

AN ABSTRACT OF THE THESIS OF

GEORGE CAMPBELL HOUCK for the MASTER OF SCIENCE
(Name of student) (Degree)

in Civil Engineering presented on May 22, 1970
(Major) (Date)

Title: THE USE OF POLYMERS FOR BETTER SETTLING IN
DOMESTIC WASTE TREATMENT SYSTEMS
Redacted for Privacy

Abstract approved: _____
Donald C. Phillips

The author presents a "state of the art" of the use of polymers for better settling in domestic waste treatment and evaluates the published research in the field.

Polymers have only recently been used to obtain better settling in domestic waste treatment. Due to the number of polymer types available and to the varying compositions of domestic waste, the multitude of possible results are confusing to the practitioner. A purpose of this paper is to organize the available information so as to aid in its understanding.

The most valuable function of polymers is the flocculation of the colloidal fraction of wastewater. Thus the theories of colloids and their interactions with polymers are presented.

The paper summarizes the bench scale results of five researchers in some detail and includes many of their tables and

figures. Results of numerous other researchers are given in tabular form.

One investigator found that 0.5 mg/l of a cationic polymer added to raw sewage caused 61% BOD and 85% suspended solids removals by settlement. Furthermore 5 mg/l of the same polymer caused 3.5 times faster settling of activated sludge. Several investigators successfully settled bulked activated sludge with small dosages of polymer. One researcher reported remarkable improvement in settling of wastes when bentonite clay was added in conjunction with a cationic polymer.

Results with the many different specific types of polymers are tabulated and compared. Cationic polymers were more successful than the anionic or nonionic polymers, and moreover the latter were only effective when multivalent cations were present. Specifically cationic polyamines and a cationic polydiallyldimethylammonium were the most effective polymers which were reported in the literature.

Although polymers are used at many domestic waste treatment plants today, there is a paucity of published information giving the results. The author concludes that it would be most valuable to gather and publish this information.

The Use of Polymers for Better Settling in
Domestic Waste Treatment Systems

by

George Campbell Houck

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1971

APPROVED:

Redacted for Privacy

Professor of Civil Engineering
in charge of major

Redacted for Privacy

Head of Department of Civil Engineering

Redacted for Privacy

Dean of Graduate School

Date thesis is presented May 22, 1970

Typed by Barbara Glenn for George Campbell Houck

ACKNOWLEDGMENT

The author wishes to acknowledge the invaluable assistance received from Dr. Donald C. Phillips, Professor of Civil Engineering and my major professor, and Dr. Frank D. Schaumburg, Associate Professor of Civil Engineering. Furthermore the author acknowledges the support provided for his year of graduate work by the Federal Water Pollution Control Administration through a training grant. He extends his appreciation to his wife, Lou Anne, for her diligent typing of the various drafts of the thesis.

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION	1
THEORY	4
Colloids	5
Hydrophobic Colloids	6
Hydrophilic Colloids	7
Coagulation	10
Polymers	12
Metal Coagulants	17
WASTEWATER COMPOSITION	20
Domestic Sewage	21
Kraft Mill Wastewater	22
PHOSPHATE REMOVAL	24
RESULTS	28
Investigations Reported in the Literature	30
Rebhun, <u>et al.</u> , 1969	30
Jones, 1966	37
Dixon and Zielyk, 1969	46
Busch and Stumm, 1968	52
Tenney and Stumm, 1964	58
Additional Results	62
Water Treatment Results	67
Cohen, <u>et al.</u> , 1958	67
Pressman, 1967	68
DISCUSSION	71
Polymer Effect on Soluble versus Colloidal Organics	71
Observations	71
Observations on Industrial Wastes	73
Hypothesis	74
Polymer Effect in Various Treatment Systems	75
Primary Clarifier	75
Activated Sludge	75
Trickling Filter	78
Cost Considerations	79
Success of Different Polymer Types	82

TABLE OF CONTENTS (continued)

	<u>Page</u>
Basic Types	82
Specific Chemical Types	87
CONCLUSIONS AND RECOMMENDATIONS	89
Conclusions	89
Recommendations for Future Work	91
BIBLIOGRAPHY	93
APPENDIX A. Polymer and Coagulant Prices	102
APPENDIX B. Selected List of Researchers and Their Respective Projects	103

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.	Colloidal electrical charge due to adsorbed ions (after Argaman).	8
2.	Dissociation of carboxyl and amino groups (after Rich).	10
3.	Chemical structure of polymers (after O'Melia).	13
4.	Schematic representation of the effect of varying polymer concentration on floc size (after La Mer).	16
5.	Chemical cost comparison of phosphorus removal (after Malhotra).	26
6.	Removal of turbidity from secondary effluents by cationic polyelectrolyte purifloc C-31 in absence and presence of bentonitic clay (after Rebhun).	34
7.	Removal of apparent turbidity from secondary effluents by alum in absence and presence of bentonitic clay (after Rebhun).	34
8.	Removal of total and soluble COD by Purifloc C-31 in absence and presence of bentonitic clay (after Rebhun).	35
9.	Removal of phosphates by cationic polyelectrolyte PVPB in absence and presence of bentonitic clay (after Rebhun).	35
10.	Effect of Cat Flocc on removal of BOD and suspended solids in primary effluent (after Jones).	41
11.	Effect of Cat Flocc on removal of BOD and suspended solids in raw sewage (after Jones).	43
12.	Effect of revolutions of mixing on removal of suspended solids in raw sewage (after Jones).	44

<u>Figure</u>	<u>Page</u>
13. Effect of pH and Cat Flocc on removal of suspended solids in raw sewage (after Jones).	45
14. Effect of three Cat Flocc samples on the settling rate of activated sludge (after Jones).	47
15. Effect of three Cat Flocc samples on the settling rate of activated sludge (after Jones).	48
16. Effect of <u>E. coli</u> concentration on amount of polymer to initiate flocculation (after Dixon).	51
17. Effect of polymer on electrophoretic mobility and filtration time of <u>E. coli</u> (after Dixon).	51
18. Aggregation and redispersion of bacteria by anionic and nonionic polymers (after Busch).	54
19. Aggregation of SiO ₂ and of <u>A. aerogenes</u> with polymers of bacterial origin (after Busch).	57
20. Flocculation of dispersed microorganisms with cationic Purifloc 602 (after Tenney).	60
21. Flocculation of dispersed microorganisms with Al ³⁺ (after Tenney).	60
22. Effect of pH on flocculation of dispersed microorganisms by alum (after Tenney).	61
23. Removal of phosphorus by Al ³⁺ at pH 6 (after Tenney).	63
24. Effect of coagulant aids on pond water (after Cohen).	69
25. Flocculation of various waters treated with polymer A (after Pressman).	69
26. Effect of Dow C-31 on removal of BOD and suspended solids in raw sewage (after Jones).	72

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1	Typical strength parameter distributions among sewage fractions.	21
2	Mean characteristics of a kraft mill wastewater.	23
3	Average composition of the effluent from Haifa Sewage Treatment Plant.	31
4	Summary of additional results.	64
5	Analyses of waters used in laboratory studies.	70
6	Results with activated sludge.	77
7	Results using different polymer types.	83

THE USE OF POLYMERS FOR BETTER SETTLING IN DOMESTIC WASTE TREATMENT PROCESSES

INTRODUCTION

The scope of this paper is to present a "state of the art" of the use of polymers for increased settling in domestic waste treatment, and to analyze the published research by exploring the possible beneficial engineering applications. Direction for fruitful additional research in this field will be recommended. The writer believes that valuable service is done by simply organizing in one report the knowledge in this confusing and rapidly developing field. The confusion has been compounded due to the great number of polymer types available today and the variety of wastes that are treated.

The theories of the chemistry of colloids and their coagulation by the use of metal coagulants and the more recent polymers were first developed in relation to the treatment of raw water to make it potable, that is by removing turbidity, color, and other noxious substances. These theories are outlined in this report to give background to a knowledge of polymer interactions.

The results of research into the settling of several industrial wastes by polymers and also by metal coagulants are reported herein to give additional background to the subject of this paper. Also, for

the same reason a brief look is taken into the field of phosphate removal from domestic waste by the use of coagulants.

Polymers have already been established as invaluable flocculants to several domestic waste treatment processes involving sludges. Thus they are used successfully in sludge elutriation, sludge conditioning prior to vacuum filtration, and flotation thickening. Today it is an area where polymer use is growing rapidly. It is a vast field in itself and is not discussed at all in this report. Study of the field yields little information of value to the subject of domestic waste settling.

Although the literature is short of actual published research on the use of polymers for better settling of domestic wastes, several major chemical companies have within their files much information about their respective synthetic polymers and tests performed on settling at many waste treatment plants. Unfortunately the bulk of this information is rather tightly held as each company does not want to release any findings that might be helpful to a competitor. The writer has communicated by telephone and letter to the major companies in this field, i. e., Dow Chemical Co., Hercules Inc., Nalco Chemical Co., Calgon Corporation, and American Cyanamide Co. The information that was released is presented herein. Additional information has been gleaned from U. S. patents owned by these companies.

Much institutional research is presently ongoing. The Federal Water Pollution Control Administration has six research grants to American universities within this field. A list of each professor and his research project is appended. The majority of the professors have been major contributors to the literature of the coagulation of colloids. The writer communicated with each researcher and the information received has been included in this report.

THEORY

The main purpose in treating a domestic waste with a polymer is to obtain settling of the colloidal fraction of the waste. The particles larger than colloids will settle by themselves with no polymer being added, and the particles smaller than colloids are little affected by polymers. These smaller particles are defined as the soluble fraction. Thus it follows that the science of colloids must be briefly explained for the reader to gain an understanding of the subject of this report.

The field of colloidal science is a separate and distinct discipline. The presence of such publications as the Journal of Colloid and Interface Science, Journal of Physical and Colloid Chemistry, and Journal of Polymer Science attest to this. Several of the scientists who have contributed most to our knowledge of colloids and their coagulation are specialists in this field. So it is that such men as Black, La Mer, Matijević, Stumm, and Rebhun appear over and over again in the literature.

Colloidal systems have been investigated intensively for more than a century, but the major share of our knowledge of them has been developed in the last ten years. Since this knowledge is indispensable to the practice of water treatment it is not surprising that research involving colloids has emphasized the dilute concentrations

found in raw water supplies and synthesized single substance concentrations. The need for more effective water treatment has been present for some time, but only in the last few years has a need been acknowledged for more effective waste treatment. Domestic waste simply contains suspensions, colloids, and solutions in much higher concentrations than does a raw water supply. When a polymer or coagulant is added to waste water the number of possible resulting reactions and interactions is increased many times over those occurring in the treatment of water for potable supplies. Naturally, this makes the study involving wastes much more difficult.

Colloids

A colloid is a dispersion of fine particles which is intermediate in particle size between a suspension and a true solution. It has quite different properties than either of these latter two dispersions. The arbitrary size range of a colloidal particle set by most researchers today is approximately $1\text{ m}\mu$ to $1\ \mu$. These limits only serve as a guide and are not meant to be exact values. The $1\ \mu$ size corresponds roughly to the maximum size of particles that will stay in suspension for a reasonable time. The $1\text{ m}\mu$ size is roughly the upper limit for size of particles in a solution.

It is important to visualize the tremendous surface area of a colloidal dispersion. It is this large surface area which gives

colloids their unique properties. If a cube having a side length of 1 cm is subdivided into colloidal sized cubes having side lengths of 10 μ the surface area is increased from 6 sq cm to 6,000,000 sq cm or 600 sq meters.

There are two types of colloids, hydrophobic and hydrophilic. In general it can be said that inorganic colloids are hydrophobic and organic colloids are hydrophilic. The main property that sets the hydrophobic colloid apart is its extreme sensitivity to electrolytes such as the coagulants $\text{Al}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$. Small amounts of these salts will cause the particles to flocculate. Hydrophilic colloids on the other hand will only flocculate with massive doses of these coagulants.

Hydrophobic Colloids

All particles of a hydrophobic colloid have the same electrical charge and it may be positive or negative. Silicate materials such as clays have a negative charge, while the hydrated oxides of aluminum and iron are usually positively charged. This charge is the main reason for the stability of the colloid. It is the result of selective adsorption of ions from the solution onto the surface of the particle. Since the charge on the particle can be reversed by a change in pH, it has been postulated that hydrogen or hydroxyl ions are selectively adsorbed, depending on pH (43, p. 11). The

prevailing physical theory, called the diffuse-double layer theory, pictures the foregoing layer of adsorbed ions surrounded by a layer of diffused ions of opposite charge in the liquid side of the solid-liquid interface (2, p. 2). When the solid particle moves in an electrolyte it carries with it a stationary film of liquid extending to the surface of shear. See Figure 1. The electrical potential at this surface of shear is termed the zeta potential.

The magnitude of the zeta potential can be determined by electrophoretic mobility measurements whereby the velocity and direction of the particles in a known electric field is observed by microscope. The electrophoretic mobility is reported in microns/sec/volts/cm. Since like charges repel, the zeta potential acts as a repulsive force keeping the particles from approaching each other. It counters the Van der Waals force of attraction, a type of molecular cohesive force, that increases significantly as the particles approach each other. The purpose of coagulation is to destroy this zeta potential and enable the particles to come together.

Hydrophilic Colloids

Since colloidal organic material in domestic waste water is largely hydrophilic, this type of colloid is of more interest to this report than the hydrophobic colloid. Most hydrophilic colloids are products of plant or animal life. They are more difficult to

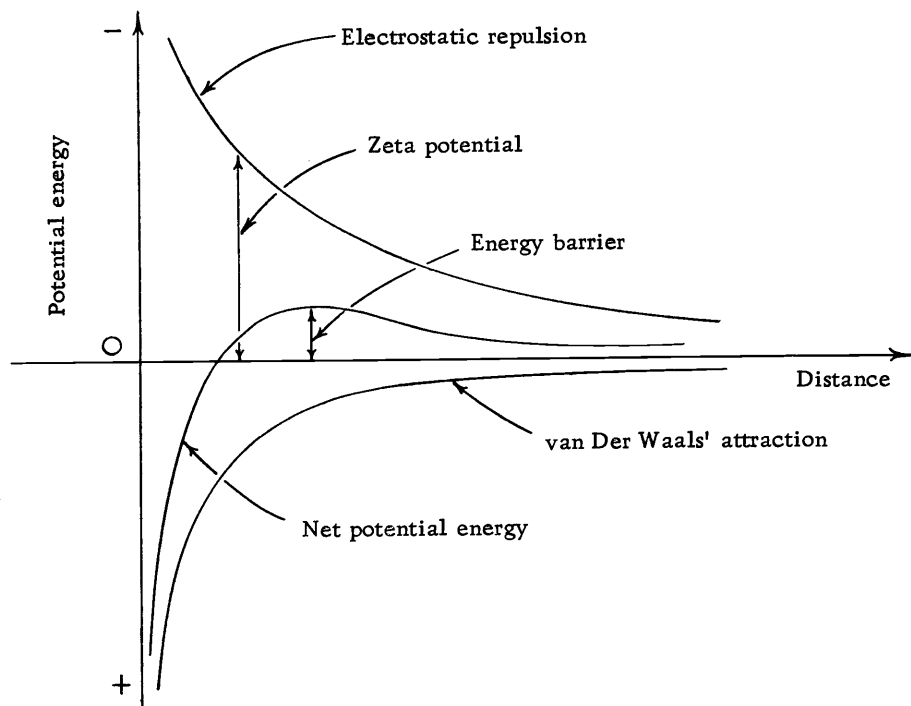
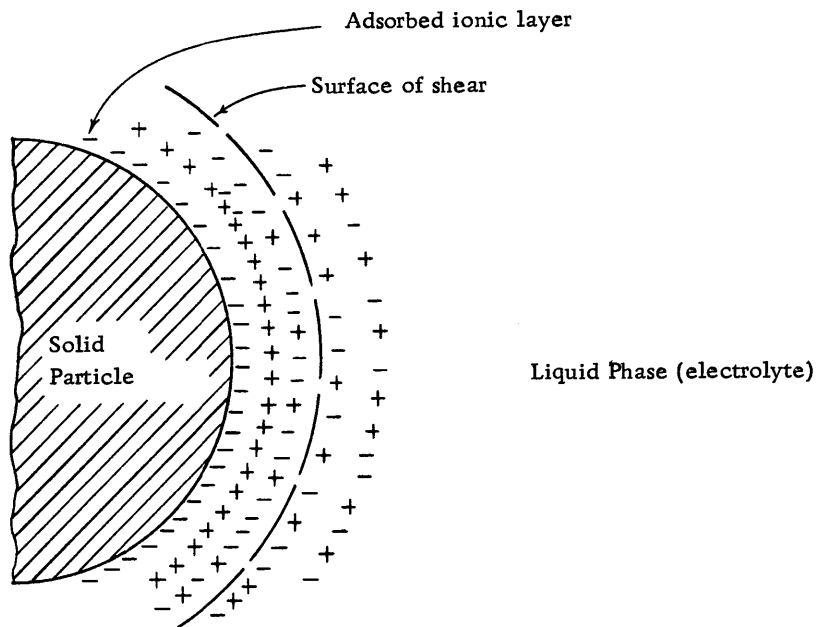


Figure 1. Colloidal electrical charge due to adsorbed ions (after Argaman).

flocculate than hydrophobic colloids largely due to their absorption of water.

Hydrophilic colloids may be true solutions, as single molecules or reversible aggregates of them, and are termed colloids because of the large size of their molecule which gives them colloidal properties (87). The weights of these large molecules fall within the range of colloidal particle weight.

Most hydrophilic colloids are electrolytic and in natural water have a negative charge. The charge is not produced by adsorption of ions on the surface of the particle, as with hydrophobic colloids, but rather by the ionization of functional groups such as carboxylic, aliphatic, aromatic, hydroxyl, sulfato, phosphato, or amino acids which are attached to the particle. Thus starch cellulose derivative, polysaccharide gums, and mucoproteins contain ionized carboxylic groups, while potato starch and nucleic acid contain phosphate or pyrophosphate ester groups (87).

As an example, protein molecules and their hydrolysis products contain both carboxylic and amino groups. Depending on the pH one or both of the groups dissociate. This is shown in Figure 2. It can be seen that in more basic solutions protein particles are negatively charged because of the COO^- group, while in more acidic solutions they are positively charged due to the NH_3^+ group.

Hydrophilic colloids also exhibit electrophoretic mobility.

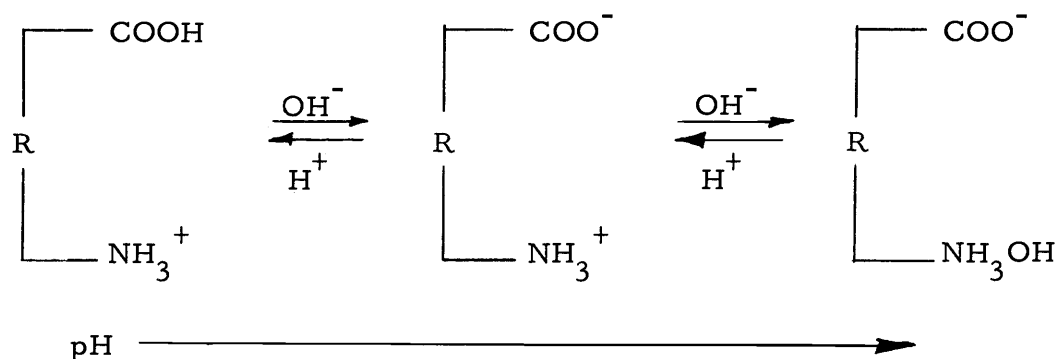


Figure 2. Dissociation of carboxyl and amino groups. (after Rich)

Thus they too have an isoelectric point wherein the net electric charge has been reduced to zero by the addition of coagulants or poly-electrolytes and there is no movement in an electric field. As will be seen later this isoelectric point is not necessarily the point of optimum flocculation.

Hydrophilic colloids, being much more difficult to coagulate than the hydrophobic, serve as protective colloids to the latter, shielding them from the action of electrolytes (76, p. 222). Thus hydrophilic colloids are adsorbed on particulate matter such as clay and impart hydrophilic properties to the material.

