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Removal of volatile organic compounds from wastewater during the coagulation process.

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REMOVAL OF VOLATILE ORGANIC COMPOUNDS
FROM WASTEWATER DURING THE
COAGULATION PROCESS

by

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To my family

ABSTRACT

The identification of increasing members of poten-
tially hazardous volatile organic contaminants discharged by
various industries into the sewerage system has raised con-
siderable concern. The process of coagulation and floccula-
tion is capable of removing certain volatile organic
contaminants; but the factors influencing such removal and
degree of removal of specific volatile organics are not well
defined. This study was undertaken to investigate the ef-
fectiveness of the coagulation/flocculation process in
removing volatile organic compounds and to explore modifica-
tions to the process to enhance removal efficiency. Five
polyelectrolytes were examined along with alum and ferric
sulfate in their ability to remove volatile organic com-
pounds from wastewater. Also, the effectiveness of powdered
activated carbon in adsorption of volatile organics was ex-
amined as a coagulant aid.

The removal of five volatile organic compounds,
Methylene Chloride, Trichloroethylene, Tetrachloroethylene,
Benzene and Toluene was very poor when all five polymers and
the two metal salts were used as sole coagulants. The
removal of volatile organics was enhanced slightly by using
the metal salts as prime coagulants and the polymers as
coagulant aids. Cationic polymers, with very high molecular
weights, were the least effective when used both as prime

coagulants and as coagulant aids.

Removal of volatile organic compounds was increased by the addition of powdered activated carbon after the application of the coagulants. The removal can be attributed to both carbon adsorption and floc entrapment. The total amount of organic matter present in the wastewater greatly affected the efficiency of the activated carbon.

ACKNOWLEDGMENTS

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I. INTRODUCTION

The rapid increase of organic contaminants in the environment in recent years has caused a grave concern regarding possible health risks associated with some of these chemicals. Many of these organic compounds have been recognized to cause serious adverse effects, including cancer, even when present at trace levels. Our standard of living has advanced to a stage where many of our daily products are associated with organic chemicals. It is now recognized that serious action must be taken to control these contaminants in the environment.

Among a wide a variety of organic contaminants, Volatile Organic Compounds, VOCs, are increasingly posing a threat to the water resources. A large portion of these volatile organics enter the sewerage system from a variety of sources. Most of the discharges stem from domestic and industrial activities and some through agricultural runoff. Generally, these chemicals are present in trace concentrations and are poorly removed by conventional water and wastewater treatment methods.

Removal of volatile organics in wastewater treatment processes has only recently been investigated. Effective treatment has been obtained by the use of a number of operations such as adsorption, ion exchange, air stripping and reverse osmosis. All these methods are very effective in

removing large percentages of VOCs; however, their high cost

makes them impractical for most wastewater treatment plants

across North America. Only in special cases, when the con-

taminant concentrations are very high, are one or more of

these operations used. For the remaining wastewater treat-

ment facilities, any removal of VOCs is achieved through

the traditional treatment methods.

It is believed that the coagulation and flocculation

process is capable of removing some of the VOCs from the

wastewater. This removal is assumed to occur by two dif-

ferent methods: (i) the entrapment of some of the VOCs

within the flocs and subsequent sedimentation, and (ii) the

adsorption of some of these organics onto the

polyelectrolytes used as primary coagulants or coagulant

aids. Coagulation processes are usually operated to maxi-

mize turbidity removal. Previous researchers have shown

these operating conditions to be different from the optimum

conditions required for VOCs removal (Amy and Chadik 1983,

Semmens and Ayers 1985, Semmens and Field 1980). However,

an understanding of the behavior of different coagulants

and coagulant aids at various concentrations is lacking.

This makes it difficult to asses the potential of the

coagulation process in removing VOCs and limited any pos-

sibilities of modifying the process.

This study was designed and conducted to investigate

the behaviour of VOCs in the coagulation process. The

primary objectives were to:

1. investigate the performance of the existing coagula-

tion process in removing volatile organics,

2. determine the removal efficiencies of volatile organics with different polymers, and

3. explore modifications in the coagulation process that will enhance its efficiency in VOCs removal.

II. LITERATURE SURVEY

2.1 Volatile Organics in the Environment

2.1.1 Organic Matter

Volatile organic compounds, VOCs, contribute only a small percentage of the total organic content that can be introduced into the environment. The term organics stands for a general class of chemicals composed of carbon, C, and one or more of the following: hydrogen, H, nitrogen, N, and oxygen, O. Organic molecules may also include a number of other atoms such as sulfur, S, chlorine, Cl, and iodine, I, as well as many others. Most of the organic substances occurs naturally and are frequently referred to as humic substances. These substances are amorphous, highly aromatic, hydrophobic and generally acidic. Humic material, as found in most natural waters, are usually negatively charged (AWWA Committee Report 1979). These macromolecules are found in water as suspended matter and/or dissolved matter. Often, humic substances are referred to as colloids regardless of whether or not they are in solution. This classification is attributed to the range of molecular weights which stretches from a few hundred to tens of thousands (Semmens and Field 1980).

