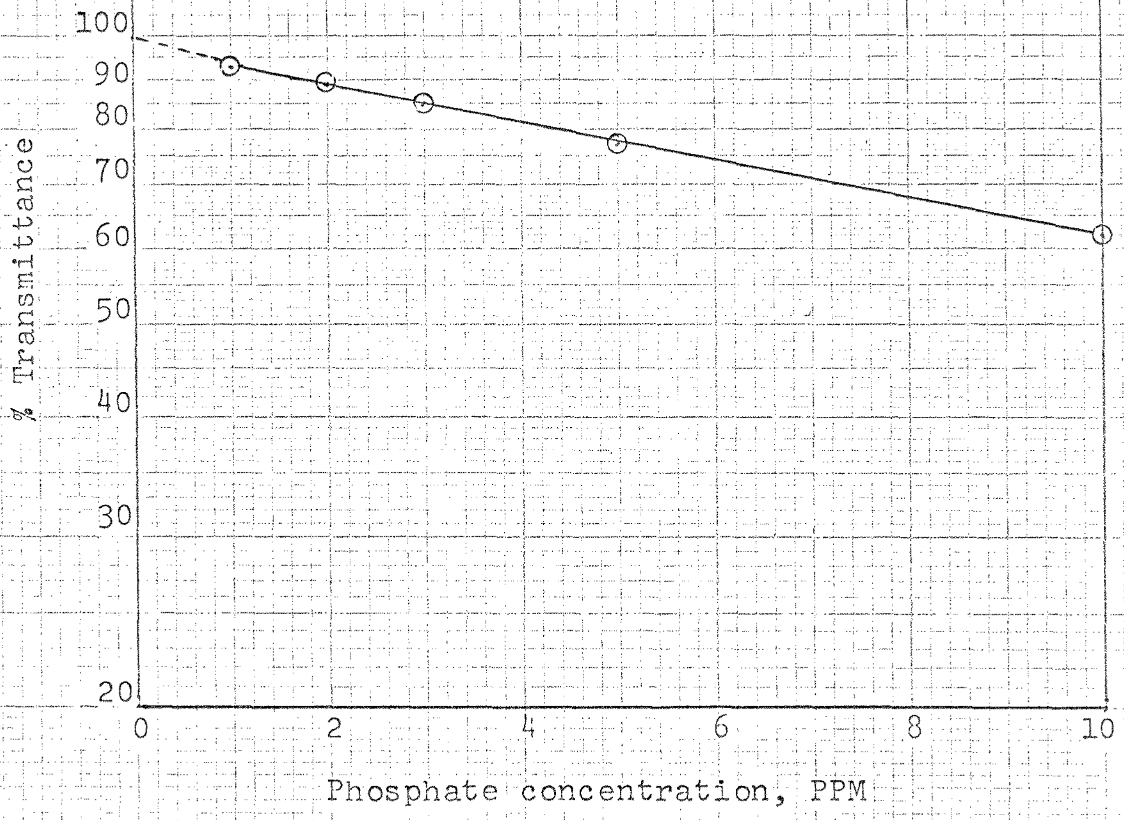
$$Y=39.6X^{0.251}$$

Figure IV-10

Calibration curve--
Phosphate concentration vs. %
transmittance

Drawn by: R.C. Patel, Date: 5/2/70

Source of phosphate used was
Potassium Dihydrogen Phosphate.



REFERENCES

(1) Baylis, J.R., "Effect of Microorganisms on Length of Filter Runs," Water Works Eng., 108, (1955), p. 127.

(2) Bogan, R.H., Albertson, O.E. and Pluntez, J.C.,"Use of Algae in Removing Phosphorus from Sewage,"J. Sanitary Engineering Division, Proc. ASCE, 86, No. SA 5, (1960) pp. 1 to 20.

(3) Bogan, R.H., "The Use of Algae in Removing Nutrients From Domestic Sewage," in Algae and Metropolitan Waste, R.A. Taft San. Engr. Center Report, W61-3, (1961), p. 140.

(4) Cole, C.V. and Jackson, M.L., J. Phys. and Colloid Chem. 54, (1950), p. 128.

(5) Corsaro, G., Ritter, H.S., Hrubik, W. and Stephens, H.L., "Mechanism of Phosphate Threshold Action," J. AWWA, 48, (1956),p. 683.

(6) Culp, R.L., "Wastewater Reclamation by Tertiary Treatment," Jr. of Water Pollution Control Fed., 35, (1963), pp. 799-806.

(7) Eberharde, W.A. and Nesbit, J.B., "Chemical Precipitation of Phosphate Within a High Rate Bio-Oxidation System," Presented at 22nd Annual Purdue Inc. Waste Conference, Lafayette, Inc., May, 1967.

(8) Eliassen, R., Reclamation of Reusable Water from Sewage, Progress Report, Demonstration Project Grant WPD-21-01 (USPHS), Stanford University,(August 9, 1963).