Coagulation

The removal of colloidal material from water during coagulation-flocculation takes place in two steps. The first, termed coagulation, includes the addition of coagulant and the series of chemical reactions and physical interactions that take place between the

particle, coagulant, and water. In the second step, termed flocculation, the particles come into contact with each other and agglomerate into flocs. Obviously the precise point where coagulation becomes flocculation is rather indefinite.

Coagulation has been explained for some time by what should be called the physical theory. In short by this theory, when electrolytes such as $\text{Al}_2(\text{SO}_4)_3$ or $\text{Fe}_2(\text{SO}_4)_3$ are added to a solution containing a hydrophobic colloidal dispersion, counter ions of charge opposite to that on the surface of the colloidal particle are adsorbed, the diffuse part of the double ionic layer is compacted, and the charge is neutralized. Thus the zeta potential is destroyed.

As part of this theory the valence of the coagulant ion of opposite charge has an important effect. The well known Schulze-Hardy rule states that a bivalent ion is 50-60 times more effective than a monovalent ion, and a trivalent ion is 700-1000 times more effective than a monovalent ion (3). This is the reason that $\text{Al}_2(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ are the most commonly used coagulants.

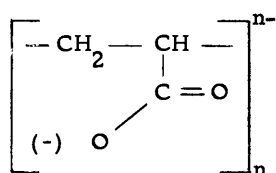
By 1968 it was apparent that this double layer model and the physical theory of coagulation just described were restricted in their application to only hydrophobic colloids and their coagulation by simple electrolytes (86). The introduction of synthetic organic polyelectrolyte coagulant aids for water treatment processes in the late 1950's had resulted in revised theories of coagulation. Indeed in

1962 La Mer (36, p.1838) was to say, "Electrostatic effects are not to be ignored but the subject of flocculation has suffered from overemphasis on electrostatics to the neglect of chemical forces. "

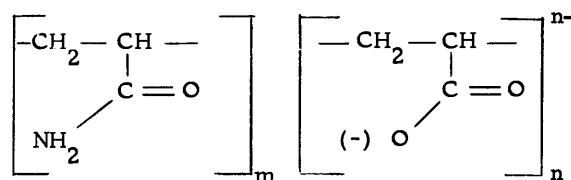
Polymers

A polymer molecule is one which has a number of repeating chemical units held together by covalent bonds. Many synthetic polymers contain only one type of repeating unit or monomer, while others contain two or three types. The total number of units can vary and thus different molecular weights result. The polymer chains may be linear or branched.

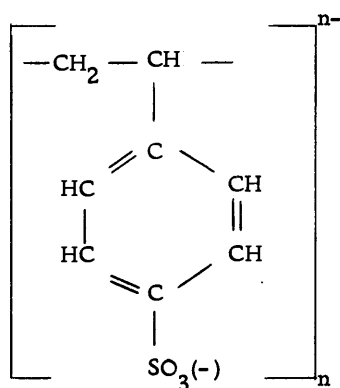
A polyelectrolyte is a special class of organic polymer which is soluble in water and has functional groups that will ionize along the polymer chain. Hence when a polyelectrolyte is dissolved in water the functional groups dissociate and the molecule is charged either positively or negatively. Thus we have cationic or anionic polyelectrolytes respectively. A polymer without ionizable groups is termed nonionic. Although common usage names all polymers used in water and waste treatment as polyelectrolytes, the proper term, when referring to all three types, is polymer. Polyelectrolyte refers to only cationic and anionic polymers. This report makes use of this more precise definition. Figure 3 shows a few examples of polymers.



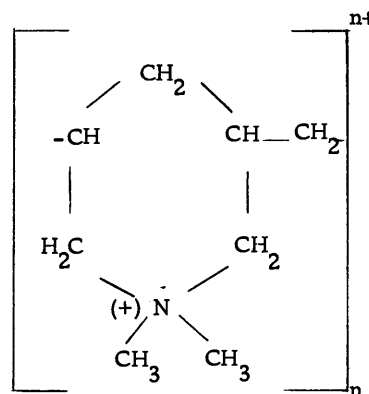
a. Polyacrylic Acid (PAA)
ANIONIC



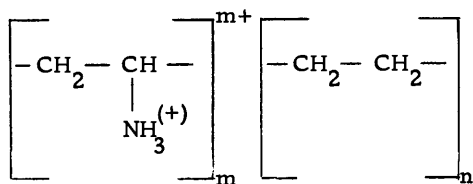
b. Hydrolyzed Polyacrylamide (HPAM)
ANIONIC



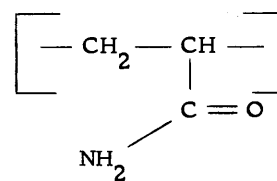
c. Polystyrene Sulfonate (PSS)
ANIONIC



d. Polydiallyl dimethylammonium
(PDADMA, Cat-Floc)
CATIONIC



e. Polyethyleneimine*
(a polyamine)
CATIONIC



f. Polyacrylamide (PAM)
NONIONIC

Figure 3. Chemical structure of polymers. (After O'Melia). *Inserted by author.

Polymers are termed macromolecules because of their large size, and are most usually long and linear. They have a great range in molecular weight, from perhaps 300 to 3,000,000. A typical molecular weight might be 10,000.

La Mer and others have developed a chemical bridging model to explain how polymers destabilize colloidal suspensions (47, 54). According to this theory a polymer molecule attaches itself to the surface of a colloidal particle at one or more adsorption sites and the remainder of the molecule segments extend out into the solution. These extended segments then interact with vacant sites on other colloidal particles and "bridges" are formed. Each polymer molecule can have many functional groups or segments that can be adsorbed or bonded and therefore one polymer molecule can attach itself to many separate particles. Usually with increasing molecular weight, and hence an increasing number of functional groups, polymers can adsorb more particles. Hydroxyl, phosphoryl, and carboxyl groups along the polymer chain are particularly effective in causing adsorption (86). The adsorption or bonding is quite specific as to the type of particle that can be adsorbed by a particular polymer functional group. Quite often anionic polymers are adsorbed on negatively charged colloids. This in itself refutes the physical theory described heretofore, which maintains that only opposite charges are attracted, and limits the use of this theory to hydrophobic colloids and their

coagulation by electrolytes. As an example of the former, hydrolyzed polyacrylamides are negatively charged but are excellent flocculants for negatively charged colloidal dispersions. It is postulated that anionic polymers can adsorb on negative colloids by hydrogen bonding, anion interchange with adsorbed anions such as OH^- , or interactions with cations on or in the immediate vicinity of the colloid surface (15, 54).

The following are important aspects of the polymer bridging model:

1. There is a definite correlation between colloid concentrations and the optimum polymer dosage for flocculation. This follows since available surface area varies directly with particle concentration. Also the optimum destabilization occurs when only a portion of the available adsorption sites on the surface of the colloid have been covered.
2. If too great a polymer dosage is used a destabilized colloidal dispersion will restabilize since the surfaces will be saturated with polymer and no more sites are available for polymer bridges. See Figure 4.
3. A destabilized colloid can be restabilized by extended agitation due to the breaking of the polymer bridges. Therefore time of agitation is an important variable.
4. The optimum flocculation does not necessarily occur at the

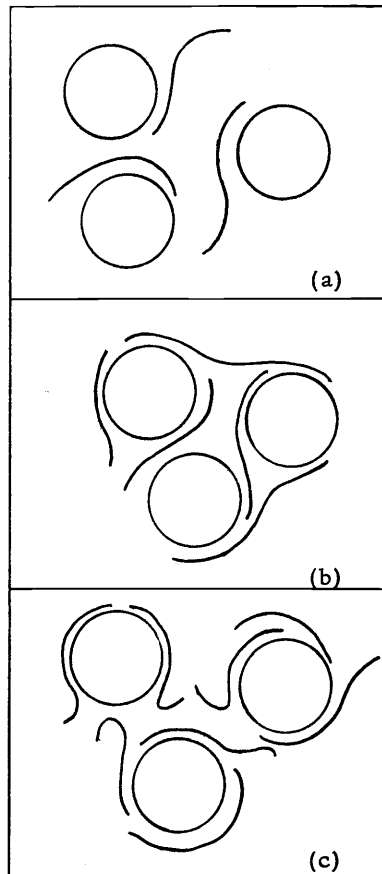


Figure 4. Schematic representation of the effect of varying polymer concentration on floc size. (a) Low polymer concentration, (b) optimum polymer concentration, (c) excess polymer concentration (after LaMer).

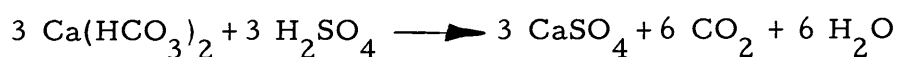
isoelectric point.

Workers in 1958 discovered that anionic and nonionic polymers were only effective in removing turbidity from natural and synthetic waters of low suspended solids concentration when used in conjunction with metal coagulants such as alum (20). However the necessary coagulant dosage was significantly reduced by the use of the polymer. It has been postulated that the metal cation reduces the negative charge on a colloidal particle to a degree where the anionic polymer can approach and become adsorbed or bonded as mentioned previously. The workers further found that cationic polymers were effective whether used alone or with a metal coagulant.

Metal Coagulants

The metal coagulants, aluminum sulfate, $\text{Al}_2(\text{SO}_4)_3 \cdot 14 \text{H}_2\text{O}$, ferric sulfate, $\text{Fe}_2(\text{SO}_4)_3$, and other iron salts have long been successfully used in water treatment. They remove dilute colloidal suspensions of negatively charged clay, organic coloring matter, and other objectionable material found in natural waters. Most of the metal cations react with alkalinity in the water to produce many species of insoluble positively charged hydroxides. The theory has been that these cations, often bearing a quite high positive charge, neutralize the negative charge of the colloid particle, whereupon both are agglomerated into floc.

The equations representing alum reaction with alkalinity are the following:



The alum reaction with water releases H^+ ions, depressing the pH. If insufficient alkalinity is present naturally as a buffer, lime or other material must be added to prevent a lowering of the pH, which would not allow formation of additional aluminum hydroxide. The pH should be kept above 5 to get nearly complete precipitation and hence effective coagulation from both alum and iron coagulants.

Investigators (87) analyzing the composition of a 10 M solution of ferric coagulant found the following:

20%	Fe^{+++}
40%	$\text{Fe}(\text{OH})^{++}$
5%	$[\text{Fe}(\text{OH})_2]^+$
35%	$[\text{Fe}_2(\text{OH})_2]^{4+}$

Recent research has determined that hydrolyzed metal ions fall into an intermediate category between simple ions and poly-electrolytes (86). The hydrolysis of the metal cations is said to continue into polymerization to multinuclear hydrolysis species which act more like polyelectrolytes. In contrast to the double layer model and its coagulation by neutralization of the charge, the more recent

literature states that coagulation by alum and iron salts is quite specific, and in addition to charge neutralization, involves chemical reactions at the colloidal surface.

The optimum coagulant dosage depends on:

1. colloid concentration and charge
2. pH
3. presence of other cations and anions
4. temperature

Other ions in solution have a profound effect on coagulation.

Since domestic wastewater contains a greater variety of substances than does natural water and in greater concentration, it is not surprising that the successful and economic coagulation of wastewater has been an elusive goal. Alum and iron salts used alone as coagulants cause many problems. The principal problems are the high dosage requirements (in the neighborhood of 150-300 ppm), and the resulting large sludge volumes which must be disposed.

WASTEWATER COMPOSITION

Knowledge of the composition of a waste is all important if the use of polymers to increase settling is contemplated. Wastes vary a great deal and since polymers are quite specific in their actions, laboratory tests (i. e. , jar tests) and trial plant runs must be performed to find the correct polymer and its dosage. Often the waste is not amenable to polymer treatment of any kind.

Polymers are most effective in causing liquid-solid separation of colloids. The settleable solids portion of suspended solids will settle without the aid of polymers. Thus it is generally held that 40-60% of suspended solids in domestic sewage are removed in a primary clarifier without the addition of a flocculant. But suspended solids, as determined by Standard Methods, include the supracolloidal fraction and a portion of the colloidal fraction of sewage since the analysis uses a filter with 0.45 μ pore openings. Supracolloidal has been defined (42) as particulate matter of a particle size greater than 1 μ (which is the arbitrary upper limit of colloidal particle size), but showing colloidal characteristics. Thus polymers will substantially increase suspended solids removal in clarification by interacting with these two fractions.

Soluble organic matter on the other hand is little affected by treatment with flocculants. Thus a waste whose organic fraction is

mostly soluble will give disappointing results with polymers.

The following paragraphs give description of the analysis of two wastes used frequently by researchers in the polyelectrolyte field.

Domestic Sewage

The results of recent investigation into the composition of domestic sewage included the findings in Table 1 (42). The table shows that colloidal and supracolloidal matter made up 29% of the organic matter in the sewage from a residential New Jersey community. The supracolloidal fraction was removed from sewage, which had previously been settled, by centrifugation at 14,000 rpm (42, 75). The colloid fraction of the remaining sewage was then

Table 1. Typical strength parameter distributions among sewage fractions (after Hunter).

Fraction	Strength Parameter		
	Total Solids % by weight	Organic Matter ^a % by weight	Nitrogenous Matter ^b % by weight
Settleable	18	30	23
Supracolloidal	11	19	34
Colloidal	7	10	11
Soluble	64	41	22

^aVolatile solids or calculated from organic carbon data

^bCalculated from Organic Nitrogen Data, assuming all nitrogenous matter was protein

removed by ultrafiltration through a cellophane membrane.

Whereas Table 1 indicates 41% of the organic matter in sewage to be soluble, McKenney (51, p. 168) states that 20% of the organic matter of fresh sewage is soluble. He further states that as sewage ages biological action converts more of the insoluble organics to the soluble form until stale sewage contains 50 to 60% soluble organics.

McKenney divides the organic matter of sewage into three major groups and gives the following breakdown:

protein	40-50%
carbohydrates	40-50%
fat	5-10%

Kraft Mill Wastewater

Colloids impart the major portion of the color and suspended solids of kraft mill wastewaters. In addition a significant proportion of the COD is in the form of colloidal particles and coarse suspensions. These materials can be removed by treatment with poly-electrolytes. However the BOD of the waste is mostly soluble and little affected by them. Table 2 shows a typical kraft mill wastewater.

Table 2. Mean characteristics of a kraft mill wastewater (after Middlebrooks).

Constituent	Concentration (mg/l)
COD	950
BOD (5 day)	96
SS	540
VSS	330
pH	6.9

PHOSPHATE REMOVAL

With the recent increased emphasis on nutrient removal, and particularly phosphate removal, from municipal waste treatment plants much research has been directed toward finding improved removal methods. Accordingly the literature contains scores of recent papers on the subject of phosphate removal. Polymers have only been used in a very few of these investigations. Since polymers used alone or in conjunction with the primary coagulants are the subject of this report, the field of phosphate removal will be reviewed only briefly to give additional background.

Recently Nesbitt published an excellent "state of the art" paper on the subject (60). The reader is referred to this article for additional information.

An approximate figure for phosphorus concentration in raw sewage is 24 mg/l PO_4 (60). A desirable goal for effluent is roughly 0.2 mg/l PO_4 (61, p. 1).

The most promising methods developed to date for phosphate removal are its precipitation with lime, alum, or iron salts. These coagulants can be added in a third, tertiary, step to domestic waste treatment, or they can be added in a secondary treatment plant to bring about precipitation in the primary or secondary clarifier. The resulting precipitates, all relatively insoluble, are $\text{Ca}_3(\text{PO}_4)_2$,

$\text{Al}(\text{PO}_4)$, and $\text{Fe}(\text{PO}_4)$ respectively.

The following figures, an approximate average of several investigations, give an idea of lime precipitation results:

$\text{Ca}(\text{OH})_2$ dosage:	250 mg/l
pH	11.0
PO_4 in effluent	3 mg/l
PO_4 removal	92%
BOD removal	70%

The fact that a high pH is necessary is advantageous in that ammonia nitrogen can then be removed by a stripping process. However a major disadvantage is that if the buffer capacity of the receiving water is not adequate the high effluent pH may need to be adjusted (52). If a minimum phosphate level in the effluent is desired a final filtration step is necessary for these precipitation methods.

Alum precipitation requires approximately the same dosage as lime and gives phosphate and BOD removals of the same magnitude. However, with alum the optimum pH is much lower.

Percentage removal of total phosphate against chemical cost in dollars per million gallons is shown in Figure 5. It is apparent that lime precipitation is the cheapest method. Nesbitt (60) concludes that most of the phosphorus removal schemes that have been proposed would double the cost of municipal waste treatment. Where new plants incorporated phosphorus precipitation within the primary

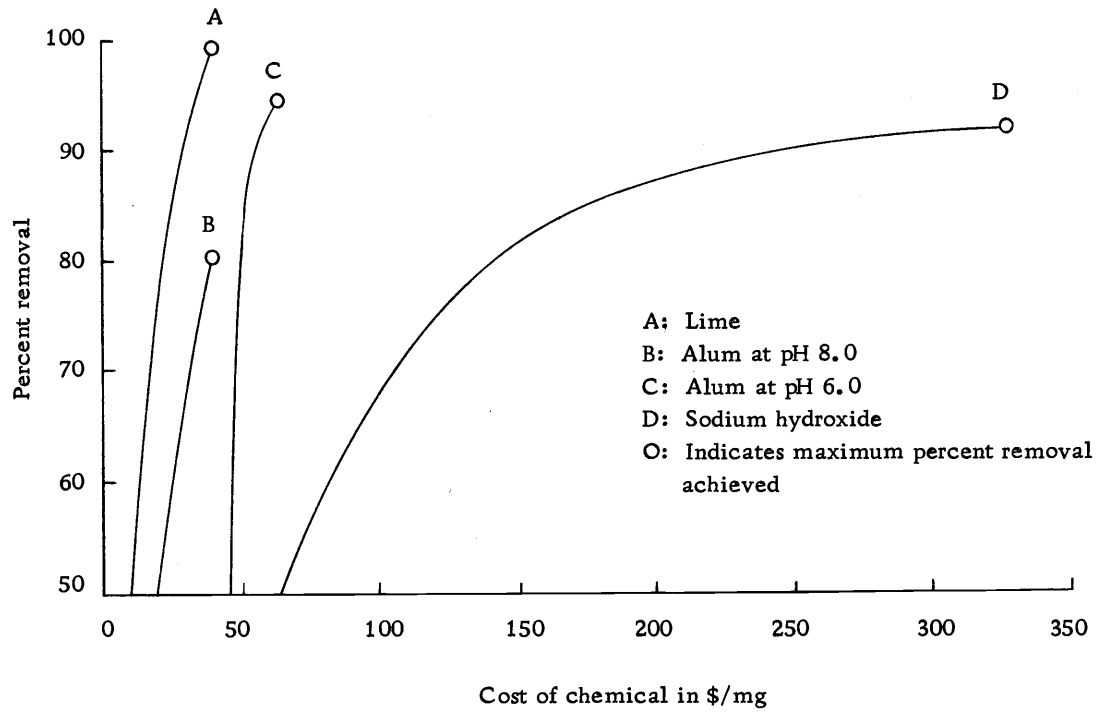


Figure 5. Chemical cost comparison of phosphorus removal (after Malhotra).

treatment units this extra cost would be considerably less.

Results of the investigators, Rebhun et al. , and Tenney and Stumm, whose work on organic waste removal included phosphate removal, are found in the chapter entitled "Results."

RESULTS

A search of the literature revealed only seven informative published papers reporting the results of researchers who investigated the use of polymers for better settling of domestic wastes. Three additional published papers gave the results of researchers using polymers and/or coagulants with paper mill and tannery wastes. The results of all ten investigations are presented in this chapter.

The seven articles dealing with domestic wastes were very complete and well done in the specific area which they covered and are sufficient to give the reader an understanding of what is possible and to be expected in this rapidly advancing field. It is noteworthy that two of the articles were published in 1969, two in 1968, and one in 1966.

During the last decade many more papers than those cited above have been published giving the results when using polymers and/or coagulants in potable water treatment. As stated before it is in this field that the chemical additives were first used and theories developed. A few of these investigations are reported in this paper merely as background information for the subject at hand, which is domestic waste water. These results give the reader an idea of the relative flocculant concentrations involved and the interactions occurring during raw water clarification.