2.1.2   Volatile Organic Compounds

Volatile Organic Compounds, VOC, generally are organic chemicals with relatively high values of Henry's Law constant, H.   The greater the H value, the greater the tendency for the organic to volatilize from water to air phase (Namkung and Rittmann 1987).   Volatile Organics are generally a supplement of the lower molecular weight range of organic matter.   It is these small and simple molecules that can become very detrimental in water environments.   The higher molecular weight organics, for the most part, are not considered to pose great harm to the environment.   The exception are such organics that may react with chlorine during the oxidation/disinfection process and potentially form trihalomethanes, THM (McCarty 1980).

Most volatile organics have relatively high vapour pressures.   A volatile organic with a low vapour pressure such as tetrachloroethylene still has a vapour pressure value of 1.9 KPa at 20° C (Environmental Health Criteria 31, 1980).   This is relativly high considering a semi-volatile organic such as di-(2-ethylhexyl)pthalate has a vapour pressure of $2.1*10^{-8}$ KPa (Environment Canada 1983).   Another volatile organic, methylene chloride, has a vapor pressure of 46.52 KPa at 20° C (Environmental Health Criteria 32, 1984).   Although there seems to be a wide spread in the volatility of these two compounds, they are both considered to be very volatile.

2.2   Sources of Volatile Organics

Volatile organics are discharged into the sewerage system from a variety of sources. However, the majority are a result of the manufacturing processes used by today's industries. Other sources include domestic discharges such as household cleaners, paints and solvents. Also automobile emissions, chemical spills, and surface runoff add to the total amount of VOCs reaching the wastewater treatment facilities.

Volatile Organic chemicals originate as a result of physical and chemical conversions of naturally occurring raw materials such as petroleum, natural gas and coal (Langer and Feiler 1982). These VOCs can be by-products of manufacturing processes or inclusive parts of products such as plastics, synthetic fibers, synthetic rubber, dyes, paints, inks, solvents, food additives, pharmaceuticals, detergents, lubricants, and cosmetics. The three major industries responsible for discharging the majority of VOCs in wastewater are the petrochemical, pharmaceuticals and the paint and ink companies.

2.2.1   Petrochemical Industry

Approximately 50 percent of the plants in the petrochemical industry discharge their wastes into municipal treatment works (Langer and Feiler 1982). These industries produce consumer goods such as chemicals, gasoline, jet fuels, heating oil, lubricating oil, asphalt, coke and ingredients for a wide range of plastic and rubber products.

Most of these are derived from crude oil by means of distil-lination, catalytic conversions, solvent extraction and chemical conversion operations (Langer and Feiler 1982, Environment Canada 1984). Other VOCs, such as toluene, can be produced from petroleum as well as through the carbonization of coal (Environment Health Criteria 52, 1985).

Through these processes and from extensive washing procedures, the concentrations of VOCs in the industrial effluents can become very high. A study of toxic pollutants entering treatment facilities as a result of the petrochemical industry revealed a wide range of concentrations of VOCs in these types of wastewaters (Langer and Feiler 1982). Some of these values are listed in Table 1. It can be seen that the chemicals that are predominant in the effluents are benzene, toluene, and methylene chloride.

2.2.2 Pharmaceutical Manufacturing

The pharmaceutical manufacturing companies produce a variety of products ranging from biological and botanical products to medicinal chemicals and cosmetics. The processing operations are accomplished by a number of methods. The most common chemical technique is chemical synthesis. Biological and natural extraction are widely used for deriving products from animal fats, plants and glands. Benzene and tetrachloroethylene are used in the extraction process. Other volatile organics, including toluene, are involved in the seed preparation and fermentation processes.

Most of the water used in this industry is required

TABLE 1

Concentrations of Major Volatile Organic Compounds discharged
from the Petrochemical Industry (Langer and Feiler, 1982)

Volatile Organics	Concentration (ug/L)	
Benzene	100	– 5,800
Chlorobenzene	31	
Chloroform	5	– 100
1-2, Dichloroethane	16	– 54
Dichlorobromomethane	24	
2,4-Dinitrotoluene	20	
1,2-trans-dichloroethylene	10	– 20
Methylene Chloride	3	– 1600
Tetrachloroethylene	50	
Toluene	10	–15,000

for cooling purposes. Therefore, the wastewater is mainly generated from spills and flushing and cleaning of equipment. Some wastewater may also come from the use of dust scrubbers, which control dust during tablet and capsule production. The VOCs in the discharge from this group of industries can be seen in Table 2 (Langer and Feiler). Some of these concentrations may reach very high levels.

2.2.3   Paint and Ink Industry

This industry manufactures mainly interior and exterior paints, varnishes, lacquer, putty, caulking compounds, sealants, paint and varnish removers, and printing inks. Most of these products are either in a solvent or a water base. Almost all these products are made in batches from material such as oil, resins, pigments and solvents.

Approximately 99 percent of the plants in this category discharge their wastewater into municipal sewerage systems. The bulk of the wastewater is generated through cleanup and rinsing of tubs and reactors. Almost all the volatile organics included in the EPA priority pollutants list are released from this industry. Table 3 lists only the major chemicals found in this type of wastewater (Langer and Feiler 1982).