(9) Eliassen, R., and Wyckoff, B.M., Reclamation of Reusable Water from Sewage. Progress Report of PHS Grant WPD-21-02164, Technical Report No. 41, Dept. of Civil Engr., Stanford University, Stanford, California, (August, 1964).

(10) Galal-Gorchev, H. and Stumm, W.J., Inorganic and Nuclear Chemistry.

(11) Henriksen, A., "Laboratory Studeis on the Removal of Phosphates from Sewage by the Coagulation Process," Schweiz. Z. Hydrol. 24, (1962), pp. 253-271.

(12) Kaufman, W.J., "Removal of Radio Active Anions by Water Treatment," A.E.C. Report, NYO 1571 Oak Ridge, Tennessee, (1951).

(13) Kehr, W.Q. and Ownby, C.R., "Water Resources Problems of the Great Lakes," J. AWWA, 56, (1964), p. 1167.

(14) Lea, W.G., Rohlich, S.A. and Katz, W.J., Sewage and Industrial Wastes, 26, (1954), p. 261.

(15) McKee, J.E. and Wolf, H.W., Water Quality Criteria, State of California Water Quality Board, Publ. No. 3-A, 2nd Edition (1963).

(16) Malina, J.F., and Tiyaporn, S., "Effect of Synthetic Detergent on Lime-Soda Ash Treatment," J. AWWA, 56, (1964), p. 727.

(17) Martinez, W.W., "Phosphate and Nitrate Removal from Treated Sewage by Exchange Resins," M.S. Thesis, Dept. of Civil Eng., The Pennsylvania State University, (December, 1962).

(18) Oswald, W.J., Golueke, C.G., Cooper, R.C., Gee, H.K., and Bronson, J.C., "Water Reclamation, Algae Production and Methane Fermentation in Waste Ponds," New York: International Conference on Water Pollution Res., London, Permagon Press, (1964).

(19) Palmer, C.M., "Algae in Water Supplies," Public Health Service Publication No. 657, (1962).

(20) Palmer, C.M., "Algae and Other Interference Organisms in New England Supplies," J. New England Water Works Association, 72, (1958), p. 26.

(21) Palmer, C.M., "Algae and Other Interference Organisms is The Waters of South Central U.S.," J. AWWA, 52, (1960), p. 897.

(22) Palmer, C.M., "Algae and Other Interference Organisms in Water Supplies of California," J. AWWA, 53, (1961), p. 1297.

(23) Palmer, C.M., "Algae in Water Supplies of Ohio," Ohio J. Sc., 62, (1962), 236.

(24) Palmer, C.M., "Algae in Water Supplies of The United States," in Algae and Man, New York: Plenum Press, (1964), p. 239.

(25) Poston, H.W., and Gamet, M.B., "Effect of Algae on Filter Runs with Great Lakes Water," J. AWWA, 56, (1964), p. 1203

(26) Priday, W., Moyer, H.E., and Culp, R.L., "The Most Complete Wastewater Treatment Plant in The World," The American City, Vol. 79, (September, 1964), pp. 123-126.

(27) Reid, G.W., and Assenzo, J.R., "Culture and Harvesting of Attached Algae Grown on Domestic Sewage," Part I, Water and Sewage Works, 108, (1961), pp. 248 and 264.

(28) Reitmeir, G. B., and Buehrer, T.F., "The Inhibiting Action of Minute Amounts of Sodium Hexametaphosphate on the Precipitation of Calcium Carbonate from Ammonical Solutions. I. Quantitative Studies on the Inhibition Process, J. Phys. Chem., 44,(1940), II. Mechanism of the Process with Special Reference to the Formation of Calcium Carbonate Crystals," J. Phys. Chem., 44, (1940), p. 552.

(29) Rudolphs, W., "Phosphates in Sewage and Sludge Treatment, Quantities of Phosphates." Sewage Works Jr., 19, 1, (January, 1967), p. 43.

(30) Sawyer, C.N., "Biological Engineering in Sewage Treatment," Sewage Works Jr., 16, 5, (September, 1944), p. 925.

(31) Skulberg, O.M., "Algal Problems Related to the Eutro-

phication of European Water Supplies, and a Bio-Assay Method to Assess Fertilizing Influence of Pollution on Inland Waters," Algae and Man, New York, Plenum Press, (1964), p. 262.

(32) Stumm, W.,Department of Water Resources and Sanitary Engineering, Cambridge, Massachusetts: Harvard University.

(33) Stumm, W., and Morgan, J.J., J. AWWA, (1962)

(34) Tenney, M.W., and Stumm, W., "Chemical Flocculation of Microorganisms in Biological Waste Treatment," Jr. WPCF, 37, (October, 1965), p. 1370.

(35) Yee, W.C., "Selective Removal of Mixed Phosphates by Activated Alumina," J. AWWA, (February, 1966), pp. 239-247.

(36) Water Quality and Treatment, Second Edition, American Water Works Association, New York: (1951).