The writer communicated by telephone and subsequently by two letters to each of five chemical companies, all major producers of synthetic organic polymers used in water and waste treatment. These companies were Calgon Corporation, Dow Chemical Company, Hercules Incorporated, Nalco Chemical Company, and Permutit Company. The writer asked for "case histories" on the successful use of polymers and coagulants at domestic waste treatment plants which, hopefully, would include BOD, COD, and suspended solids removals, names and dosages of the flocculants, and type of waste treated. Unfortunately he received only brochures written in general terms with no specific information. The companies gave various reasons explaining why they could not release more information.

This writer's experience parallels that of other investigators in the literature. Thus Jones (43, p. 3) wrote: :

. . . most of the research work on polyelectrolytes for water and waste water treatment has been done by major chemical producers, who have closely guarded their results for proprietary reasons. In reviewing the literature, especially for waste treatment, it was found that most of the papers have been authored by personnel of these chemical producers who report on plant scale tests of their polymers in vague although favorable terms and present little useful data.

Included later in this chapter is a table showing results found by the chemical companies as reported rather incompletely in the literature or in brochures and bulletins.

Investigations Reported in the Literature

Rebhun, et al. , 1969 (69)

Summary

Rebhun investigated the use of polyelectrolytes in combination with bentonite clay for treating effluent from the Haifa, Israel municipal waste treatment plant. This plant consists of high rate trickling filters and primary and secondary clarifiers. He found that cationic polyelectrolytes cause flocculation of suspended particles and reacted with soluble anionic organic material to produce colloids that were difficult to settle. If bentonite clay was added it caused removal of these reaction products and also necessitated a smaller polyelectrolyte dosage. In addition he found that bentonite clay used by itself caused some removal of organic matter. Rebhun also experimented with alum and with anionic and nonionic polymers. He had good results with the alum but not with the latter two types of polymers.

Waste Composition

The quality of the plant effluent is shown in Table 3. The water had a quite high organic content, color, salinity, and hardness. This is due to the low per capita water use in Israel.

Table 3. Average composition of the effluent from Haifa Sewage Treatment Plant (after Rebhun).

Constituent	Units	
Total suspended solids	mg/l	32
Total dissolved solids	mg/l	1318
pH		7.8-8.0
Color	color units	165
BOD	mg/l	29
ABS	mg/l	21.9
Alkalinity (M. O.)	mg/l as CaCO ₃	578
Total hardness	mg/l as CaCO ₃	479
Ca ⁺⁺	mg/l as CaCO ₃	252
Mg ⁺⁺	mg/l as CaCO ₃	227
Total N	mg/l as N	73.9
NH ₄ ⁺	mg/l as N	59.9
Organic N	mg/l as N	14.0
NO ₃ ⁻	mg/l as N	6.2
Cl ⁻	mg/l	402
SO ₄ ⁻⁻	mg/l	91.1
PO ₄ ⁻⁻⁻	mg/l	21.6

Flocculants

1. Alum
2. Cationic polyelectrolyte, Purifloc C-31, manufactured by Dow Chemical. It is a polyethyleneimine having a molecular weight of 30,000.
3. Cationic polyelectrolytes, PVPB, a polyamine synthesized by Rebhun, poly-4-vinyl-N-butylpyridonium bromide. Molecular weight is 32,800.
4. Nonionic polymer, Magnifloc 972, manufactured by American Cyanamide. It is a polyacrylamide having a molecular weight of 2,000,000. Both polymers were added as 0.1% solutions.
5. A bentonite clay named Wyoming M-26.

Methods

Rebhun used jar tests in his work and employed a mixing rate of 100 rpm for 5 minutes followed by flocculation at 25 rpm for 25 minutes and various settling periods. He used optical density (absorbance) measured with a Hilger-Spekker electrophotometer as his main analytical test. This gave him "apparent turbidity," the sum of the effects of turbidity and color. To obtain true turbidity he centrifuged the samples at 8000 rev/min for 20 minutes; the optical

density of the centrifuged sample represented true color which was subtracted from the original apparent turbidity to give true turbidity.

Results

Figures 6 and 7 show flocculation results with and without bentonite clay. Impractical and uneconomic doses of cationic polyelectrolyte and alum were necessary for turbidity removal without clay. When clay was added in the amount of 500 mg/l prior to dispersing the polyelectrolyte, 0.5 mg/l of Purifloc C-31 was able to remove 93% of true turbidity. The flocs were larger and settled at faster rates. The increased turbidity seen in Figure 6, resulting when Purifloc C-31 was added without clay, was explained by Rebhun to be a consequence of a reaction between the polycation and various components in solution.

Figure 8 presents removal of total and soluble COD by flocculation with Purifloc C-31 with and without bentonite clay. The total COD results were obtained with a 30 minute settling time. A 34% removal of total COD occurs when no flocculant is added, simply due to additional settling caused by the agitation. Eighty-five percent total COD removal is obtained when 500 mg/l clay is added followed by 20 mg/l Purifloc C-31. Results using centrifuging rather than settling are also shown. Rebhun states that the curve showing soluble COD removal after centrifugation proves that the polymer

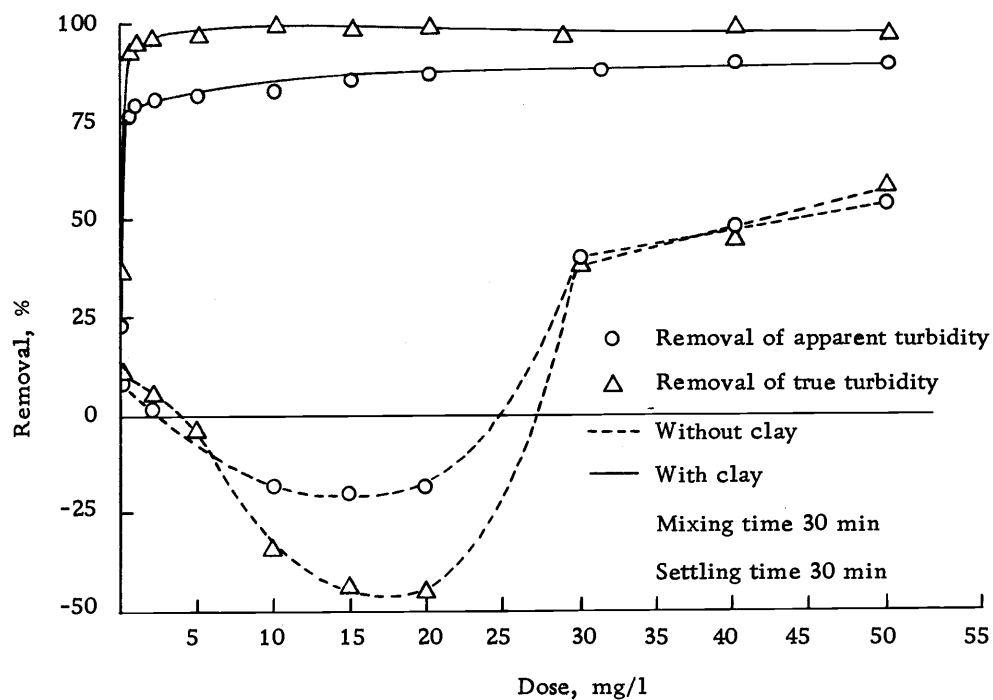


Figure 6. Removal of turbidity from secondary effluents by cationic polyelectrolyte purifloc C-31 in absence and presence of bentonitic clay (after Rebhun).

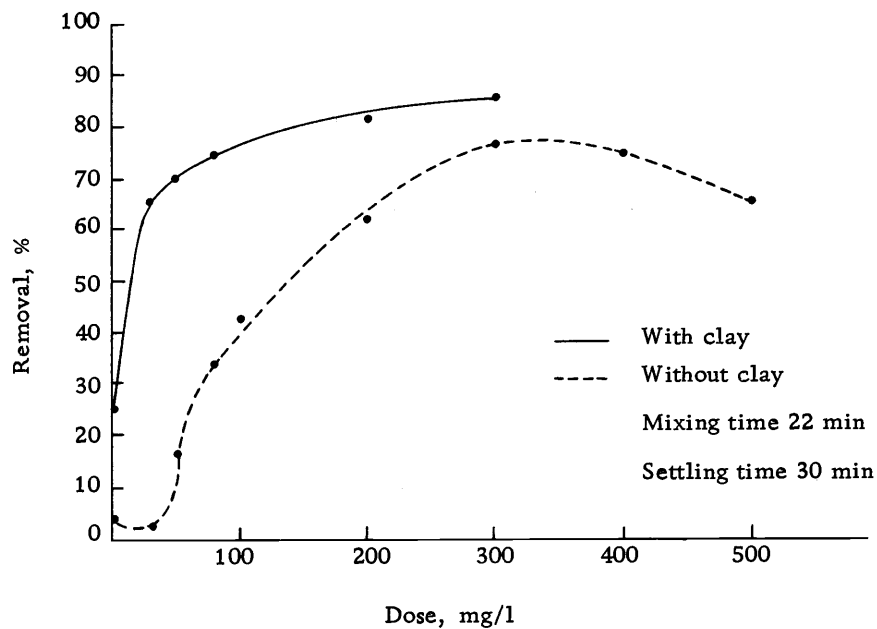


Figure 7. Removal of apparent turbidity from secondary effluents by alum in absence and presence of bentonitic clay (after Rebhun).

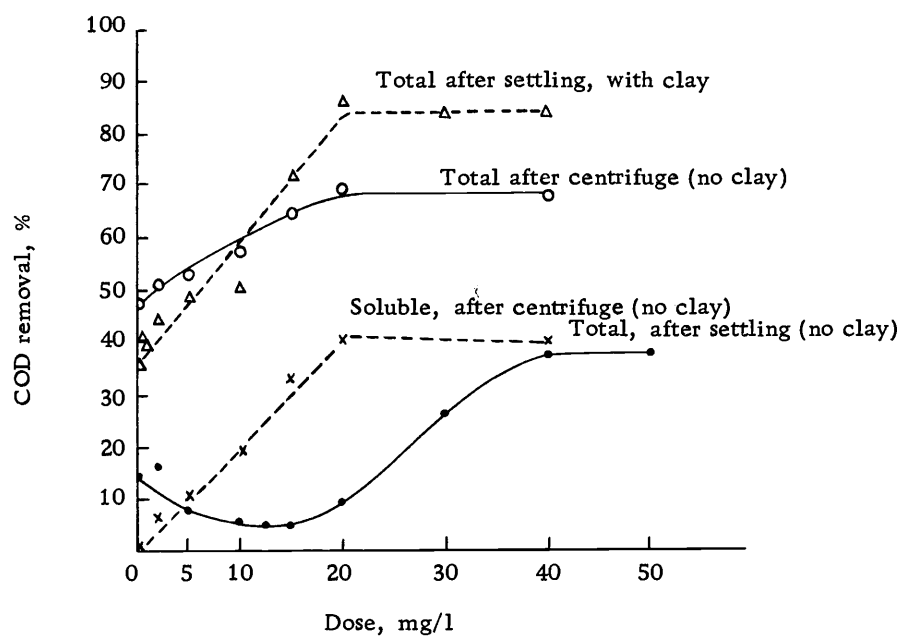


Figure 8. Removal of total and soluble COD by Purifloc C-31 in absence and presence of bentonitic clay (after Rebhun).

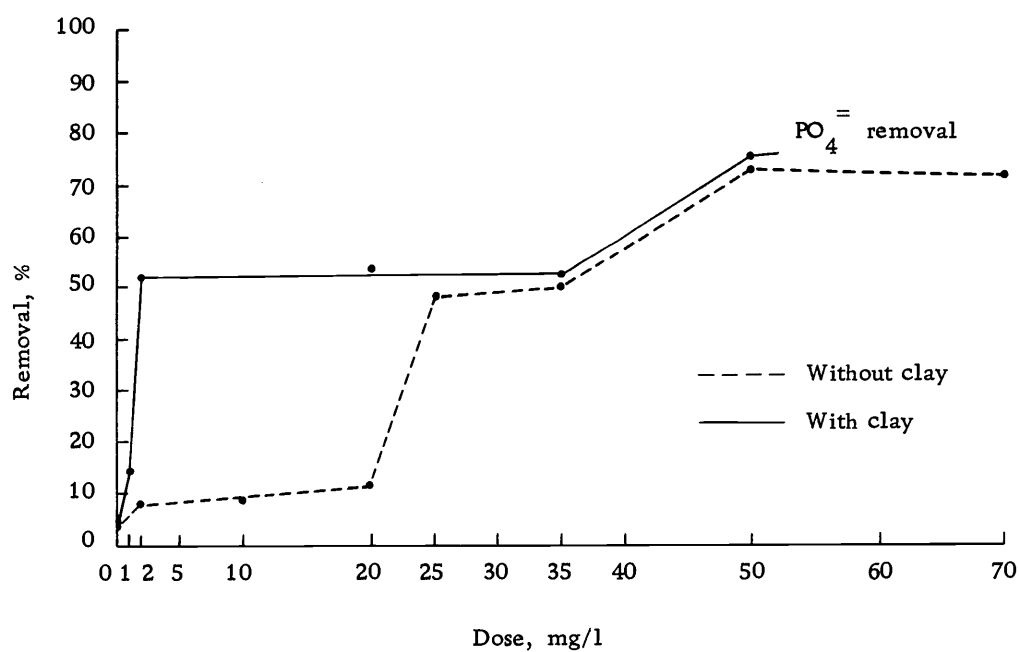


Figure 9. Removal of phosphates by cationic polyelectrolyte PVPB in absence and presence of bentonitic clay (after Rebhun).

reacts with soluble organic matter and that the reaction products being insoluble can be removed by centrifugation.

Figure 9 shows phosphate removal by the cationic polyelectrolyte PVPB with and without bentonite clay. Rebhun surmises that the quaternary amine polycation reacts with phosphates and finely dispersed colloid results. He states, "in the presence of clay, the reaction product is adsorbed by the clay and removed as it settles." (69, p. 351).

Rebhun's Discussion

Rebhun states that the cationic polyelectrolyte reacts with the dissolved anionic organic matter in the plant effluent. Because a substantial part of the organic fraction of a secondary clarifier effluent is in solution, a high dosage of cationic polyelectrolyte is necessary, 20 mg/l in this case. The reaction products are highly dispersed colloids which will settle only in the presence of clay. The clay particles serve as nuclei for flocculation. Perhaps segments of the cationic polyelectrolyte which have not reacted with the organic material form bridges to the clay particles. The clay is in a coagulative state due to the high ionic strength and Ca^{++} concentration of the effluent and settles rapidly.

Rebhun is at present studying the flocculation of hydrophilic organic suspended solids from a suspension that does not contain

dissolved organic matter.

Jones, 1966 (43)

Summary

Jones, for his Ph. D. dissertation at the University of Florida, investigated the use of a cationic polyelectrolyte, Cat Flocc, in the treatment of domestic wastewater. Dr. A. P. Black, one of the best known names in the field of coagulation, served as his committee chairman. Jones studied the effect of three different molecular weights of cationic polymer on:

1. raw sewage
2. primary clarifier effluent
3. activated sludge
4. dewatering of anaerobically digested sludge

The first three applications are of prime interest to this writer's report.

Jones obtained 61% BOD removal and 85% suspended solids removal from the raw sewage with a 0.5 mg/l dosage of Cat Flocc of all three molecular weights. Flocculating with a dosage of 8 mg/l of Purifloc C-31 and 8 mg/l of Primafloc, both cationic polyelectrolytes, gave similar BOD and suspended solids removals. Furthermore when using 5 mg/l Cat Flocc, Jones obtained 80% BOD removal

and 95% suspended solids removal. The Cat Floc polymer with the highest molecular weight formed the largest and fastest settling floc which was also most resistant to breakup due to extended mixing.

Activated sludge settling rates were found to increase considerably by flocculation with Cat Floc and once again the highest molecular weight polyelectrolyte gave the fastest settling rate.

Jones experimented further by adding lime together with Cat Floc to flocculate raw sewage. Better removals were obtained than without lime.

Jones concluded that the introduction of polyelectrolytes has been the most important development in the field of waste treatment since the activated sludge process.

Waste Composition

Grab samples from the University of Florida and Gainesville, Florida, sewage treatment plants were used for the investigations of coagulation-flocculation of raw sewage and settled sewage. Grab samples of activated sludge were obtained from the University of Florida and Daytona Beach, Florida, sewage treatment plants. The author did not indicate that any of the plants treated an industrial waste and since the wastes of the plants responded similarly to treatment, it is assumed no industrial waste load of consequence existed.

Flocculants

1. Cat Flocc, a cationic polyelectrolyte manufactured by the Calgon Corporation but originally developed and manufactured by Black Laboratories Inc. It is a linear homopolymer of diallyldimethylammonium chloride. The ionized form of this polymer is shown in Figure 3. Three different molecular weights of Cat Flocc were used: Cat Flocc No. 1 with a relative molecular weight of 1.00; Cat Flocc No. 2 with a relative molecular weight of 1.57; and Cat Flocc No. 3 with a relative molecular weight of 1.72. The molecular weight of Cat Flocc No. 3 was less than 300,000.
2. Purifloc C-31, a cationic polyelectrolyte used in Rebhun's work and described previously.
3. Primafloc C-7, a cationic polyelectrolyte manufactured by Rohm and Haas Co. It is a polyamine having a molecular weight over 1,000,000.
4. Lime.

Methods

Jones used jar tests in his investigations. Working solutions of polyelectrolytes were prepared by diluting the manufactured product until solutions of 10 mg/ml, 1 mg/ml, and 0.1 mg/ml were

obtained. Jones utilized a mixing rate of 100 rpm for 20 minutes, followed by flocculation at 20 rpm for 20 minutes. Samples were allowed to settle for 15 minutes.

The parameters measured were BOD, suspended solids, pH, and electrophoretic mobility. Settling rate of activated sludge was determined in a 30" tall by 6" diameter tube that eliminated sidewall effects.

Results

Settling of raw sewage and primary effluent. Jones ran his tests using all three different molecular weights of Cat Flocc. The results for the different molecular weights were nearly identical in all respects excepting when using extended mixing. He also ran parallel tests on sewage and settled sewage from both domestic treatment plants. These results also were similar although the University's plant had a weaker sewage and hence required less polymer dosage. Only a representative sampling of the figures depicting Jones' results are shown in this report.

Figure 10 shows a substantial reduction of BOD and suspended solids from settled sewage. Jones assumes that Cat Flocc does not remove dissolved organic matter and states that this figure shows that a large portion of the solids in settled sewage are in the colloidal form and can be removed by Cat Flocc.

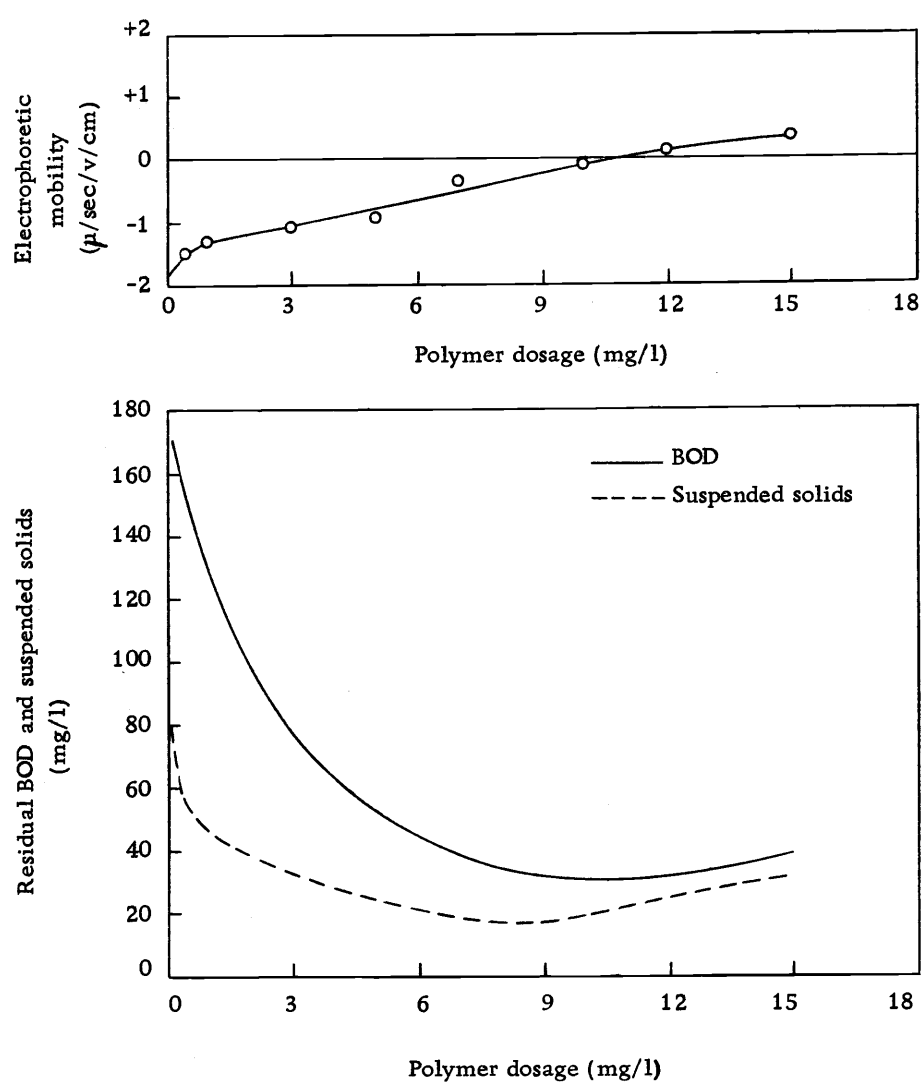


Figure 10. Effect of Cat Flocculation on removal of BOD and suspended solids in primary effluent (after Jones).