The three categories of industries mentioned above are responsible for a large portion of the total amount of VOCs entering municipal wastewater treatment plants. Other directly and indirectly related companies such as leather tanning and finishing and pulp and paper, contribute to the

TABLE 2

Concentrations of Volatile Organic Compounds discharged from
the Pharmaceutical Industry (Langer and Feiler, 1982)

Volatile Organics	Concentration (ug/L)
Benzene	100 - 10,000
1,2,Dichloroethane	100 - 15,000
Chloroform·	100 - 100,000
Ethylbenzene	100 - 50,000
Methyleny Chloride	100 - 100,000
Toluene	100 - 15,000

TABLE 3

Concentrations of Volatile Organic Compounds discharged
from the Paint and Inc Industry (Langer and Feiler, 1982)

Volatile Organics	Concentration (ug/L)	
	Paint	Ink
Benzene	1933	368
Toluene	17,966	1617
Trichloroethylene	81	1841
Tetrachloroethylene	567	1250
Ethylbenzene	7482	4151
Carbon Tetrachloride	3770	96

total emission of VOCs. In a 1979 study, VOCs were detected in the wastewater from an average of 14 industries, out of a total of 32 industrial categories analyzed for organics (Keith and Telliard 1979). The most frequently detected chemicals are listed in Table 4 along with the total number of categories in which they were present. Also listed in Table 4 are the average concentrations found in the wastewater treatment plant influent, effluent as well as in the sludge. The influent concentration also includes VOCs from surface runoff and domestic discharges.

Out of all the volatile organic compounds listed in the EPA priority list, there seems to be five major organics that are most abundant in the wastewater. These pollutants are methylene chloride, benzene, toluene, trichloroethylene and tetrachloroethylene. Based on the wide application of these chemicals and their potential toxicity, these five compounds were chosen for analysis in this study.

2.3 Toxicity of Volatile Organics

The definition of toxic and hazardous substances must be stated clearly in order to understand the health effects of volatile organics. Toxicity refers to the capacity of a chemical to cause harm. Hazardous substance represents the probability that injury will occur. Thus a substance may be classified hazardous depending on toxicity data as well as factors such as biotic and abiotic transformations and individual susceptibility. Also, the dosage at which the substance causes harm must be considered. It is highly

TABLE 4

The Most Common Volatile Organic Compounds Detected in
Municipal Wastewaters (Langer and Feller, 1982)

Volatile Organics	Number of Industrial Categories	Concentration (ug/L)		
		Influent	Effluent	sludge
Benzene	25	20	1	29
Toluene	28	214	7	3000
Ethylbenzene	24	18	1	41
Chloroform	28	16	6	9
Methylene Chloride	25	515	325	181
Tetrachloroethylene	19	126	17	47
Trichloroethylene	21	45	20	3300

unlikely that any substance is entirely safe or entirely dangerous. An excess exposure to anything is potentially harmful (Boardman and Sherrard 1983).

Exposure may be divided into three categories: acute, subacute and chronic. Acute exposure refers to exposures of short duration, usually a time length of a few hours or shorter. Chronic exposure refer to periods over three months. Any exposure period between acute and chronic is refererd to as subacute. Most exposures are simply stated in terms of acute or chronic or most often as effects of both acute and chronic.

There are a number of different terms used to express toxicity of contaminants. One of the most common terms used is maximum contaminant level, MCL,. MCL's are mandatory standards set as limits never to be exceeded (Monty 1986). In July 1984, the U.S. Environment Protection Agency proposed recommended MCLs, RMCLs, of zero for volatile organics that are considered carcinogens. These included tetrachloroethylene, trichloroethylene, benzene and methylene chloride (Sitting 1985). Maximum allowable concentrations, MACs, and threshold limit values, TLVs, are also frequently applied (Monty 1986). Another criterion used for pollutant exposure is the suggested no-adverse-effect response level, SNARLs. The EPA has adopted this term from the National Academy of Science, NAS, and is used for both long and short term exposure (Monty 1986). For long term risks, SNARLs are represented in concentrations corresponding to incremental lifetime cancer risks. All

these different terms have been developed by agencies such as the EPA, World Health Organization, WHO, Ontario Ministry of the Environment, MOE, and many others arround the globe. These are required to protect aquatic life from acute and chronic toxicity and to protect human beings from exposure toxicity, directly as well as indirectly from ingestion of contaminated species.

Information on the health effects of most VOCs is very limited. Since monitoring these chemicals has only started recently, any data on their toxicity stem from laboratory tests on organisms and any accidental human exposure. The regulated standards and criteria on the toxicity on the five VOCs investigated in this study are listed in Table 5. In the future, as more information is gathered on these chemicals, their regulations and guidelines will certanly be modified.

2.4 Properties of Volatile Organics

The treatment of any wastewater is largly dependent on the quality and quantity of the pollutants. It is also dependent on water characteristics such as temperature, pH and volume. Other factors that must be considered include government regulations, cost and availability of materials. Nevertheless, the most important elements are the properties of the contaminants. The effectiveness and the feasibility of the treatment methods that could be implemented are decided based on these properties.