Good BOD and suspended solids removal were obtained over a wide range of electrophoretic mobilities, as seen in Figures 10 and 11. Only after mobility values became positive did the particles re-disperse. Part of the removal from raw sewage shown by Figure 11 can be attributed to suspended solids that would have settled in a primary clarifier without a flocculant, but not the entire 60% BOD removal obtained with only 15 minutes settling.

Figure 12 shows the effects of extended mixing on different weight polymers. The floc formed by Cat Flocc No. 1, of lower molecular weight, tends to break up after 500 revolutions, while the floc formed by Cat Flocc No. 3 increases in size. Jones states:

This factor may be of considerable importance in design, as the kinetics of coagulation-flocculation are a function of total revolutions and not of mixing time. A higher molecular weight polymer would allow higher mixing rates and thereby shorter detention times to obtain a given removal efficiency. (43, p. 77).

Figure 13 shows the effect of adding 185 mg/l $\text{Ca}(\text{OH})_2$ to raw sewage in addition to Cat Flocc No. 3, and thus raising the pH to 10.3. The Ca^{++} ions changed the electrophoretic mobility of the sample and resulted in slightly better removal of suspended solids and BOD.

Activated sludge settling. Jones experimented with a multitude of polymer dosages, suspended solids concentrations, and sludge volume indices (SVI) to determine the effect of Cat Flocc on the

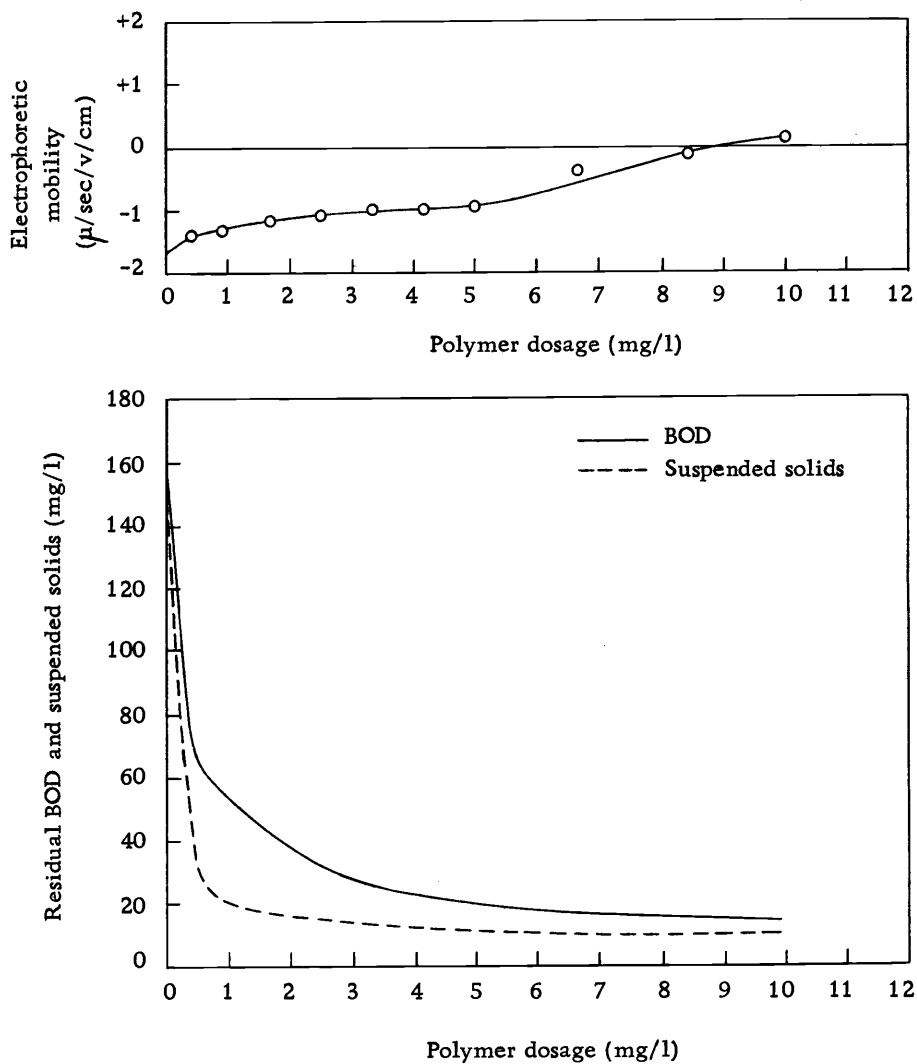


Figure 11. Effect of Cat Flocculant on removal of BOD and suspended solids in raw sewage (after Jones).

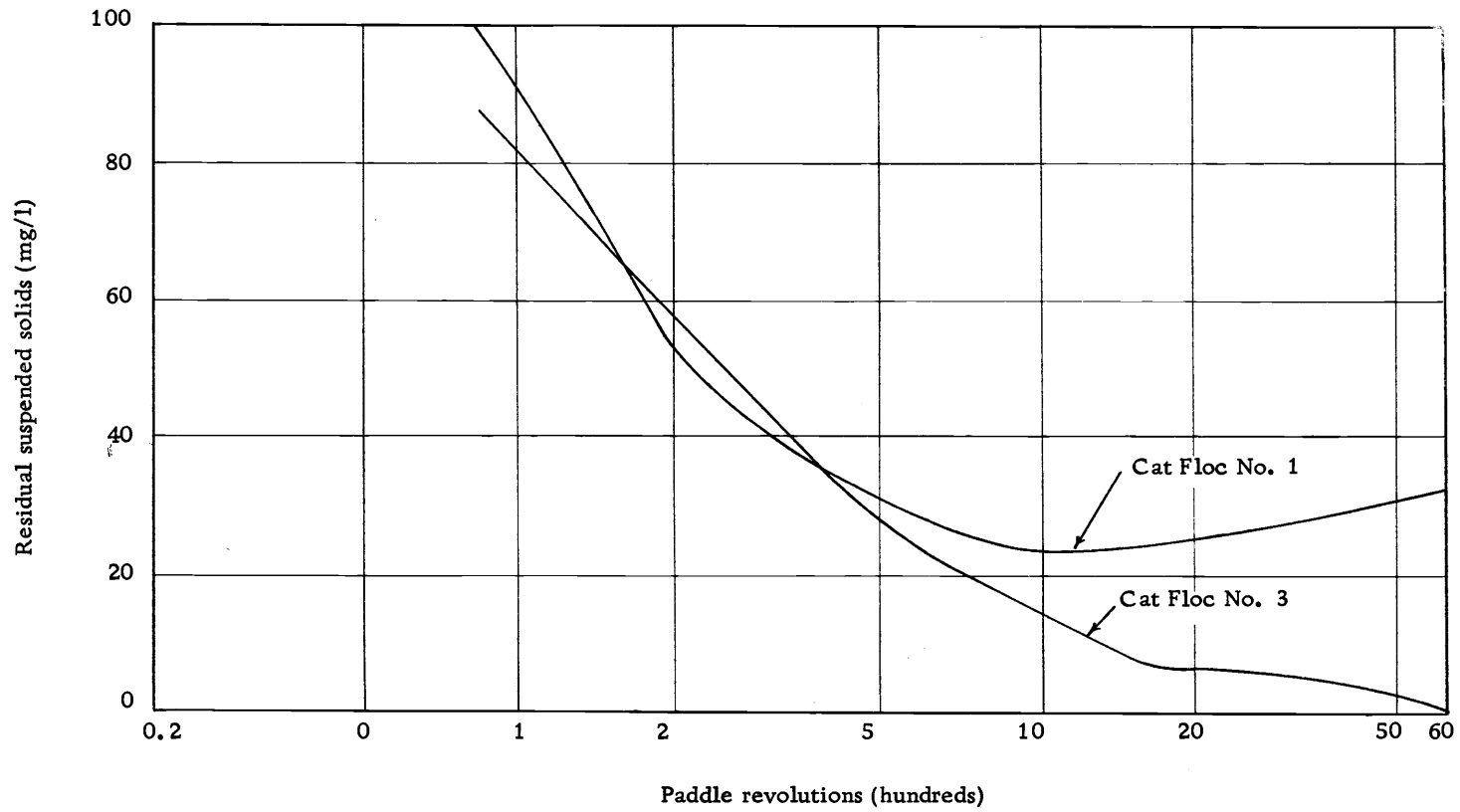


Figure 12. Effect of revolutions of mixing on removal of suspended solids in raw sewage. Initial suspended solids 136 mg/l, mixing rate 80 rpm, polymer dosage 9.4 mg/l, electrophoretic mobility - 0.6 μ /sec/v/cm (after Jones).

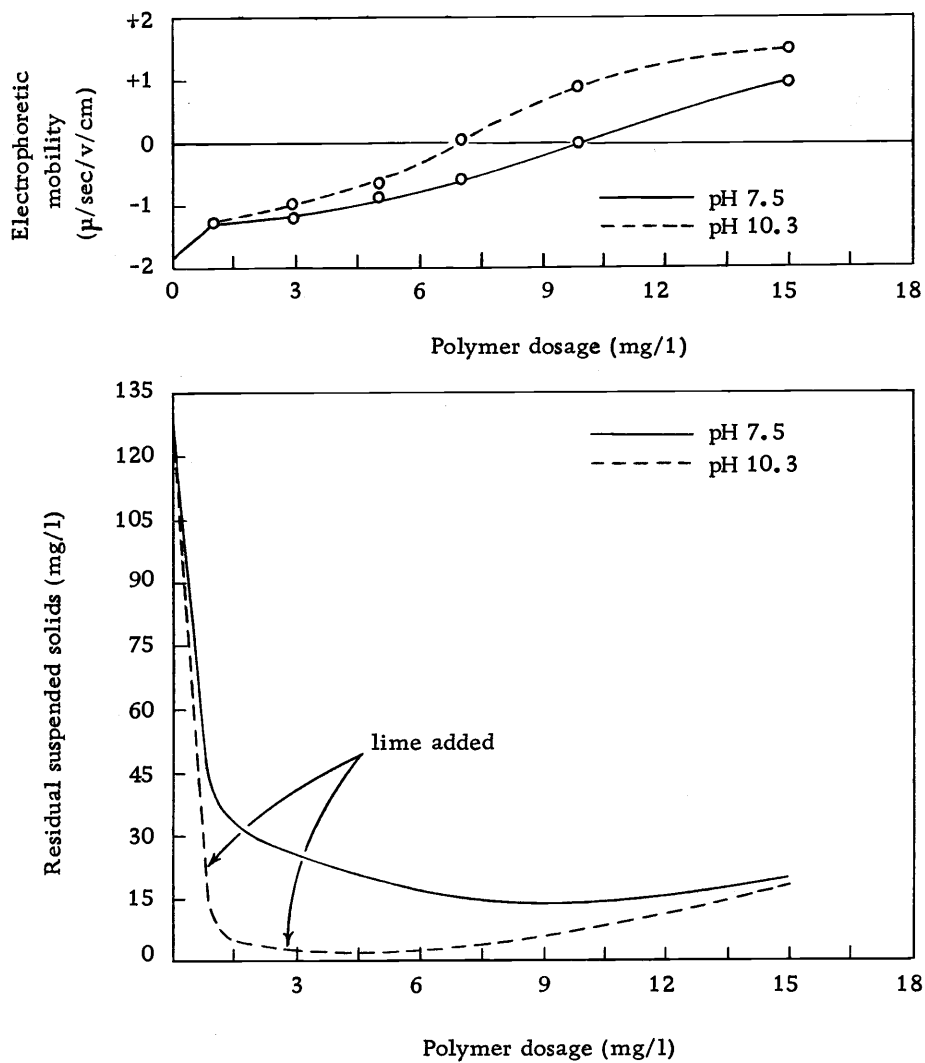


Figure 13. Effect of pH and Cat Flocc on removal of suspended solids in raw sewage (after Jones).

settling rate of activated sludge. Figure 14 is representative of his results. The sludge depicted would be considered poor settling sludge since the SVI is 170. Zone settling rate of the untreated sludge was 12.8 ft/hr while 5 mg/l of Cat Flocc increased this to an average of 42 ft/hr. Thus the required settling area for a clarifier could be reduced by a factor of 3.5.

Experiments on bulking sludge were run with polymer dosages from 1-40 mg/l, suspended solids from 1,200-1,500 mg/l, and SVI from 520-770. Figure 15 is representative of the findings and shows good results with a sludge that would barely settle without treatment.

Dixon and Zielyk, 1969 (25)

Summary

Dixon measured flocculation of E. coli, in concentrations ranging from 50 to 2700 mg/l, brought about by various dosages of non-ionic, anionic, and cationic polymers. He had poor results with the nonionic and anionic polymers but good results with cationic polymers.

Waste Composition

Pure cultures of E. coli grown for about 16 hours in a medium in which glucose was the carbon source.

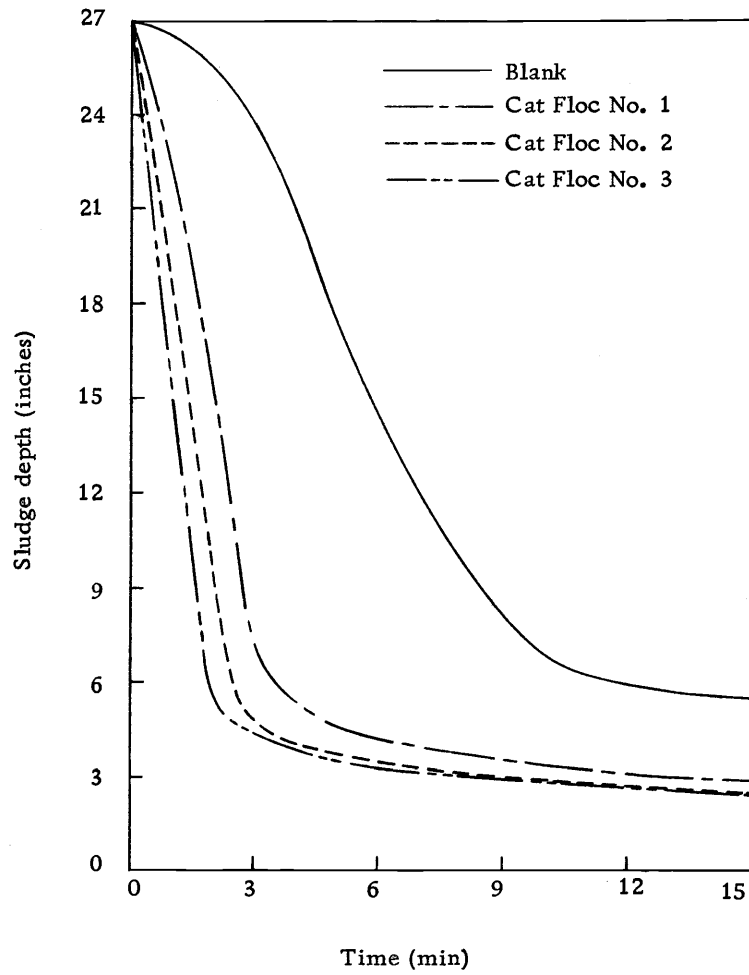


Figure 14. Effect of three Cat Floc samples on the settling rate of activated sludge. Polymer dosage 5.0 mg/l, suspended solids 785 mg/l, SVI 170 (after Jones).

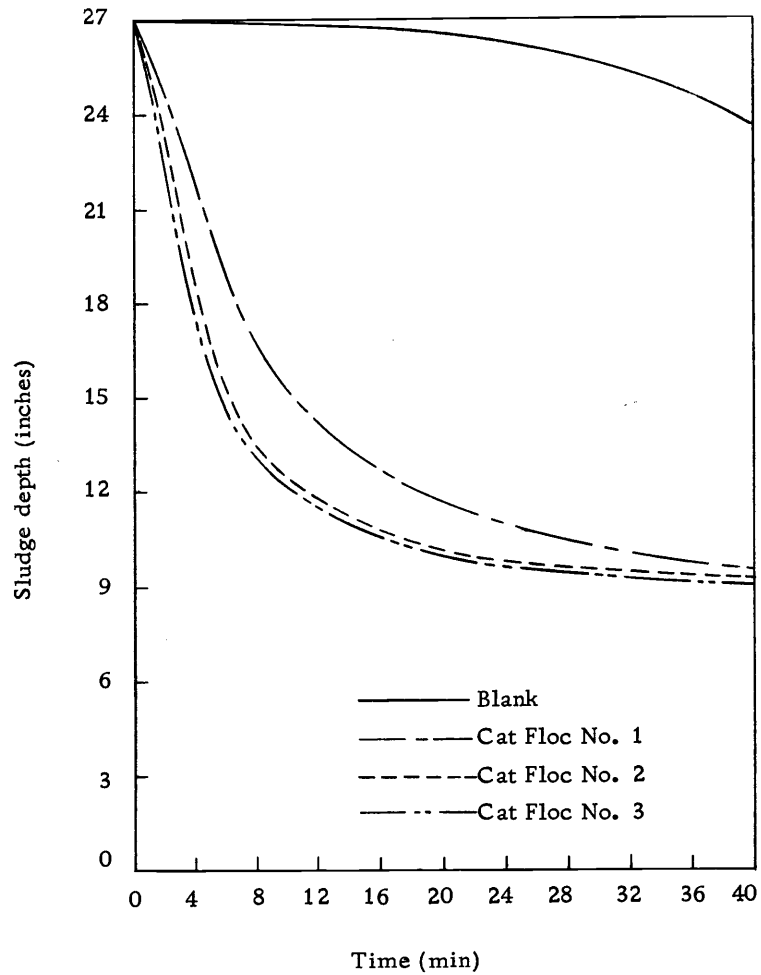


Figure 15. Effect of three Cat Floc samples on the settling rate of activated sludge. Polymer dosage 10.0 mg/l, suspended solids 1,500 mg/l, SVI 630 (after Jones).

Flocculants

Cationic. All polyethyleneimine polymers manufactured by Dow Chemical Company.

<u>Polymer</u>	<u>Designation</u>	<u>Molecular Weight</u>
1. Montrek 6	0.8 M	450-750
2. Montrek 12	1.0 M	1050-1350
3. Montrek 18	1.3 M	1650-1950
4. III-23	1.4 M	
5. Montrek 1117	1.9 M	3000-5000
6. Montrek 1612	3.4 M	10,000-15,000
7. Montrek 600	14 M	40,000-60,000
8. III-42	20 M	
9. Montrek 1120	21 M	58,000-100,000

Nonionic. All polyacrylamides manufactured by American Cyanamide Co. with molecular weights from 7000 to 3,000,000.

Anionic. All obtained by hydrolysis of polyacrylamide samples.

Methods

Jar tests were used. Dixon's procedure was to add the polymer, adjust the pH to that desired, stir for 10 minutes, and then evaluate the sample for effectiveness of flocculation. Two methods

of evaluation were used: (1) measurement of filtration rate by recording the time necessary to pass 50 ml of the sample through a Millipore filter with 0.45 μ pore diameter and (2) light transmission by a Brice-Phoenix light scattering apparatus. In the second method the sample was settled for one hour after stirring.

Results

Cationic. Dixon had successful results with cationic polyethyleneimine polymers. Figure 16 shows that as the E. coli concentration increased a larger polymer dosage was necessary to initiate flocculation. It also indicates that less polymer is necessary at pH 4 than at pH 6-9 due to the charge on the E. coli surface being less negative and therefore easier to flocculate.

Figure 17 shows that the polymer concentration that changed the charge on the bacteria was about the same as that in which the filtration time was the least, i. e., maximum flocculation.

Anionic and Nonionic. Attempts were made to flocculate E. coli with anionic hydrolyzed polyacrylamide and nonionic polyacrylamide. Many different polymer dosages, E. coli concentrations, and pH were tried to no avail. Electrophoretic mobility was not changed by the polymers. Dixon concluded:

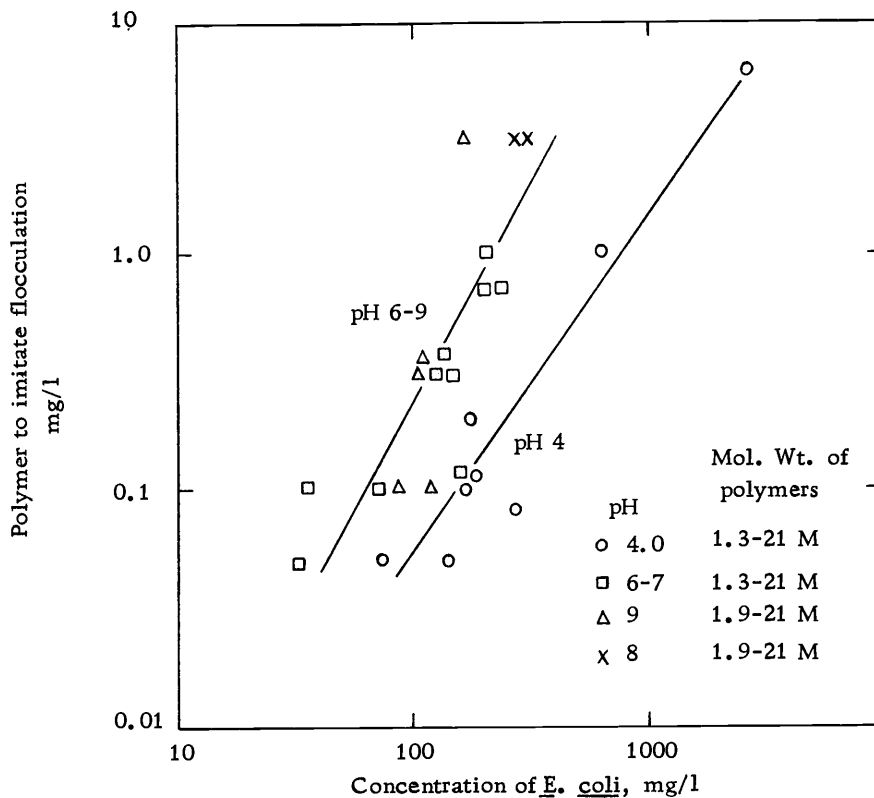


Figure 16. Effect of *E. coli* concentration on amount of polymer to initiate flocculation (after Dixon).

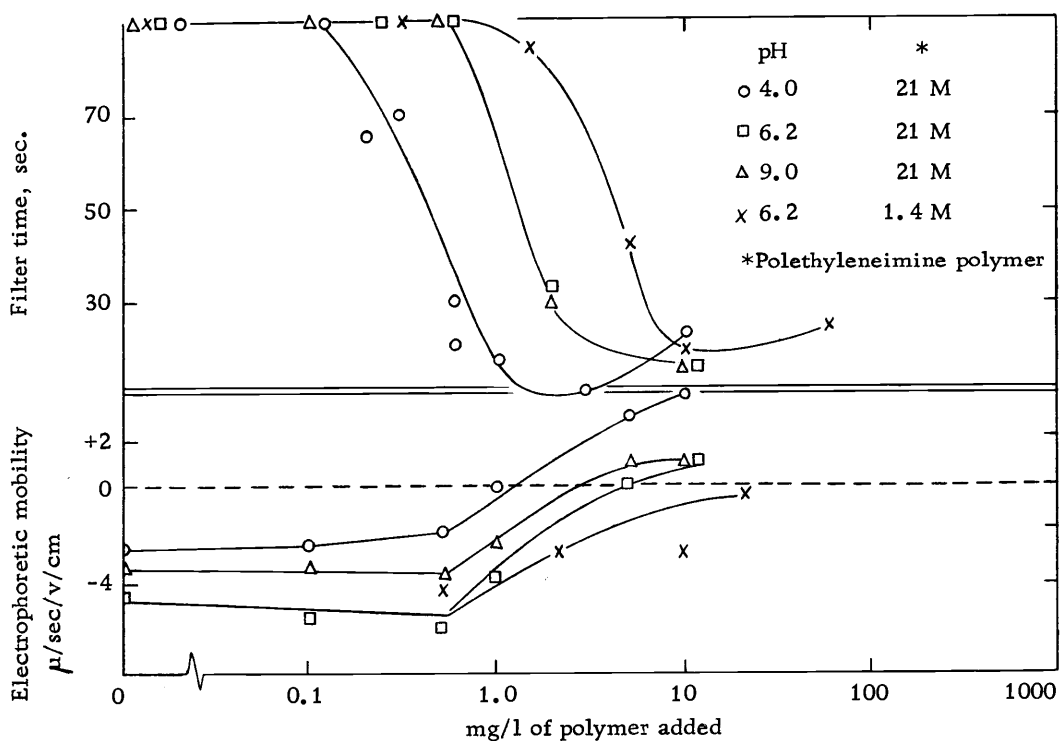


Figure 17. Effect of polymer on electrophoretic mobility and filtration time, *E. coli*. 100 mg per liter (after Dixon).

. . . polymers [anionic and nonionic] were not able to flocculate the E. coli, probably because of their failure to be adsorbed, and thus they were unable to reduce or reverse the negative charge sufficiently to permit flocculation to occur (25, p. 553).

Busch and Stumm, 1968 (15)

Summary

Busch experimented with the aggregation of pure cultures of E. coli and A. aerogenes by both synthetic anionic and nonionic polymers and also extracellular polymeric material isolated from cell free supernatant of a well flocculating activated sludge. He demonstrated the theory that bacterial aggregation is brought about by natural polymers excreted by the microbial cell. He also showed that reduction of surface potential of a colloid is not necessary for flocculation to take place.

Waste Composition

Pure cultures of E. coli and A. aerogenes grown with glucose or benzoate as the carbon source in a continuous culture apparatus.

Flocculants

Anionic. Hydrolyzed polyacrylamide, polystyrene sulfonate, and polygalacturonic acid.

Nonionic. Dextran.

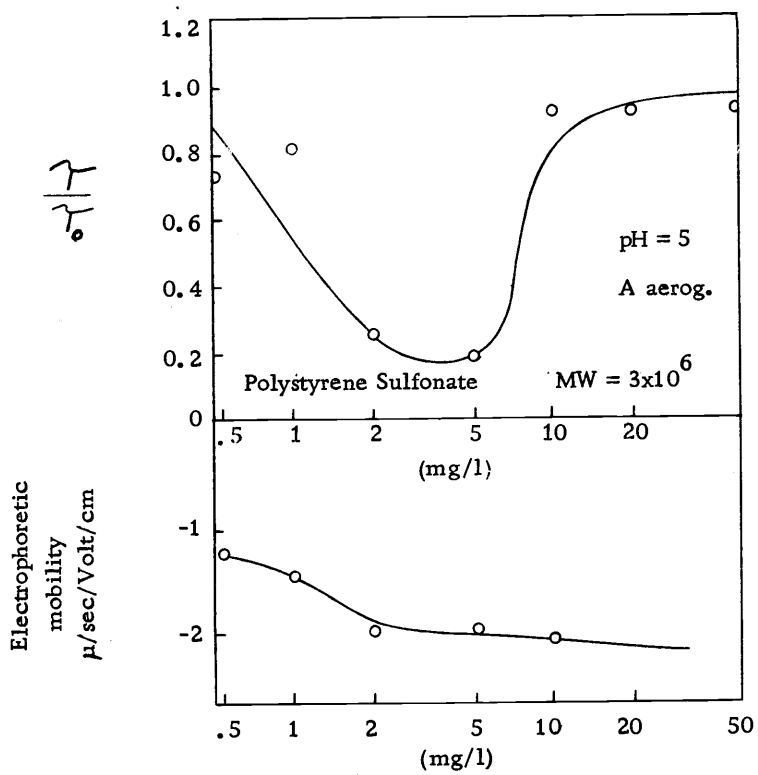
Natural polymers. Produced by bacteria. Material containing cell free flocculants was isolated by ethanol precipitation from the supernatant of a centrifuged activated sludge culture.

Methods

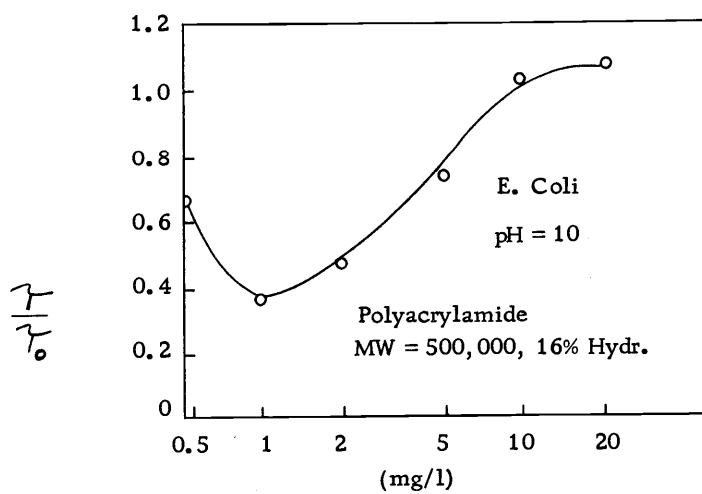
Jar tests were used. The method used to measure bacterial aggregation was the relative light scattering intensity, as determined in a Brice-Phoenix light-scattering photometer 20 minutes after addition of polymer and subsequent slow stirring. Light scattering intensity, τ , decreases with an increase in aggregation. The light scattering intensity of the sample with no polymer added is τ_0 .

Results

Busch successfully flocculated the bacterial suspensions with synthetic anionic and nonionic polymers as shown by Figure 18. One can deduce from other data in the report that a bacterial concentration of 100 mg/l was used. Figure 18a shows that the negative electrophoretic mobility of the bacterial suspension becomes more negative as anionic polymer is added, but that this has no adverse effect on flocculation. Busch explains his results by the polymer bridging model described previously. He further stated that the forces of attachment of the polyelectrolyte segments to the bacteria

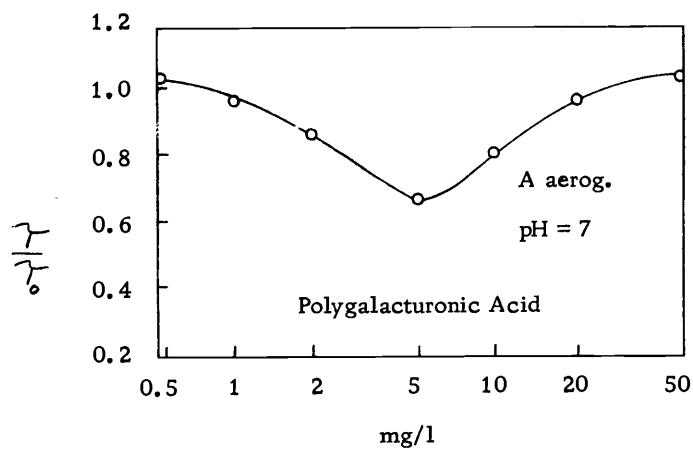


a. Anionic

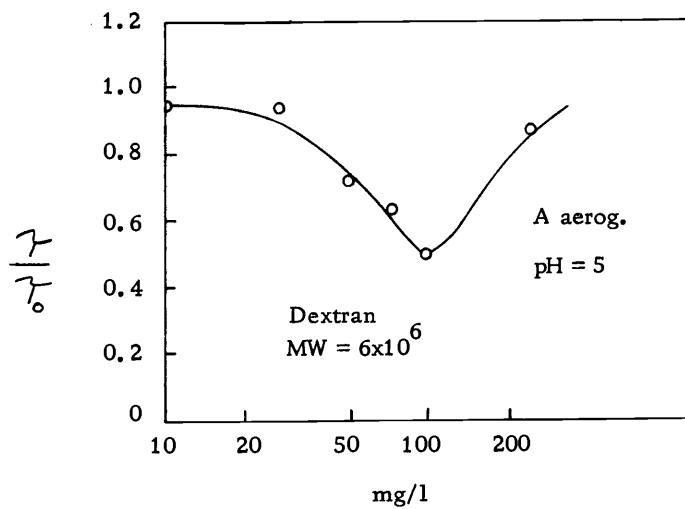


b. Anionic

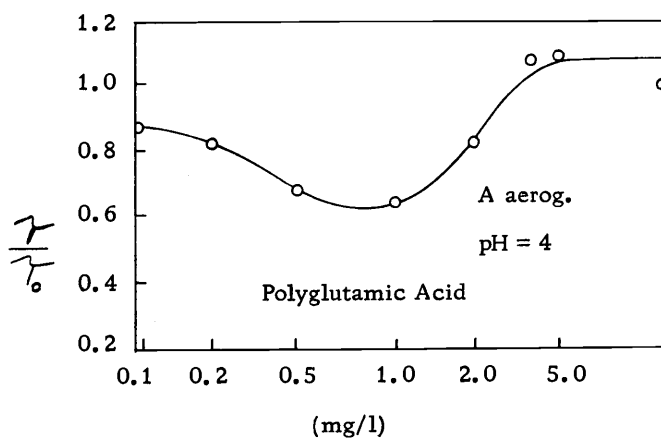
Figure 18. Aggregation and redispersion of bacteria by anionic and nonionic polymers (after Busch).



c. Anionic



d. Nonionic polysaccharide



e. No net charge at pH 4

Figure 18 Continued.

surface must be weak, because increased agitation to greater than 30 rpm results in dispersion of the aggregation.

Busch found that satisfactory flocculation with these anionic and nonionic polymers only occurred when concentrations of divalent cations, Ca^{++} or Mg^{++} , exceeded about 12 mg/l. He stated:

the authors believe that the primary role of divalent cations in the flocculation of bacteria is complex or ion pair formation between the functional groups of the polyelectrolyte and the "counter ion" in the immediate vicinity of the bacterial surface, thus enhancing the adsorption of polymer segments at the interface (15, p. 51).

He felt that although the divalent cation concentration was not high enough in the bulk solution, it was sufficiently high in the vicinity of the negatively charged bacteria due to electrostatic forces.

Busch found that material containing cell free flocculants, which presumably were natural polymers excreted by bacteria, could impart a negative electrophoretic mobility to Al_2O_3 particles which are positively charged at pH 7. This proved that the cell free supernatant had anionic components. Figure 19 shows the aggregation of SiO_2 and of A. aerogenes by natural polymers of cell free supernatant. The curves are similar to those found with synthetic anionic polymers. Busch concludes that the use of natural polymers produced by bacteria may be more expedient than the use of synthetic ones.

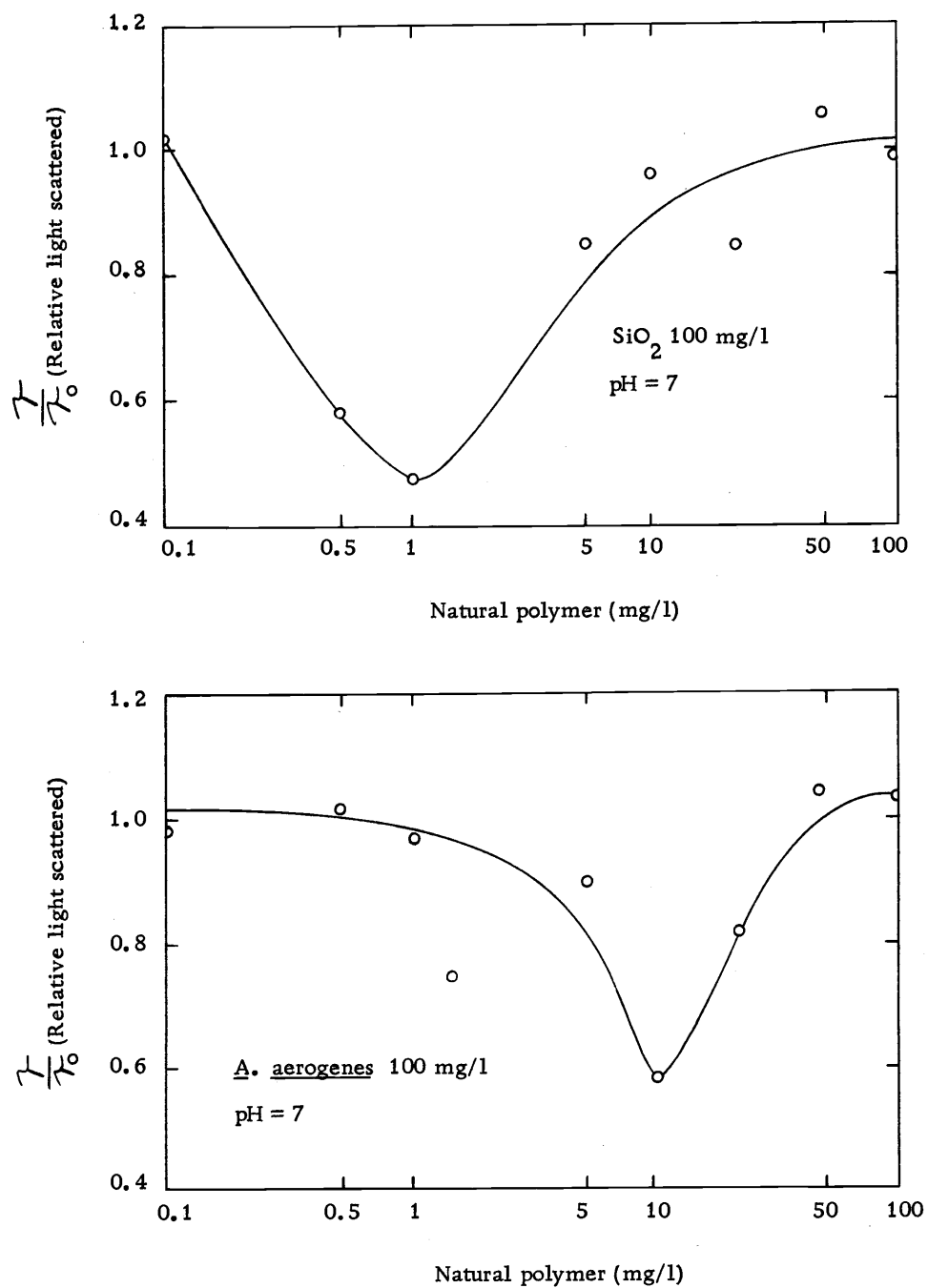


Figure 19. Aggregation of SiO_2 and of *A. aerogenes* with polymers of bacterial origin (after Busch).

Tenney and Stumm, 1964 (89)

Summary

Tenney experimented with flocculation of activated sludge by the use of polyelectrolytes and also alum. Although he tried all types of polyelectrolytes, he found that under the conditions of his experiments only cationic polyelectrolytes produced flocculation of the microorganisms. He determined that pH, amount of agitation, temperature, and ionic composition of the solution all affected the degree of flocculation by the polyelectrolytes. Tenney interpreted his results by the use of the polymer bridge model.

Tenney also investigated the removal of phosphate by precipitation with alum.

Waste Composition

Samples from continuous culture activated sludge systems of bench scale. Batch cultures were also used. A mixture of nutrient broth, glucose, and sodium oleate was the substrate.

Flocculants

Tenney experimented with 29 different polymers, with and without alum, but reported only on Purifloc 602, a cationic polymer by

Dow Chemical Company, and alum used separately. Unfortunately, he did not give the chemical name of Purifloc 602, a designation no longer used by the Dow Company.