The important properties of VOCs that play an impor-

TABLE 5

Proposed Water Quality Criteria and Standards[1]

Pollutant	Saltwater Aquatic Life Protection, (ug/L)		Drinking Water Criteria (ug/L)
	Acute	Chronic	
Benzene	5,100	-----	10
Methylene Chloride	----	-----	40
Tetrachloroethylene	10,200	450	10
Toluene	6,300	5,000	14,300
Trichloroethylene	2,000	-----	30

tant role in their removal from wastewaters are listed in Table 6 for the five organics considered in this study. As can be seen from Table 6 the only two characteristics that classify these chemicals as VOCs are: (i) the fact that they are all organic compounds and, (ii) they all have relativly high vapour pressures. Other properties such as the solubility in water vary from 20,000 mg/L for methylene chloride to a low of 150 mg/L for tetrachloroethylene. Solubility as well as the density of these chemicals can greatly affect the removal efficiencies from wastewater depending on the treatment method.

2.5 Polymers

Since the development of synthetic polymers in the fifties, many water and wastewater treatment plants have been able to improve their overall efficiency and reduce their operating costs. A survey in 1982 indicated that over 50 percent of U.S. water facilities used polyelectrolytes in their systems (AWWA Committee Report 1982). The U.S. EPA has approved over 450 types of polymers produced by more than fifty different manufacturers for use in potable water treatment (EPA Report 1975).

Polymers in water and wastewater treatment plants are used as either primary coagulants or as coagulant aids. As primary coagulants they are the agents responsible for charge neutralization and destabilization of the colloidal particles. They can be used as sole coagulants or in combination with metal salts such as alum and ferric sulfate.

TABLE 6

Properties of the Selected Volatile Organics[1]

Pollutant	Chemical Formula	Chemical Class	Boiling Point (°C)	Density (g/ml) @ 20°C	Solubility (mg/L) @ 20°C	Vapor Pressure (KPa) @ 20°C
Benzene	C_6H_6	Monocyclic Aromatic	80.1	0.879	1800	10.1
Methylene Chloride	CH_2Cl_2	Halogenated Aliphatic	40.0	1.33	20,000	46.52
Tetrachloroethylene	C_2Cl_4	Halogenated Aliphatic	121.0	1.63	150	1.9
Toluene	C_7H_8	Monocyclic Aromatic	110.6	0.867	500	3.7
Trichloroethylene	C_2HCl_3	Halogenated Aliphatic	86.7	1.46	1070	7.7

@ 25°C
[1] (WHO, 1984,1985; Environment Canada, 1983)

As coagulant aids they are added after the primary coagulant to increase the size of the floc and its strength and hence improve settling. Polymers used as coagulant aids generally have high molecular weights to enable bridging of destabil-ized colloids.

2.5.1 Properties of Polymers

Synthetic polymers used in water treatment can be classified in three general classes: polymer charge, molecular weight, and product form.

2.5.1.1 Polymer Charge

The polymer charge may be anionic, cationic, or non-ionic. Anionic and nonionic polymers are generally used as coagulant aids. They usually have high molecular weights which enable interparticle bridging. Cationic polymers are most often used as primary coagulants. They usually replace the traditional coagulants such as alum and ferric sulfate. They can also be applied in conjunction with these metal coagulants to reduce the amount of alum or ferric sulfate required. Dosage of cationic coagulants are usually a direct function of the total amount of colloidal material present in the wastewater. The dosage required is usually determined by the cationic charge density. The total charge added to the water must be enough to reduce the negative zeta potential (electrophoretic mobility) of the particles. Any excess polymer remaining in solution after destabiliza-tion (overdosing) can result in charge reversal and res-

tabilization.

2.5.1.2 Molecular Weight

The molecular weights of polymers are never exact values representing all the chains of a polymer type. Molecular weights more or less indicate mean values of the wide range of chain lengths of a polymer. It is not unreasonable for polymer strands in a commercial polymer to have a molecular weight be several times its number average molecular weight (Mangravite 1982). For this reason molecular weight comparisons are realistically impossible, but in relative terms they are important charecteristics. Polymers used in water treatment can have molecular weights as low as 10^4 g/mole and can go as high as tens of millions g/mole.

2.5.1.3 Polymer Form

All polymers used for water treatment are available in one of three forms. The most common are the dry powders. These are often high molecular weight anionic or nonionic polymers (Amirtharajah and Kawamura 1983). In this form the polymers can be conveniently transported and stored. Powdered polymers require special feeding systems which mix the polymer into a water solution prior to application. Other forms of polymers which are becoming more and more popular are emulsions. This is a mixture of polymer particles and water suspended in oil (Mangravite 1982). The polymer content typically ranges from 20 to 45 percent by mass and the

water content from 0 to 50 percent by mass. These polymers are easier to handle than dry polymers because they do not require any special feeders. However, shipping polymers in an emulsion form is more difficult and thus more expensive. The third form in which polymers for water and wastewater treatment is used is the liquid form. Usually only low molecular weight cationic polymers are mixed into water solutions. High molecular weight polymers can be very unstable and break dawn in very short periods of time. Handling liquid polymers eliminates the difficult problem of setting and dissolving dry polymers. The big disadvantage with liquid polymers is associated with transportation methods and costs. Special tankers or large barrels are required to transport the solution of which the majority is water. Also, most liquid polymers have a shelf life ranging from 3 to 12 months while emulsions and powders, if properly maintained, can be stored for longer periods (Amirtharajah and Kawamura 1982).