Methods

Jar tests were used. The samples were mixed at 30 rpm for 15 minutes and then allowed to settle for one hour. Parameters measured were COD and estimates of bacterial numbers in the supernatant. Tenney kept the pH of the sample constant during each flocculation experiment by the use of an automatic titrator.

Results

Figure 20 shows the flocculation obtained with different dosages of Purifloc 602 when the pH is held constant. The results when alum is substituted for the polymer are shown in Figure 21. The effect of pH on flocculation of microorganisms by alum is shown in Figure 22. Tenney found that the most effective range for removal of both microorganisms and phosphates was pH 5-6.

Tenney determined that when alum was added to a suspension of microorganisms containing phosphate it first reacted with the phosphate and then the remainder flocculated with microorganisms. He stated that alum precipitated the phosphate rather than coagulated it. One mole of Al^{3+} was necessary to precipitate one mole of

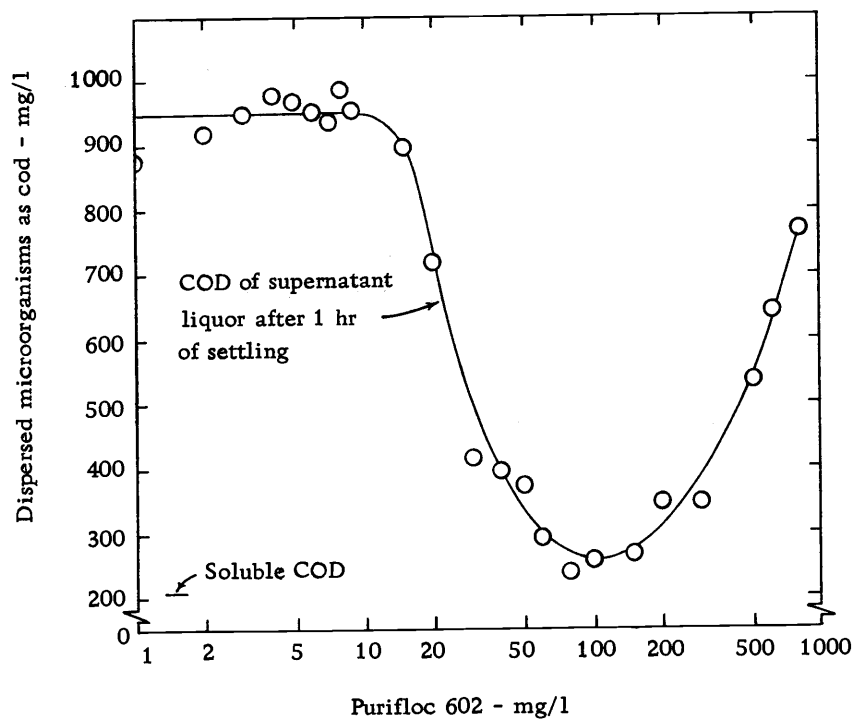


Figure 20. Flocculation of dispersed microorganisms with cationic Purifloc 602 (after Tenney).

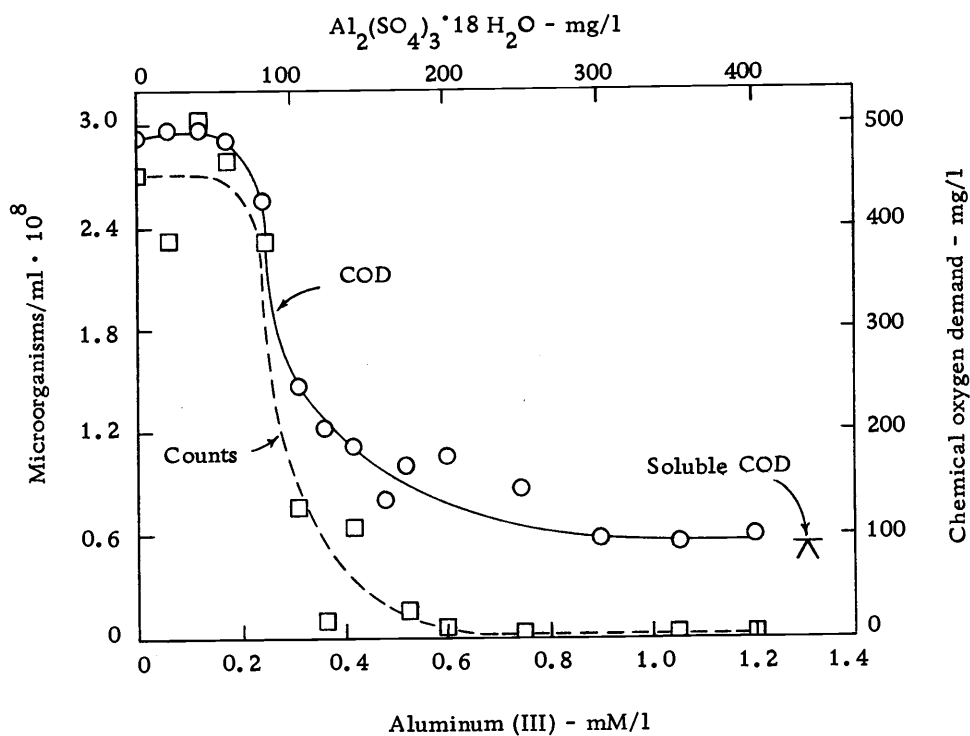


Figure 21. Flocculation of dispersed microorganisms with Al^{3+} (after Tenney).



Figure 22. Effect of pH on flocculation of dispersed microorganisms by alum (after Tenney).

phosphorus, as can be seen in Figure 23.

Additional Results

Table 4 is a compilation of additional results showing increased settling of wastewaters by the use of polymers. The data has been gathered from the literature and from informational brochures published by the various chemical companies. Together with the five previously reported results it represents the sum total of the investigative results found by the author in the Oregon State University Library. Most probably the library contains most of the published information in this field.

Industrial wastes having somewhat similar characteristics to domestic waste are included in Table 4. Results of investigations in the use of polymers for better flotation, sludge elutriation, and sludge thickening are not incorporated in this report. Although polymers used in these processes substantially enhance good floc formation, the processes are quite different from the settling process which is the subject of this report. They are a separate field whose main difference is the magnitude of the suspended solids concentration.

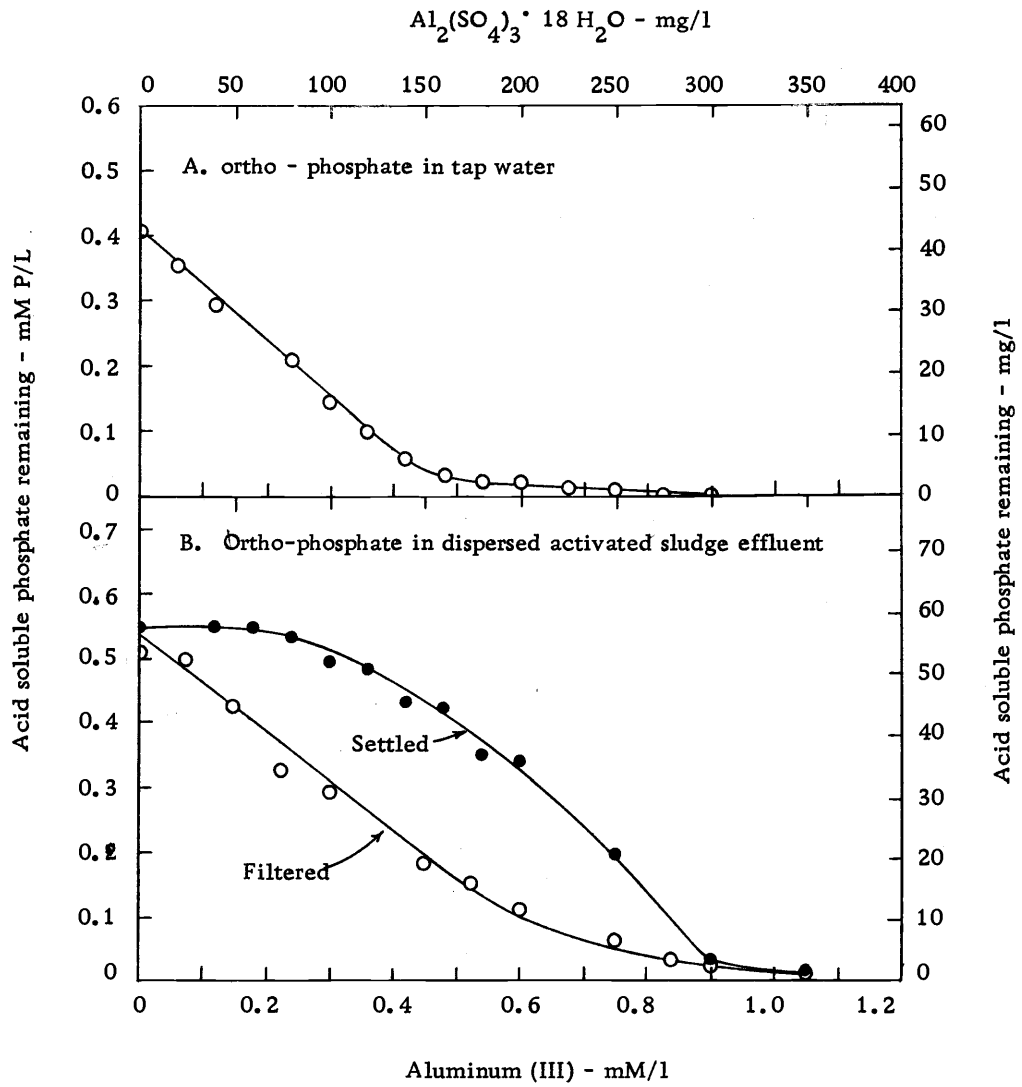


Figure 23. Removal of phosphorus by Al^{3+} at pH 6 (after Tenney).

Table 4. Summary of additional results.

No.	Investigator	Waste	Flocculants	Optimum dosage	Results
1.	Williamson <u>et al.</u> (95)	filtered secondary effluent of domestic trickling filter plant	Wyoming Bentonite	416 mg/l	COD reduced 206 to 139 mg/l
			Panther Creek Bentonite	416 mg/l	COD reduced 206 to 122 mg/l
2.	Dorr-Oliver (19)	Sewage @ primary clarifier	lime, enough dosage into primary clarifier to bring pH to 9.5-10.0		increased removals of SS 60 to 85% and BOD 30 to 70%
3.	Singer <u>et al.</u> (81)	bulked activated sludge	Purifloc 601, cationic	2 mg/l	SV1 reduced 400 to 160
			Purifloc 602, cationic	3 mg/l	SV1 reduced 630 to 170
			Purifloc 501, anionic aromatic sulfonate		no effect
			alum	50 mg/l	SV1 reduced 597 to 218
4.	Rebhun <u>et al.</u> (70)	paper mill in Israel:			
		1. newsprint production waste	alum	30-40 mg/l	good clarification
		2. offset paper production waste (contains starch)	Wyoming bentonite clay	200 mg/l	good clarification. Starch in waste makes impossible to floc with other flocculants.
5.	Middlebrooks <u>et al.</u> (55)	Kraft mill waste	alum	20 mg/l	55% COD, 95% SS, 20% BOD removals
			Dow A-21, A-22, A-23 N-11, N-12	all 2 mg/l ⁺	50-60% COD, 95% SS, 20% BOD removals

Continued

Table 4 Continued.

No.	Investigator	Waste	Flocculants	Optimum dosage	Results
6.	Dow Chemical Co. Brochure (26)	Kraft pulp mill waste (primary settling only)	Purifloc C 31, cationic polyethyleneimine	15-20 mg/l	Suspended solids reduced 20,000 lb/day to 7500 lb/day
7.	Hercules Inc. Brochure (38)	paper mill waste	Hercofloc 812 + alum	1 mg/l 60 mg/l	Suspended solids reduced 200-700 ppm to 60 ppm
8.	Schaffer (77)	meat packing wastes	Purifloc 601, cationic	10-15 mg/l	increased settling rate by 25 percent
9.	Dow Chemical Co. Brochure (26)	meat packing wastes at air flotation unit	Purifloc A 21, anionic sulfonated polymer	20 mg/l	increased SS removal 44 to 63% increased BOD removal 31 to 61%
10.	Sproul <u>et al.</u> (85).	cattleskin tannery wastes	alum	100 mg/l	93% BOD, 45% SS removals
			alum	250 mg/l	94% BOD, 57% SS removals
			Seperan AP30, anionic polyacrylamide	1.0 mg/l 0.5 mg/l	61% BOD, 84% SS removals 57% BOD, 74% SS removals
			cationic, nonionic polymers		ineffective, thus conclusion that wastes have positive charge
11.	Jones (43)	1. creosote wastes	Cat Flocc, cationic diallyldimethylammonium chloride	40 mg/l	75% COD removal
		2. organic chemical plant wastes	Cat Flocc	3.5 mg/l	36% COD, 99% SS removals

Continued

Table 4 Continued.

No.	Investigator	Waste	Flocculants	Optimum dosage	Results
12.	Burke and Dajani (14)	automotive assembly plant. Waste contains paints, chromates, oil, etc.	nonionic polyer + FeCl ₃ + NaOH	2 mg/l	Total solids reduced 2,000 to 800 mg/l

Water Treatment Results

As stated previously polymers were first introduced in the water treatment field. In the last decade many investigations in this area have been reported in the literature. It is not the intent of this report to present a substantial number of these findings since they have limited applicability to wastewater treatment. Rather, two representative results are depicted.

Cohen, et al. , 1958 (20)

Cohen studied many water supplies in Ohio by the use of jar tests, among them a pond having the following characteristics:

pH	7.4
alkalinity	36 mg/l
hardness	55 mg/l
turbidity	300 units

Three different polymers were introduced together with 30 mg/l alum. They were:

- Anionic A: A hydrolyzed acrylamide polymer
- Cationic B: An unspecified organic polymer which was a viscous liquid and in a 1N caustic solution.
- Nonionic C: A naturally derived polymer which was a mixture of polymer and clay. The active

ingredient was a cellulose derivative,
carboxymethylcellulose.

Figure 24 shows that Cationic B gave good results with this particular water and at this alum dosage, whereas the other two polymers clarified the water less than did the alum used alone. However, the author stated all three coagulations would be acceptable for application to a sand filter.

Pressman (1967) (66)

Pressman investigated using several different cationic polymers with five natural waters in Virginia. Table 5 lists the characteristics of these waters.

The most successful cationic polymer was Polymer A, a polyquaternary ammonium. The results when adding Polymer A to the different waters are shown in Figure 25. The optimum dosage for the less turbid waters was in a range of 2-5 ppm, while the more turbid Occoquan Creek required 15 ppm for optimum clarification.

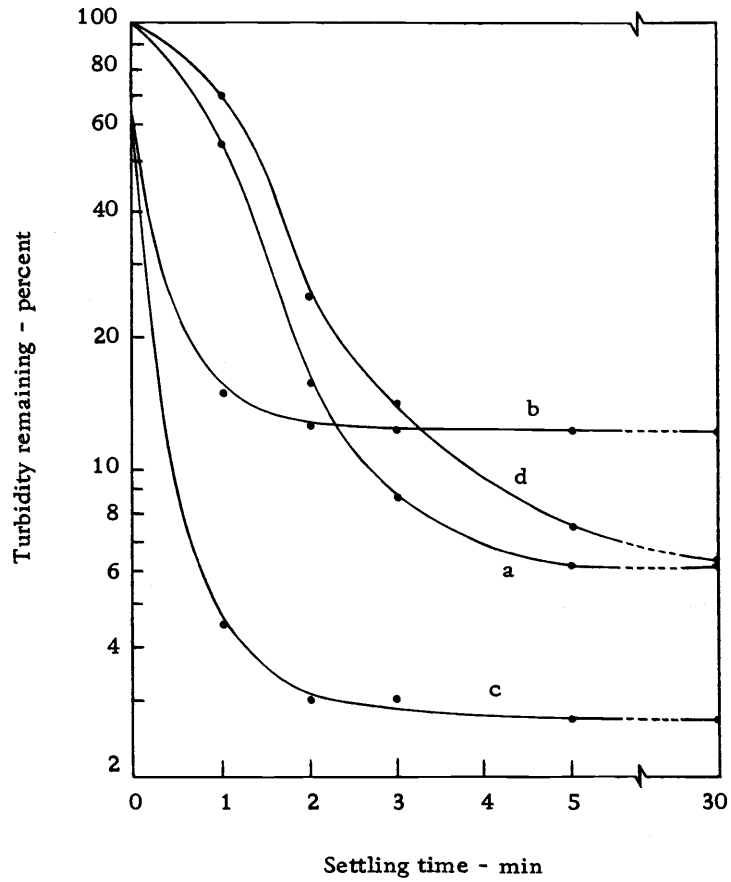


Figure 24. Effect of coagulant aids on pond water. Each solution contained 30 mg/l alum. Curves represent coagulations obtained with: a, alum alone; b, 0.5 mg/l Anionic A; c, 2 mg/l Cationic B; and d, 2 mg/l Nonionic C. (after Cohen)

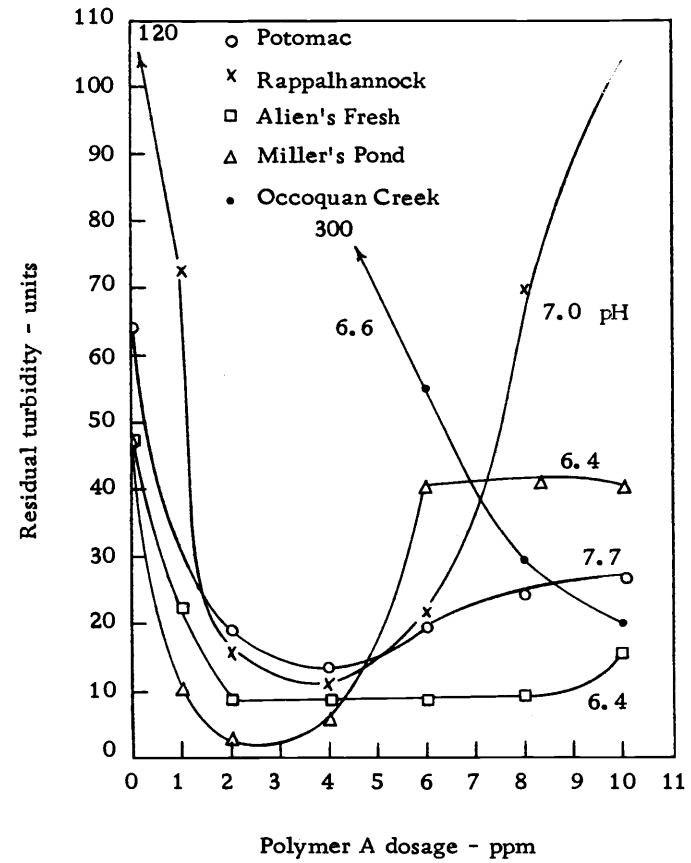


Figure 25. Flocculation of various waters treated with Polymer A. The curves above, labeled with pH values, show the results of tests with Polymer and five natural waters. (after Pressman)

Table 5. Analyses of waters used in laboratory studies (after Pressman).

Characteristic	Water				
	Potomac River	Allen's Fresh Creek	Miller's Pond	Occoquan Creek	Rappahannock River
pH	7.3	6.2	6.4	6.6	6.6
Turbidity--units	67	54	39	300	135
Color--units	5	30	25	50	45
Conductivity--micromhos/cm	180	136	47		60
Total hardness--ppm CaCO ₃	72	24	14	28	23
Alkalinity--ppm CaCO ₃	50	4	6	16	12
Chloride--ppm Cl	7	26	4	5	4
Sulfate--ppm SO ₄	14	11	6	17	9
Detergent--ppm ABS	0.10	0.06	0.05	0.08	0.03
Chemical oxygen demand--ppm	5	13	11		11
Zeta potential-mv	-24	-22	-25	-23	-21

DISCUSSION

Polymer Effect on Soluble Versus Colloidal OrganicsObservations

The results show that the most important factor affecting the success or relative failure of polymer induced coagulation-flocculation of the organic matter in a waste is the proportion of this matter that is soluble. Polymers have not been successful in flocculating soluble organic matter. They have had substantial success flocculating suspended solids and colloids. Thus the greater the amount of soluble organics in a waste, the more disappointing the results with polymers. Rebhun's, et al. (69) results with Dow C-31 (a polyamine named polyethyleneimine), shown in the Figure 8 curve entitled "total, after settling," show that 20 mg/l of the polymer used alone with the effluent from a trickling filter plant's secondary clarifier was unable to remove COD. This waste contained a high proportion of soluble organics.

On the other hand Jones (43) found that 20 mg/l of the identical Dow C-31 used on raw sewage was able to remove 68% of the BOD and 98% of the suspended solids. This is depicted in Figure 26. Obviously a trickling filter secondary effluent contains a much higher proportion of soluble organics than does a raw sewage.

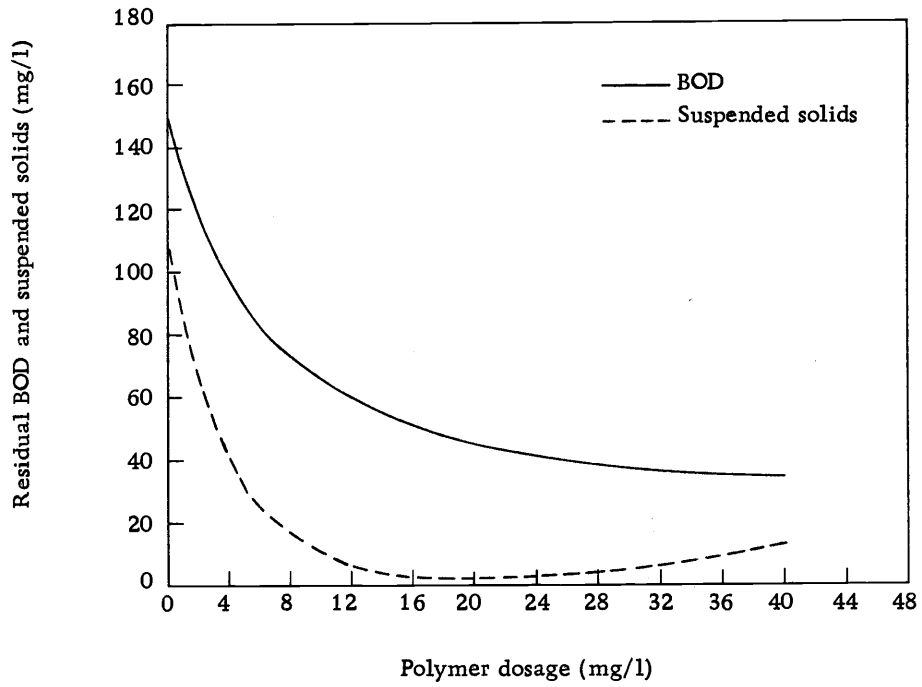


Figure 26. Effect of Dow C-31 on removal of BOD and suspended solids in raw sewage (after Jones).

Close inspection of Jones' Figure 26 reveals further proof of the slight effect of a polymer on soluble organics. The original raw sewage BOD concentration was approximately 40 mg/l greater than the original suspended solids concentration. After flocculation with 20 mg/l of Dow C-31, the remaining BOD was still approximately 40 mg/l greater than the suspended solids concentration although only 2% of the suspended solids remained. Thus, in effect, only BOD that was in the form of suspended solids was removed. Recalling that suspended solids measures all supracolloidal and a portion of the colloidal material besides settleable solids, it is apparent that the remaining BOD in Jones' experiment consisted of soluble organics plus an unknown amount of colloidal organics. Since the soluble fraction of a typical raw sewage is 20-40% of the total organics, and since 32% of the original BOD remains in this experiment, the author would conclude that substantially all of the BOD remaining is soluble.

Observations on Industrial Wastes

Results with various industrial wastes bear out the foregoing in regards to polymer effects on soluble organics. Many communities in the Willamette Valley of Oregon are faced each summer with a temporary overloading of their sewage treatment plants due to large volumes of waste from local canneries. These canneries

process beets, corn, peas, beans, cherries, and other vegetables and fruits in lesser amounts. Recent investigations (78, 18) with the use of polymers at Salem, Corvallis, and Forest Grove have been relatively unsuccessful. In each case the very high concentration of soluble organic wastes has deterred this type of treatment.

Work on potato wastes has shown that polymers will flocculate the waste if the treatment is not delayed to the extent that hydrolysis takes place. Hydrolysis causes the potato waste to dissolve.

Middlebrook's, et al. (55) results with kraft mill wastewater, shown in Table 4, show that 50-60% of the COD is removed by polymers, but only 20% of the BOD. Whereas a significant proportion of the COD is in the form of colloidal particles and suspensions, most of the BOD is soluble and therefore unaffected.

Hypothesis

The author would postulate the reason polymers are unsuccessful in flocculating soluble organics. A soluble substance's particles are of much smaller size than those of a colloid. A solution is composed of ions whereas a colloid usually consists of particles each containing many molecules. When a polymer is introduced and causes flocculation, one functional group along the polymer chain has been used up whether it attaches to an ion or to a colloidal particle. Thus a given amount of polymer will flocculate much less weight of

soluble material than colloidal material. Soluble organics can be flocculated by polymers but the large polymer dosage which is required, according to today's knowledge, makes it impractical.

Polymer Effect in Various Treatment Systems

Primary Clarifier

Jones (43) found that 0.5 mg/l Cat Flocc caused 61% BOD and 85% suspended solids removal with raw sewage. When this is compared to the usual primary settling removals of 25-35% BOD and 40-60% suspended solids, the ramifications are apparent. As one example, overloaded sewage treatment plants, both trickling filter and activated sludge, could be relieved by decreasing the loading to the secondary units.

Activated Sludge

Five researchers investigated the use of polymers to increase the settling rate of activated sludge. Thus Jones (43) and Dixon and Zielyk (25) used activated sludge in their research, Singer et al. (81) used bulked activated sludge, and Busch and Stumm (15) and Tenney and Stumm (89) used pure cultures of E. coli and A. aerogenes. All had good results with at least one polymer, cationic in four cases and anionic in one. Dixon's Figure 16 shows that the amount of

polymer necessary for flocculation increases with an increasing concentration of cells. Since none of the five researchers used the same polymer on similar activated sludge or cells it is difficult to draw conclusions on the amount of polymer needed to flocculate a given microorganism concentration.

Table 6 is a retabulation of these five researchers' results in a more convenient form for comparison.

No statistical inference can be drawn from these results. The table does indicate that for an activated sludge having a MLSS of 1000 mg/l perhaps 1-5 mg/l of cationic polymer would be a typical dosage to achieve better settling.

The important point here is that by the use of polymers a high rate activated sludge can be utilized rather than the usual low rate activated sludge, and solids reduction can still be obtained. The food to microorganism ratio can be kept high, and thus the microorganisms will be between the log growth phase and the declining growth phase, rather than the endogenous phase as in the usual activated sludge system. Thus food uptake and cell synthesis will occur at a high rate. Whereas, without polymers, such a sludge would flocculate poorly, by the use of polymers, flocculation equal to that of cells in the endogenous growth phase will occur.

Very likely aeration periods of two hours or so can replace the usual six hour aeration time with the same overall results,

Table 6. Results with activated sludge.

Investigator	Concentration	Polymer Dosage	Results
Jones (43)	activated sludge 810 mg/1 SS, SVI 150	1 mg/1 Cat Flocc (polydiallyldi- methylammonium)	3 times faster settling
Jones (43)	activated sludge 785 mg/1 SS, SVI 170	5 mg/1 Cat Flocc	3 times faster settling
Jones (43)	activated sludge 835 mg/1 SS, SVI 200	10.0 mg/1 Cat Flocc	4.5 times faster settling
Jones (43)	activated sludge 980 mg/1 SS, SVI 170	20.0 mg/1 Cat Flocc	6 times faster settling
Jones (43)	bulkied sludge 1200 mg/1 SS, SVI 650	5.0 mg/1 Cat Flocc	efficient settling of unsettleable sludge
Jones (43)	bulkied sludge 1500 mg/1 SS, SVI 630	10.0 mg/1 Cat Flocc	efficient settling of unsettleable sludge
Dixon (25)	500 mg/1 <u>E. coli</u> pH 6-9	2 mg/1 cationic polyethyleneimines	initiate flocculation
Busch (15)	100 mg/1 <u>E. coli</u> pH 10	1 mg/1 anionic polyacrylamide	optimum flocculation
Busch (15)	100 mg/1 <u>A. aerog.</u> pH 5	3 mg/1 anionic sulfonate	optimum flocculation
Tenney (89)	100 mg/1 activated sludge	100 mg/1 cationic Purifloc 602	Insoluble COD (cells) re- duced 95% by 1 hr. settling
Singer (81)	bulkied activated sludge	3 mg/1 cationic Purifloc 602	SVI reduced 630 to 170

meaning that the aerator size need be only one-third the volume as heretofore. The MLSS could be much less than the more typical 2000 mg/l concentration, perhaps more on the order of 700 mg/l.

On the other hand, through the use of polymers a designer could reduce the size of the secondary clarifier and keep the aerator size equal to that of a traditional design. Similar results would be obtained due to the faster settling rate.

Bulking sludge was investigated by Jones and also Singer and their results are seen in Table 6. The bulking problem has been one of liquid solid separation in the secondary clarifier, not one of biological metabolism of the organic waste. The two cases shown indicate that the problem may now have a good practical solution. It would appear that a 3-10 mg/l dose of cationic polymer will cause bulked sludge to settle satisfactorily. Singer has proposed that since filamentous organisms are quite efficient degraders of high carbohydrate wastes, such as those from the beet sugar or pulp and paper industries, they might well be cultivated intentionally in an activated sludge system. A polymer could then be added to the sludge to achieve the necessary settling in secondary clarification.

Trickling Filter

The only published research found on the use of polymers with the effluent from a trickling filter plant was that of Rebhun (69). As

brought out earlier in this chapter the effectiveness of polymers on a waste is inversely dependent on the amount of soluble material present. Activated sludge consists of a high concentration of microorganisms in suspension and thus is readily amenable to polymer treatment. Raw sewage consists of a high proportion of colloids and suspended solids and is also amenable to polymer treatment in primary clarification. The underflow from a trickling filter contains suspended, colloidal, and soluble organics and undoubtedly polymers would increase the settling rate and efficiency in the subsequent secondary clarifier. Thus a trickling filter plant, overloaded with strictly domestic wastes, could thereby produce an acceptable effluent. Or simply the size of a secondary clarifier could be reduced.

The effluent from the secondary clarifier of a trickling filter plant, on the other hand, has a high proportion of soluble organics and hence polymer results will be unsatisfactory. Although Rebhun achieved 85% COD removal when using clay along with a cationic polymer, his 20 mg/l polymer dosage was economically impractical.

Cost Considerations

The literature included no information on the actual costs involved in using polymers. This is understandable since each polymer is a proprietary product and the price per pound is different for each. However, it is of utmost importance to undertake a cost

analysis for an understanding of what is economically possible in this field. One must put in proper perspective, for instance, information that a given polyelectrolyte can bring about amazing BOD and suspended solids removals when its use is two times the cost of a traditional design, yielding equal results, that does not use polyelectrolytes. This comparison can only be done by cost analysis.

As brought out earlier in this chapter the use of polymers make possible several alternate design approaches. These include:

1. Activated sludge system: a smaller aerator by use of high rate activated sludge.
2. Activated sludge system: a smaller secondary clarifier due to faster settling.
3. Both activated sludge and trickling filter systems: a smaller biological unit, made possible by obtaining greater removals in primary clarifier.

The author has amortized the construction cost savings for typical examples of each of these three design approaches and has compared this to the annual cost of polymer application. The results indicate that polymer application to a treatment system utilizing a smaller unit and polymers may be less expensive than the traditional design. The number of assumptions necessary to calculate the construction costs are so great that it would be misleading to present them in this paper. The point is made, however, that cost savings

may be possible and that a thorough cost analysis should be undertaken as part of the universal search for more economical waste treatment.

The following is a list of points that need to be considered in a meaningful cost analysis:

1. A treatment plant operates at less than design flow for most of its life. Thus the actual amount of polymer used will be much less than the amount calculated by using design flow. The economic study should include calculations that project the average daily flow for each year of the expected life of the plant, and from these figures compute the pounds of polymer to be used each year.
2. Since the application of polymers constitutes an additional sophistication in waste treatment, it can be expected that the application is only worthwhile in plants which have skilled operators. Thus it may be restricted to plants of greater than 10 mgd design flow.
3. Of prime importance is the cost of the polymers. A short list of polymers and their August, 1969 prices is included in the appendix.
4. State regulatory agencies have certain design criteria which are not to be exceeded in the design of domestic waste treatment plants. At present these criteria include no

provisions for the more efficient settling which can be obtained with polymers. For the purposes of this paper it is assumed that, with demonstrated results, the state agencies will relax their criteria to allow the use of smaller sized units when polymers are to be employed. Most likely requirements would include a dual feed system and alarm controls to assure uninterrupted polymer application.

These costs must be considered in the analysis.

5. The costs of polymer feeding equipment, flocculation paddles in the clarifier, and necessary operator time to maintain the additional equipment must be included in the cost comparison.

Success of Different Polymer Types

Basic Types

Table 7 is a tabulation of the most pertinent research efforts reviewed in this paper and shows the success or failure of the various polymers used by the investigators. It is seen that cationic polyelectrolytes proved to be by far the most successful of the three basic types of polymers used for settling domestic wastes. Undoubtedly this is because most colloidal substances in domestic wastes carry a negative charge.

Table 7. Results using different polymer types.

Type	Specific Kind	Brand Name and Manufacturer	Waste	Investigator	Results
Cationic	Polyethyleneimine, a polyamine, with and without clay	Purifloc C-31 Dow	Secondary clarifier effluent from trickling filter plant	Rebhun	good
Cationic	Polyamine	PVPB, a synthesized polyamine	Secondary clarifier effluent from trickling filter plant	Rebhun	good
Cationic	Polyethyleneimine, a polyamine	Purifloc C-31 Dow	Raw sewage and primary clarifier effluent	Jones	good
Cationic	Polyamine	Primaflor C-7 Rohm and Haas	Raw sewage and primary clarifier effluent	Jones	good
Cationic	All polyethyleneimines a type of polyamine	Montrek series Dow	<u>E. coli</u>	Dixon	good
Cationic	Polydiallyldimethylammonium	Cat Flocc Calgon	Raw sewage Primary clarifier effluent	Jones	good
Cationic	Polydiallyldimethylammonium	Cat-Flocc Calgon	Activated sludge	Jones	good

Table 7. Continued

Type	Specific Kind	Brand Name and Manufacturer	Waste	Investi- gator	Results
Cationic	unknown	Purifloc 601, 602 Dow	Bulked activated sludge	Singer	good
Cationic	unknown	Purifloc 602 Dow	Activated sludge	Tenney	good
Anionic	Hydrolyzed polyacrylamides	American Cyanamid	<u>E. coli</u>	Dixon	failed
Anionic	Hydrolyzed polyacrylamides	American Cyanamid	<u>E. coli</u> and <u>A. aerogenes</u>	Busch	good
Anionic	Polystyrene sulfonate	Dow	<u>E. coli</u> and <u>A. aerogenes</u>	Busch	good
Anionic	Aromatic sulfonate	Purifloc 501 Dow	Bulked activated sludge	Singer	good
Anionic	Polygalacturonic acid	Sigma Chemical Co.	<u>E. coli</u> and <u>A. aerogenes</u>	Busch	good
Nonionic	Polyacrylamide	Magnifloc 972 American Cyanamid	Secondary clarifier effluent from trickling filter plant	Rebhun	failed
Nonionic	Polyacrylamides	American Cyanamid	<u>E. coli</u>	Dixon	failed

Table 7. Continued

Type	Specific Kind	Brand Name and Manufacturer	Waste	Investi- gator	Results
Nonionic	Dextran	Sigma Chemical Co.	<u>E. coli</u> and <u>A. aerogenes</u>	Busch	good
	Various anionic and nonionic		Activated sludge	Tenney	failed

Busch and Stumm (15) found that anionic and nonionic polymers were only effective in settling microorganisms when Ca^{++} or Mg^{++} cations were present in concentrations greater than 12 mg/l. Moreover the established practice when using polymers for water treatment is to use anionic and nonionic polymers only in conjunction with alum or an iron coagulant. Cationic polymers, on the other hand, are used alone. Very likely the poor results that Rebhun, Dixon, Tenney, and Singer experienced when using anionic and nonionic polymers would have been averted if divalent or trivalent cations had been added. As stated previously it has been postulated that the metal cation reduces the negative charge on a colloid particle to a degree where the anionic or nonionic polymer can approach and become adsorbed or bonded.

A letter from Dr. Ronald Wukasch, manager of the Dow Company's Technical Service and Development for Environmental Control Systems, sheds more light on the subject. He states in part:

It has been our broad experience that the suspended solid systems coming from secondary biological treatment had a streaming current potential well into the negative regime and that cationic coagulants or polyelectrolytes are definitely indicated. Exceptions to this rule can usually be attributed to unusually large concentrations of divalent and particularly trivalent metals present in the waste stream which act as effective counter-ions so that flocculation can be accomplished with nonionic or anionic electrolytes (96, p. 1).

Specific Chemical Types

The chemical structures of most of the polymers to be discussed in the following paragraphs have been shown in Figure 3.

The most successful of the cationic polyelectrolytes have been the polyamines, particularly the polyethyleneimines, and a polydiallyldimethylammonium (Cat Floc). The polyamines dissociate in water to yield positively charged amine groups along the molecular chain. Waste particles are adsorbed or bonded at these positively charged amine groups. Cat Floc is a linear homopolymer of diallyldimethylammonium chloride. When it ionizes in water a positive charge is located at the nitrogen atom of each ring in the chain.

Hydrolyzed polyacrylamides have been the anionic polyelectrolytes reported most often as flocculants. The long polymer chain consists of repeating amide and carboxyl units. The negative charge is located at the carboxyl group as the polyacrylamide ionizes in water.

Sulfonates are also important anionic polyelectrolytes. The negative charge is located at the SO_3 radical when the compound dissociates in water.

The most successful nonionic polymers have been polyacrylamides. Dextran has also often been reported as somewhat successful.

The chemical constituents of domestic waste vary widely from one community to another. Of course the most important factor causing this is the nature of the industrial wastes, if any, added to the system. This diversity of wastes makes it impossible to say that a certain polymer will be most successful with a given domestic waste without first running a series of jar tests. The various ions present have a pronounced effect on the reactions a polymer initiates. One can hope that as more experience is gained in this field, sufficient information will be available so that one will be able to prescribe the very best polymer for a given waste after analyzing its composition.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Based upon the investigations analyzed in this report the following conclusions can be drawn:

1. Polymers have proven remarkably successful in settling the colloidal and settleable fraction of domestic wastes. Moreover they efficiently agglomerate and settle the microorganisms of activated sludge, even when the bacteria are in the log growth to declining growth phase. Relatively small polymer dosages are involved.
2. Alternate designs for waste treatment plants can be considered which utilize polymers and thereby reduce the size of the biological units or clarifiers. The activated sludge system is particularly amenable to these cost savings.
3. Polymers can be utilized at treatment plants which each year are overloaded for short durations due to seasonal industries. Unfortunately the wastes of food processing, a major seasonal industry, are high in soluble organics and have not been successfully flocculated by polymers.
4. The service life of an overloaded treatment plant can be extended by the use of polymers. However, since in most

communities money for new construction is more readily available than money for operation, only slight use of this advantage will probably be made. Federal and State grant money is available for new construction, but not for operation and maintenance.

5. Soluble organic wastes are not efficiently settled by polymers. Extremely large polymer dosages are necessary to remove this waste fraction. Thus polymers have not proved successful in treating food processing wastes.
6. Cationic polyelectrolytes are much more effective with typical domestic wastes than are anionic and nonionic polymers.
7. In order for anionic or nonionic polymers to successfully flocculate domestic wastes, a multivalent cation must be present. Occasionally a waste will contain multivalent metals in sufficient concentration. On most occasions the cation must be added.
8. At least one researcher has found bentonite clay to be a valuable aid when using polymers. It served as a nucleus for flocculation.

Recommendations for Future Work

The following recommendations for future work are made:

1. As shown in this report the published literature includes several papers giving results of jar tests involving the use of polymers in the settling of domestic wastes. However, there is a paucity of published information on full plant scale results in this field. At many treatment plants today polymers are quite successfully used to obtain better settling. However the only persons cognizant of the polymer used and its dosage, the waste composition, and the results obtained are the municipality, consulting engineer, and polymer manufacturer directly involved. No clearing house for this type of information exists.