2.5.2   Polymers as Coagulants

The use of polymers in water and wastewater treatment has been around for a long time. It has been reported that as early as 2000 B.C. turbid water was treated by the use of a number of vegetable substances (Cohen 1958). Since then, many natural organic material of polymeric nature have been applied in aiding the coagulation of suspended particles. Substances such as starch, cellulose, gums and proteinaceous materials have been found to be effective

coagulants.   The principal property that explains the be-
haviour of all these natural polymers is simply the presence
of ionizable sites (Ruehrwein and Ward 1952).

It was not until 1952 that the synthetic polymers
were analyzed for their potential as coagulants.   Ruehrwein
and Ward, 1952, examined both anionic and cationic polymers
in the flocculation of bentonite.   They concluded that
cationic polymers could induce flocculation by physically
adsorbing onto the clay particles.   They found anionic
polymers did not flocculate the suspended particles but im-
proved the rate of flocculation when the anionic polymers
were added after floc formation.   Ruehrwein and Ward, 1952,
were also the first to propose that single polymer chains
can adsorb onto more than one clay particle.   This even-
tually led to the polymer bridging model.   Three years later
Michales and Morelos, 1955, concluded that adsorption and
subsequent flocculation of cationic polymers is a result of
electrostatic attraction to the negatively charged colloidal
particles.   In the case of anionic polymers, they were
generally found ineffective in removing negative colloids.
They also stated that the adsorption mechanism along with
intramolecular association to be controlled by hydrogen
bonding.   Their study also supported the theory of polymer
bridging; however, they admitted that the entire floccula-
tion process was poorly understood.

The adsorption of suspended particles onto polymer
chains was studied by a number of researchers.   Miller and
Goahame, 1961, were able to confirm the model of polymer

bridging. They showed that only a part of the polymer chain attached to a particle while the remaining part extended through the solution. From this discovery it was concluded that the free chain in solution can form bridges between other particles. Fontana and Thomas, 1961, found that a single polymer chain in solution can extend and intertwine thus allowing a number of suspended particles to be adsorbed.

Solid proof on the mechanism of polymer bridging did not exist until the work of LaMer, 1956. LaMer concluded that polymer concentration was independent of the number of adsorbed sites on each polymer chain. Optimum flocs seemed to form when approximately half of the active sites on the suspended particle were amalgamated with the polymer. He also observed that the bridging action increased with increase in polymer molecular mass. Further work by LaMer, 1963, brought about the theory of particle restabilization due to polymer overdosing. Excessive polymer in solution causes a form of polymer coating on the particles and thus prevents bridging.

2.6 Coagulation and Flocculation

2.6.1 Application

The process of coagulation and flocculation plays an important role in wastewater treatment. Many contaminants, particularly those harmful to the environment, are removed by this process. Removal of parameters such as suspended solids, SS, biochemical oxygen demand, BOD, phosphorqus and

heavy metals is greatly enhanced. During flocculation tiny particles suspended in solution are caused to collide and form into larger and heavier thus more settelable flocs. These collisions are brought about by random Brownian motion (perikinetic), velocity gradients caused by fluid shear (orthokinetic) and the differential settling rates of particles. Generally, the larger flocs formed by flocculation can then be removed by settling followed by filtration.

The physical aspects of flocculation are very complex. The process involves many variables which to date are not fully understood. These variables include the properties of the particles, properties and quality of the water and the engineering of particle contact. In the design and operation of flocculation basins, many factors that influence the process such as temperature, floc density, water viscosity, particle distribution and concentrations and other characteristics are not controlled. Only a few factors are directly controlled. These include detention time, velocity gradients and the coagulant types and dosages.

2.6.2   Volatile Organics Removal

During the coagulation/flocculation process, trace organic compounds are believed to be removed by one or more of the following mechanisms: charge neutralization and adsorption, adsorption and bridging or sweep flocculation with enmeshment and co-precipitation (Semmens and Field 1980, Semmens and Ayers 1985). Trace organics in the wastewater

can become adsorbed onto metal coagulants, polyelectrolytes or other organics or suspended solids. During flocculation some trace organics may become trapped within forming flocs and hence settle out. Some of the organic matter may also form complexes with the coagulant or coagulant aids and hence precipitate out (Semmens and Ayers 1985).

There has been very little research conducted on the removal of specific organic compounds from water. In almost all the studies cited, the organics removal has been reported in terms of total organic carbon, TOC, (Preising 1962, Amy and Chadik 1983). TOC is a collective measure of organics in water and provides no information on the composition and identification of the wide array of organic pollutants. Other more categorized terms are total organic halogens, TOX, and trihalomethanes precursors, THMPs. These types of analyses give no indication on the types of organic compounds being removed and at what concentrations. Volatile organic compounds in concentrations of parts per billion, ppb, contribute a negligible amount to the total organic content in wastewater. At the same time, if VOCs are not removed in the same ratio as TOC, the volatile organic content in the treated water could possibly become a major contributor to total organic content.

Generally, volatile organic compounds are poorly removed by primary treatment. An EPA study of a publicly owned treatment facility revealed the following percentage removals of VOCs by primary treatment (Crowford and South-worth 1982):

Benzene	7 %
Methylene Chloride	16 %
Trichloroethylene	25 %
Toluene	10 %
Tetrachloroethylene	42 %

Hannah et. al., 1986, evaluated VOCs removal by different treatment processes. Their results also concluded poor removal by primary clarification with alum. They reported an average of 14 percent removal for the seven volatile organics they observed. These results are based on an alum dosage of 250 mg/L.

The removal of organics from wastewater has been generally found to increase with increasing coagulant dosages. Semmens and Field, 1980, noted that alum dosages higher than those normally used for turbidity removal are needed to obtain best organic removal. The two most important variables affecting the performance were found to be coagulant dosage and pH. They also stated that the actual mode of operation including rapid mix, flocculation time and the order of coagulant additions appeared to have little effect on organics removal. Although the work of Semmens and Fields focused on TOC removal, it still provided a good indication of the general behaviour of the overall family of organic compounds.

A more recent study by Semmens and Ayers, 1985, conducted on the removal of low molecular weight organic compounds indicated poor removal by coagulation. Any removal was assumed to be caused by the formation of complex

molecules from trace organics and the metal salts, alum or ferric sulfate. Adsorption did not appear to be a sig-nificant mechanism at any dosage level: Semmens and Ayers, 1985, did indicate that overall removal was slightly en-hanced in the absence of natural organics indicating com-petition between other organic matter for adsorption sites.

2.6.3 Effects of pH

Perhaps one of the most important variables as-sociated with removal of organic material is the pH of water. Many researchers have reported that there exists an optimum pH for TOC removal while using alum and ferric sul-fate (AWWA Committee Report 1979, Semmens and Field 1980). The optimum pH ranges from 4.0 to 5.0 for alum and a slightly higher range of 5.0 to 6.0 for ferric sulfate. Semmens, 1980, reported TOC and THMP reduction of 60 percent at pH of 5.0 but only 15 percent at pH of 8.0 using alum coagulation. Edzwald, 1978, in a study on coagulation of humic acids with a cationic polymer reported optimum removal at pH of 5.0. The work of O'Brien and Navak, 1979, also concluded that cationic polymers work most efficiently at pH values of 7.0 or below. However, nonionic polymers were found to function effectively over a pH range of 6.5-8.5. The acidity of water required for organics removal is slightly lower than that needed for optimum turbidity removal (Black and Willems 1961).

The reason for the increase in organics removal at low pH values is attributed to the fact that lower pH values

reduce the negative charge on the organics. Black and Wil-
lems, 1961, noted that flocs produced in the range of op-
timum coagulation had low values of zeta potential. Semmens
and Field, 1980, reported that equivalent TOC removal at pH
of 5.0 by alum can be obtained at higher pH values by in-
creasing the coagulant dosage. This procedure will require
the use of more coagulants and therefore is not an optimum
solution.

3.3 Adsorption

3.3.1 Application

Adsorption of contaminants from water and wastewater
is not a new process. Powdered activated carbon, PAC, was
used in the 1920s to control taste and odour in water sup-
plies (Montgomery 1985). However, it was not until the late
sixties that adsorption was recognized as an effective
method for removal of organics. Today, although adsorption
is still being used largely to control taste and odour in
water, it is increasingly becoming popular in removing trace
organic contaminants.

Adsorption is defined as a physical and/or chemical
process by which a substance is accumulated at an interface
between the two phases. This process occurs due to forces
that attract the adsorbate to the solid surface in solution.
These forces are derivatives of the adsorbant driven to the
solid surface which occupies a lower energy state. Every
substance adsorbs differently on different adsorbents. This
is attributed to the properties of the contaminants such as

molecular mass and solubility. Generally adsorption is very effective over a wide range of pollutant solubility but is restricted to relativly low molecular mass compounds.

2.7.2   Activated Carbon

In water and wastewater treatment the most widely used adsorbent is activated carbon. Activated carbons are carbonaceous materials subjected to selective oxidation to produce a highly porous structure (Sanks 1978). These carbons can be thermally or chemically activated to produce surface areas in excess of 2000 m^2/g. It is the high porosity and massive surface area that make activated carbon a good adsorbent.

2.7.3   Plastic adsorbents

The use of plastic (polymeric) adsorbents in the removal of organic material from water is becoming increasingly popular as more information is gathered on their capacities and performance. Recent advancements in polymer chemistry is producing more and wider varieties of potential adsorbents (Webber and Vliet 1981). One advantage of plastic adsorbents over activated carbon is that they can be manufactured with predetermined surface conditions. Thus, certain polymers can be tailored for specific adsorption applications. Another advantage is that these polymers may be regenerated with basic, acidic, or salt solutions or certain solvents.