An indication of some of the reasons for this lack of published information is contained in a letter received by the author from one of the major manufacturers in response to his request for information. The letter says in part:

. . . the application technology of polymers is in many cases as important as the ability to manufacture molecules which exhibit superior properties. As () is primarily a service oriented company, we are in the business to sell our technology as much as our chemicals. With this in mind, I must say that it is not our policy to divulge data to the extent which you request in your letter.

A major breakthrough toward better waste treatment techniques and designs would be made by the gathering and publishing of the information outlined above. The author recommends that a nationwide survey on the subject be undertaken by an organization such as the Water Pollution Control Federation or the Federal Water Pollution Control Administration. Questionnaires would be sent to every municipality where the likelihood existed that polymers were used for better domestic waste settling.

2. Only one investigator, Rebhun, reported on using bentonite clay in conjunction with a polymer. Five hundred mg/l clay along with a cationic polyelectrolyte gave highly successful results with trickling filter plant effluent. More research with clay, using different wastes, polymers, and clay dosages is needed. The success Rebhun found with clay should be investigated further.
3. Several researchers have found that a multivalent cation must be present for anionic and nonionic polymers to successfully settle wastes. More research is needed to determine the minimum amounts of the various cations which are necessary.

BIBLIOGRAPHY

1. Application of Reten 205 in sewage treatment. *Water and Sewage Works* 111:64-66. 1964.
2. Argaman, Y. and W. J. Kaufman. Turbulence in orthokinetic flocculation. Berkeley, 1968. 164 p. (University of California. College of Engineering and School of Public Health. Sanitary Engineering Research Laboratory. SERL Report no. 68-5. Federal Water Pollution Control Administration Research Grant no. WP-00658)
3. Black, A. P. Basic mechanisms of coagulation. *Journal of the American Water Works Association* 52:492-504. 1960.
4. Black, A. P., F. Birkner and J. J. Morgan. Destabilization of dilute clay suspensions with labeled polymers. *Journal of the American Water Works Association* 57:1547-1560. 1965.
5. Black, A. P. and S. A. Hannah. Electrophoretic studies of turbidity removal by coagulation with aluminum sulfate. *Journal of the American Water Works Association* 53:438-452. 1961.
6. Black, A. P. and A. L. Smith. Determination of the mobility of colloidal particles by microelectrophoresis. *Journal of the American Water Works Association* 54:926-934. 1962.
7. Black, A. P. and M. R. Vilaret. Effect of particle size on turbidity removal. *Journal of the American Water Works Association* 61:209-214. 1969.
8. Black, A. P. et al. Effectiveness of polyelectrolyte coagulant aids in turbidity removal. *Journal of the American Water Works Association* 51:247-263. 1959.
9. Blaisdell, D. S. and R. E. B. Klaas. Separating solids from sewage. U. S. Patent 3,142,638. July 28, 1964. (Abstracted in *Chemical Abstracts* 61:14347-14348. 1964)
10. Borchardt, J. A. Coagulant aids. *Water and Sewage Works* 108 (Reference number):R. 173-R180. 1961.

11. Braithwaite, R. L. Polymers as aids to the pressure flotation of waste activated sludge. *Water and Sewage Works* 111:545-547. 1964.
12. Bramer, H. C. and R. D. Hoak. Zeta potential and sedimentation practice. *Proceedings of the 19th Industrial Waste Conference, Lafayette, Indiana, 1964.* p. 977-985. (Purdue University. Engineering Extension Series no. 117)
13. Bunch, R. L., E. F. Barth and M. B. Ettinger. Organic materials in secondary effluents. *Journal of the Water Pollution Control Federation* 33:122-126. 1961.
14. Burke, J. T. and M. T. Dajani. Organic polymers in the treatment of industrial wastes. *Proceedings of the 21st Industrial Waste Conference, Lafayette, Indiana, 1966.* p. 303-313. (Purdue University. Engineering Extension Series no. 121)
15. Busch, P. L. and W. Stumm. Chemical interactions in the aggregation of bacteria. *Bioflocculation in waste treatment. Environmental Science and Technology* 2:49-53. 1968.
16. Carr, R. L. Polyelectrolyte coagulant aids. Dry and liquid handling and application. *Water and Sewage Works* 114 (Reference number):R64-R72. 1967.
17. Cassell, E. A. et al. Removal of organic colloids by microflotations. *Proceedings of the 23rd Industrial Waste Conference, Lafayette, Indiana, 1968.* p. 966-977. (Purdue University. Engineering Extension Series no. 132)
18. Chapman, R. Sanitary Engineer, Cornell, Howland, Hayes, and Merryfield, Incorporated. Personal communication. Corvallis, Oregon. September 12, 1969.
19. Chemical-biological process removes phosphorus. *Chemical and Engineering News* 45:25-26. 1967.
20. Cohen, J. M., G. A. Rourke and R. L. Woodward. Natural and synthetic polyelectrolytes as coagulant aids. *Journal of the American Water Works Association* 50:463-478. 1958.
21. Conley, W. R. and R. H. Evers. Coagulation control. *Journal of the American Water Works Association* 60:165-174. 1968.

22. Conway, R. A. Cationic organic coagulants in waste water treatment. *Water and Sewage Works* 109:342-344. 1962.
23. Culp, G. L. and A. F. Slechta. The Lake Tahoe water reclamation plant waste water reclamation by tertiary treatment. *Journal of the Water Pollution Control Federation* 35:799-806. 1963.
24. Dean, R. B. et al. An electron microscope study of colloids in wastewater. *Environmental Science and Technology* 1:147-150. 1967.
25. Dixon, J. K. and M. W. Zielyk. Control of the bacterial content of water with synthetic polymeric flocculants. *Environmental Science and Technology* 3:551-558. 1966.
26. Dow Chemical Company. Let Purifloc settle your waste problems. Midland, Michigan, 1968. n.p.
27. Dickerson, B. W. and P. T. Farrell. Laboratory and pilot plant studies on phosphate removal from industrial wastewater. *Journal of the Water Pollution Control Federation* 41:56-62. 1969.
28. Eliassen, R. and G. Tchobanaglou. Removal of nitrogen and phosphorus from wastewater. *Environmental Science and Technology* 3:536-541. 1969.
29. Garwood, J. Polyelectrolytes in sewage treatment. *Effluent and Water Treatment Journal* 7:380-382. 1967.
30. Goodman, B. L. Chemical conditioning of sludges: six case histories. *Water and Wastes Engineering* 3(2):62-65. 1966.
31. Goodman, B. L. and C. P. Witcher. Polymer-aided sludge elutriation and filtration. *Journal of the Water Pollution Control Federation* 37:1643-1656. 1965.
32. Green, J. Coagulating composition. (to Nalco Chemical Company) U. S. Patent 3,130,167. April 21, 1964. (Abstracted in *Water Pollution Abstracts* 39:no. 1360. 1966)
33. Ham, R. K. and R. F. Christman. Agglomerate size changes in coagulation. *Proceedings of the American Society of Civil Engineers, Journal of the Sanitary Division* 95:481-502. 1969.

34. Hannah, S. A., J. M. Cohen and G. G. Robeck. Control techniques for coagulation-filtration. *Journal of the American Water Works Association* 59:1149-1163. 1967.
35. Harris, H. S., W. J. Kaufman and R. B. Krone. Orthokinetic flocculation in water purification. *Proceedings of the American Society of Civil Engineers, Journal of the Sanitary Division* 92(SA6):95-111. 1966.
36. Healy, T. W. and V. K. La Mer. The adsorption-flocculation reactions of a polymer with an aqueous colloidal dispersion. *Journal of Physical Chemistry* 66:1835-1838. 1962.
37. Hennessy, P. V., L. R. Williams and Y. S. Lin. Tertiary treatment of trickling filter effluent at Orange County, California. *Journal of the Water Pollution Control Federation* 39:1819-1833. 1967.
38. Hercules Incorporated. Hercofloc flocculant polymers for industrial water and waste treatment. Wilmington, Delaware, 1969. 10 p.
39. Heukelekian, H. and J. Balmat. Chemical composition of the particulate fractions of domestic sewage. *Sewage and Industrial Wastes* 31:413-423. 1959.
40. Hiebenthal, F. and D. Spetch. The use of high-polymer flocculants for water and trade waste treatment. *Effluent and Water Treatment Journal* 7:308-312. 1967.
41. House, R. R. and S. T. Moore. Clarification of industrial waters. (to American Cyanamid Company) U. S. Patent 2,980,609. April 18, 1961. (Abstracted in *Water Pollution Abstracts* 37:no. 1809. 1964)
42. Hunter, J. V. and H. Heukelekian. The composition of domestic sewage fractions. *Journal of the Water Pollution Control Federation* 37:1142-1163. 1965.
43. Jones, R. H. Liquid-solids separation in domestic waste with a cationic polyelectrolyte. Ph.D. thesis. Gainesville, University of Florida, 1966. 201 numb. leaves (Microfilm)
44. Katchalsky, A. Polyelectrolytes. *Endeavour* 12:90-94. 1953.

45. Katz, W. J. and A. Geinopolos. Sludge thickening by dissolved air flotation. *Journal of the Water Pollution Control Federation* 39:946-957. 1967.
46. Kleber, J. P. Field use of a cationic polymer for clarification. *Water and Wastes Engineering* 6(6):42-45. 1969.
47. La Mer, V. K. and T. W. Healy. Adsorption-flocculation reactions of macromolecules at the solid-liquid interface. *Reviews of Pure and Applied Chemistry* 13:112-121. 1963.
48. Lesinski, C. A. and E. J. Sullivan. Method of employing dextrans. (to Dow Chemical Company) U. S. Patent 3,085,853. April 16, 1963. (Abstracted in *Water Pollution Abstracts* 39: no. 135. 1966)
49. Logan, J. A. et al. An analysis of the economics of wastewater treatment. *Journal of the Water Pollution Control Federation* 34:860-882. 1962.
50. Louis, L. Bentonite clay as a coagulant aid. *Water and Sewage Works* 104 (Reference and data):R83-R86. 1957.
51. McKinney, R. E. *Microbiology for sanitary engineers.* New York, McGraw-Hill, 1962. 293 p.
52. Malhotra, S. K., G. F. Lee and G. A. Rohlick. Nutrient removal from secondary effluent by alum flocculation and lime precipitation. *International Journal of Air and Water Pollution* 8:487-500. 1964.
53. Matijević, E. and L. H. Allen. Interactions of colloidal dispersions with electrolytes. *Environmental Science and Technology* 3:264-268. 1969.
54. Michaels, A. S. Aggregation of suspensions by polyelectrolytes. *Industrial and Engineering Chemistry* 46:1485-1490. 1954.
55. Middlebrooks, E. J., W. E. Phillips and F. J. Coogan. Chemical coagulation of kraft mill wastewater. *Water and Sewage Works* 116(3):IW7-IW9. 1969.
56. Middleton, A. B. Activated silica sol applications. *Water and Sewage Works* 110:251-253. 1963.

57. Mueller, K. C. and M. C. Burbank. Effects of polyelectrolyte coagulant aids on removal of Missouri River turbidity with ferric sulfate. *Journal of the American Water Works Association* 56:333-346. 1964.
58. Narkis, N., M. Rebhun and H. Sperber. Flocculation of clay suspensions in the presence of humic and fulvic acids. *Israel Journal of Chemistry* 6:295-305. 1968.
59. Nemerow, N. L. Theories and practices of industrial waste treatment. Reading, Massachusetts, Addison-Wesley, 1963. 557 p.
60. Nesbitt, J. B. Phosphorus removal - the state of the art. *Journal of the Water Pollution Control Federation* 41:701-713. 1969.
61. Nesbitt, J. B. Removal of phosphorus from municipal sewage plant effluents. University Park, 1966. 58 p. (Pennsylvania State University. College of Engineering. Sanitary Engineering Laboratory. Engineering Research Bulletin B-93)
62. Ockershausen, R. W. Chemical treatment of sewage and industrial wastes. Proceedings of the eighth Southern Municipal and Industrial Waste Conference, Chapel Hill, North Carolina, 1959. p. 85-102.
63. O'Melia, C. R. A review of the coagulation process. *Public Works* 100(5):87-98. 1969.
64. Perrin, F. R. and C. P. Blakeley. For cold, low-hardness water . . . jar tests with coagulant aid. *Water Works Engineering* 115:724-726. 1962.
65. Polymer use for waste treatment grows. *Chemical and Engineering News* 44:40-41. Oct 10, 1966.
66. Pressman, M. Cationic polyelectrolytes as prime coagulants in natural water treatment. *Journal of the American Water Works Association* 59:169-181. 1967.
67. Pye, D. J. and G. F. Schurz. Method of clarifying water. (to Dow Chemical Company) U. S. Patent 3,128,249. April 7, 1964. (Abstracted in *Water Pollution Abstracts* 39: no. 1359. 1966)

68. Rebhun, M. and N. Narkis. Advanced treatment of effluents from municipal waste-water treatment plants for reuse. *Israel Journal of Chemistry* 4:99-100. 1966. (Abstracted in *Water Pollution Abstracts* 40: no. 668. 1967)
69. Rebhun, M., N. Narkis and A. M. Wachs. Effect of polyelectrolytes in conjunction with bentonitic clay on contaminants removal from secondary effluents. *Water Research* 3:345-355. 1969.
70. Rebhun, M., H. Sperber and C. Saliternik. Purification of paper mill effluents by flocculation. *Tappi* 50(12):62A-64A. 1967.
71. Rhame, G. A. Polyelectrolytes as ABS suppressors. *Water and Sewage Works* 111:44-45. 1964.
72. Rice, A. H. Sewage and industrial waste purification process. U. S. Patent 3,171,804. March 2, 1965. (Abstracted in *Water Pollution Abstracts* 38: no. 1937. 1966)
73. Rich, L. G. Unit processes of sanitary engineering. New York, Wiley, 1963. 190 p.
74. Riddick, T. M. Zeta potential and polymers. *Journal of the American Water Works Association* 58:719-722. 1966.
75. Rudolfs, W. and J. L. Balmat. Colloids in sewage. I. Separation of sewage colloids with the aid of the electron microscope. *Sewage and Industrial Works* 24:247-256. 1952.
76. Sawyer, C. N. and P. L. McCarty. *Chemistry for sanitary engineers*. New York, McGraw-Hill, 1967. 518 p.
77. Schaffer, R. B. Polyelectrolytes in industrial waste treatment. *Proceedings of the 18th Industrial Waste Conference, Lafayette, Indiana, 1963*. p. 447-459. (Purdue University Engineering Extension Series no. 115)
78. Schaumburg, F. D. Associate Professor, Oregon State University, Dept. of Civil Engineering. Personal communication. Corvallis, Oregon. July 17, 1969.

79. Schmid, L. A. and R. E. McKinney. Phosphate removal by a lime-biological treatment scheme. *Journal of the Water Pollution Control Federation* 41:1259-1275. 1969.
80. Sennett, P. and J. P. Oliver. Colloidal dispersions, electrokinetic effects and the concept of zeta potential. *Industrial and Engineering Chemistry* 57(8):33-50. 1965.
81. Singer, P. C., W. O. Pipes and E. R. Hermann. Flocculation of bulked activated sludge with polyelectrolytes. *Journal of the Water Pollution Control Federation* 40:R1-R9. 1968.
82. Slechta, A. F. and G. L. Culp. Water reclamation studies at the South Tahoe Public Utility District. *Journal of the Water Pollution Control Federation* 39:787-814. 1967.
83. Smellie, R. H. and V. K. La Mer. Flocculation, subsidence, and filtration of phosphate slimes. *Journal of Colloid Science* 13:589-599. 1958.
84. Smith, R. Cost of conventional and advanced treatment of wastewater. *Journal of the Water Pollution Control Federation* 40:1546-1574. 1968.
85. Sproul, O. J., P. F. Alkinds and F. E. Woodard. Investigations on physical and chemical treatment methods for cattleskin tannery wastes. *Journal of the Water Pollution Control Federation* 38:508-516. 1966.
86. Stumm, W. and C. R. O'Melia. Stoichiometry of coagulation. *Journal of the American Water Works Association* 60:514-539. 1968.
87. Stumm, W. and J. J. Morgan. Chemical aspects of coagulation. *Journal of the American Water Works Association* 54:971-994. 1962.
88. Sven, T. J. and A. M. Schiller. Flocculation of sewage. (to American Cyanamid Company) U. S. Patent 3,171,805. March 2, 1965. (Abstracted in *Water Pollution Abstracts* 40: no. 1670. 1967)

89. Tenny, M. S. and W. Stumm. Chemical flocculation of microorganisms in biological waste treatment. Proceedings of the 19th Industrial Waste Conference, Lafayette, Indiana, 1964. p. 518-539. (Purdue University. Engineering Extension Series no. 117)
90. Tomlinson, H. D. et al. Laboratory studies of tannery waste treatment. Journal of the Water Pollution Control Federation 41:660-678. 1969.
91. U. S. Federal Water Pollution Control Administration. Advanced waste treatment research. Summary report--advanced waste treatment, July, 1964-July, 1967. Cincinnati, 1968. 96 p. (FWPCA Publication no. WP-20-AWTR-19)
92. U. S. Federal Water Pollution Control Administration. Water pollution control-research, development, demonstration, and training projects. 1968 Grant and contract awards. Washington, D. C. , n. d. 140 p.
93. Walker, J. F. H. and J. H. Dougherty. Use of polyelectrolyte coagulants to enhance settling characteristics of activated sludge. Proceedings of the 20th Industrial Waste Conference, Lafayette, Indiana, 1965. p. 715-723. (Purdue University. Engineering Extension Series no. 118)
94. Weiss, C. M. Relation of phosphates to eutrophication. Journal of the American Water Works Association 61:387-391. 1969.
95. Williamson, J. N., A. H. Heit and C. Calmon. Evaluation of various adsorbents and coagulants for wastewater renovation. Cincinnati, Ohio, 1964. 91 p. (U. S. Public Health Service. Publication no. 999-WP-14. Environmental Health Series, Water Supply and Pollution Control no. AWTR-12)
96. Wukasch, R. F. Manager, Technical Service and Development, Environmental Control Systems, The Dow Chemical Company. Personal communication. Midland, Michigan. August 4, 1969.

APPENDICES

APPENDIX A

POLYMER AND COAGULANT PRICES

Product	Manufacturer	Price	
		Minimum amount per lb	>20,000 lbs* (i. e. average customer) per lb
Purifloc C-31	Dow	\$.50**	\$.38
C-32	Dow	.33	.25
A-21	Dow	1.60	1.00
A-22	Dow	2.00	1.15
A-23	Dow	2.60	1.35
N-17	Dow	2.75	1.40
N-11	Dow	2.00	.95
N-12	Dow	2.50	1.50
Cat Flocc	Calgon	.50	.40
St 266	Calgon	.55	.50
bentonite clay		> 2000 lb:	\$.09/lb
alum		liquid	\$.035/lb
lime, hydrated			\$.03/lb

*20,000 pounds is a truck load.

**Prices are FOB @ factory. Add approximately 8% for freight to Oregon plants.

APPENDIX B

Selected list of researchers and their respective projects from FWPCA report on grant and contract awards (92):

<u>Name</u>	<u>Project</u>
1. Kaufman, Warren J. , Sc. D. Division of Hydraulic and Sanitary Engineering U. of California, Berkeley	Orthokinetic flocculation of heterodispersed systems
2. Linford, Henry B. , Ph. D. Dept of Civil Engineering Columbia University, N. Y.	Cationic polymers as flocculant aids in water
3. Maier, Walter J. , Ph. D. Dept of Civil Engineering U. of Minnesota, Minneapolis	Removal of colloidal matter from wastewater
4. Matijević, Egon, Ph. D. Dept of Chemistry Clarkson College of Technology Potsdam, N. Y.	a. Flocculation of colloids suspended in water b. Second workshop seminar on coagulation and flocculation
5. Singley, John E. , Ph. D. Dept of Environmental Engineering U. of Florida, Gainesville	Stoichiometry and mechanisms of coagulation
6. Stumm, Werner, Ph. D. Division of Engineering and Applied Physics Harvard University Cambridge, Mass.	Chemical aspects of coagulation