2.7.4   Volatile Organics Removal

2.7.4.1 ·Activated Carbon

The capacity of activated carbon in adsorbing volatile organics has been found to be very high. A five year study detailing the design of a granular activated carbon, GAC, facility in Cincinatti reported removals of at least 94 percent for a large number.of VOCs (Westerhoff and Miller 1986). The only poorly removed organic was toluene with a 52 percent removal. Toluene, although not adequatly removed when concentrations were low, was removed more readily when initial concentrations were increased. Amy et. al., 1986, studied the removal of trichloroethylene and carbon tetrachloride by GAC. They concluded that although both were effectivly removed, carbon tetrachloride required a deeper GAC bed to achieve equal removal. Amy et. al. also found that background levels of organic carbon significantly effected adsorption capacity.   In a small township[1] in New Jersey, where a GAC system was installed to remove trichloroethylene from groundwater, excellent percentage removal was obtained (McKinnon and Dyksen 1984).   However, the carbon became exhausted after very short periods of time. This required regular costly carbon regeneration and system slowdown. Activated carbon has been found very effective in VOCs removal and has been applied specifically for this purpose in a number of treatment works where pollutant levels warrant the high cost of this adsorbent.

2.7.4.2   Plastic Adsorbents

The use of polymeric adsorbents for VOCs removal has recently warranted investigations in an attempt to achieve better performance and cheaper overall costs than activated carbon.   Kong and DiGiano, 1986, compared the adsorption power of activated carbon with a polymeric adsorbent. The type of adsorbent was a carbonaceous resin. The study revealed that the resin had a higher capacity for adsorbing the VOCs tested.   The dosage of resin required to remove equal quantities of trichloroethylene, tetrachloroethylene and carbon tetrachloride was three to five times smaller by mass than that required by activated carbon.   Love and Gilers, 1982, reported the findings from a USEPA study of GAC versus synthetic resin in VOGs removal.   Their results also concluded that the capacity of the resin was two to three times that of GAC.

Not all synthetic adsorbents have surpassed GAC in removing VOCs from water. An unsuccessful attempt by Urano and Kno, 1984, compared the adsorption of aromatic compounds on activated carbon and polystyrene.   In all cases the activated carbon was found more effective than the polystyrene.   Cook and Hartz, 1983, conducted batch adsorption experiments using polyvinyl chloride, polyethylene, neoprene and polyurethane foam as adsorbents.   Granular activated carbon was included in the study for comparison purposes. In all cases the GAC outperformed all the plastic adsorbents in the removal of methylene chloride, chloroform and carbon tetrachloride.   Methylene chloride was the least

removed by all adsorbents including activated carbon. This was attributed to the high solubility of methylene chloride. Removal of carbon tetrachloride and chloroform ranged from only 2 percent to a high of 78 percent using the various plastic adsorbents.

Adsorption capacity of plastic materials will most likely improve as the polymer production technologies advance.

III. EXPERIMENTAL METHODS

The experimental set-up and procedures followed in conducting this study are described in this chapter. Figure 1 provides a flowchart for the sequence followed in conducting experiments.

3.1 General Approach

This study was divided into three phases. Phase one was designed to find the optimum dosage required for each of the polyelectrolytes and the metal coagulants, alum and ferric sulfate. Phase two embodied the combination of alum or ferric sulfate as primary coagulants along with one of the several polymers used as coagulant aids. A narrow range of coagulant dosage based on the results obtained in phase one were employed. Finally, phase three icorporated the use of powdered activated carbon as an adsorbent in addition with the best combination found in phase two. In each cases, the optimum coagulant dose was regarded as the one giving the maximum overall removal of organic compounds.

In addition to analyzing the removal of volatile organics, several other parameters, such as BOD, suspended solids, alkalinity, pH, phosphorus and heavy metals were determined. This was necessary in order to evaluate the overall performance of the system.

RAW WATER
(approx. 8 L)

Add 100 ug/L of

Add 1000 ug/L of

Copper
Nickel
Zinc
Cadmium
Lead

Methylene Chloride
Benzene
Trichloroethylene
Toluene
Tetrachloroethylene

SPIKED WASTEWATER

*Remove samples for
analysis of*

Heavy Metals
Phosphorous
Suspended Solids
BOD
Alkalinity and pH

JAR TEST ASSEMBLY

COAGULANTS

B   1   2   3   4   5

*Remove samples to repeat above tests
plus samples for analysis of VOCs*

Figure 1. Flowchart of General Experimental Procedures

3.2   Jar Tests

All coagulation/flocculation tests were performed using the traditional jar test.   This is the most common technique used to determine the optimum dosage for plant operation because it is simple, easy to run and requires no sophisticated equipment.   The main disadvantage with jar tests is the difficulty of reproducing conditions similar to those found in full scale treatment systems.

All the jar tests were conducted on a Phipps and Bird multiple laboratory stirrer.   One liter standard Pyrex beakers were used with a final sample volume of 1000 mL.   In each beaker a total of four mixing paddles were positioned 25 mm above the bottom of the beakers.   The paddles had a surface area of 1900 sq. mm (76 mm wide and 25 mm in height).

The jar test experiments in phase one of the study included rapid mixing at 100 rpm for 90 seconds.   Subsequently, the speed was reduced to 20 rpm for a twenty minute flocculation period.   Finally, the paddles were removed and the flocs were allowed to settle for thirty minutes before samples were collected for analysis.   In all cases the coagulants were injected into the vortex at the beginning of the rapid mix mixing.

For the second phase an initial rapid mixing time of 90 seconds at 100 rpm was employed for the first coagulant. At the end of this mixing period the coagulant aid was added and mixed at the same speed for an additional 90 seconds. The flocculation and settling characteristics were the same

as in phase one.

Phase three was run similarly to phase two, with the exception that, after the second rapid mixing period, powdered activated carbon was added and mixed at 100 rpm for one additional minute. Therefore, the total rapid mixing time for this phase was four minutes.

3.3 Materials

3.3.1 Raw Wastewater

The wastewater used for this study was obtained from the West Windsor Wastewater Treatment Plant which services most of the industries in the City of Windsor. The samples were collected from a sampling station from the main sewer prior to entering the treatment facility.

The volatile organic content in this raw water was usually very low and fluctuated considerably. For this reason, it was decided to spike the original samples with 1000 ug/L of each of the five organic compounds, benzene, methylene chloride, tetrachloroethylene, toluene and trichloroethylene. The wastewater was also spiked with 100 ug/L of each of the metals Cu, Cd, Zn, Pb, and Ni. This was required to ensure minimum detectable amount of these inorganics since the heavy metal content in this wastewater also varied considerably on a daily basis (Zytner 1980).

The wastewater was collected in 10 L glass bottles with an aluminum covered cap. Immediately after the wastewater was collected it was brought back to the laboratory, spiked and used in the jar tests.

3.3.2 Polymers

The properties of the five polymers used in this study are listed in Table 7. Three of these were cationic polymers with a wide range of molecular weights and cationic charges. The remaining two polymers were anionic. One had a molecular weight of approximatly 10,000,000 and the other had an infinite molecular weight. The recommended range of dosage for four polymers was obtained from the suppliers. Polymer CX-617 was a new polymer obtained from the McMaster Institute for Polymer Production Technology, MIPPT. This polymer's jell like behaviour in water tempted the author to investigate its performance in wastewater treatment.

Stock solutions of each of the polymers were prepared based on the dosage required. Polymers 8103, 603, and 7607 were received in an emulsion form. They were further diluted with deionized water into more usable solutions. The final concentrations of stock solutions are given Table 8. Polymers CX-617 and 2790 were obtained in a powder and granular forms respectivly. Predetermined amounts of these polymers were dissolved in 100 mLs of deionized water and mixed overnight. These solutions were not stored for more than one day (Amirtharajah and Kawamura 1983). Two key points were kept in mind when making the polymer solutions. First, the polymer solution added to the beakers had to be large enough to pipet accurately. Second, it was essential that the volume added was small enough not to alter the concentration of the contaminants in the

TABLE 7

Polymer Properties

Polymer	Type	Cationic Charge (meg/gm)	Molecular Weight	Recommended Dosage (mg/L)
Alchem 8103	Cationic	1.1	100,000	10 - 50
Alchem 603	Cationic	4.0	30,000	10 - 50
Alchem 7607	Cationic	3.1	600,000	10 ʳ 50
Diafloc 2790	Anionic	---	10,000,000	0.1- 1.0
MIPPT CX-617	Anionic	---	infinite	-----

TABLE 8

Polymer Solutions

Polymer	Form	Percent Polymer	Stock Solution (mg/L)
8103	Emulsion	20	5000
603	Emulsion	25	5000
7607	Emulsion	45	5000
2790	Granular	100	100
CX-617	Powder	100	5000

beakers. All the polymers were agitated for a minimum of one hour prior to use to ensure the polymer is evenly distributed in the water.

3.3.3 Metal Coagulants

In this study both, aluminum sulfate, $Al_2(SO_4)_3 \cdot 16H_2O$, and ferric sulfate, $Fe_2(SO_4)_3 \cdot 14H_2O$, were used as chemical coagulants. These two chemicals are the most common coagulants and are used by most wastewater treatment plants (Committee Report 1982). Stock solutions of 10 g/L were prepared daily (Batchelor and Yang 1982). Each solution was agitated for at least one hour before use.

3.3.4 Powdered Activated Carbon

The powdered activated carbon, PAC, was obtained from Fisher Scientific. As received, the carbon particles varied considerably in size and posed considerable problems during preliminary jar tests. Most of the carbon particles immediately either sank to the bottom or remained floating on the surface throughout the flocculation period. Therefore, only a small percentage of the powdered activated carbon remained in suspension. Through a series of trials it was found that powder passing a 200 sieve flocculated best. Thus, this selected carbon size was washed with deionized water to remove all the fines that would otherwise float on the surface. The activated carbon was then dried and stored in a desiccator until use. This procedure prevented most of the carbon from settling and from floating

on the surface during flocculation. A 10 % slurry of carbon
by weight was prepared prior to use in order to inject it
with pipet into the vortex during coagulation (Sanks 1986).

In all cases a dosage of 500 mg/L of PAC was added.
The reason behind such a high dosage is the fact that a
large amount of organic material is present in the was-
tewater in addition to the volatile organics added. Also,
by adding such a large dosage the maximum efficiency of PAC
in removing VOCs from typical wastewater can be evaluated.
The average dosage of PAC used by most treatment facilities
is 2.8 mg/L (Sanks 1986). Amy and Chadik, 1983, used a
dosage of 50 mg/L to remove trihalomethane precursors from
raw water. In special or difficult cases dosages such as
100 mg/L and higher have been required (Montgomery 1986).
Therefore, the high concentration employed in this study are
not unrealistic.

3.3.5   Volatile Organic Compounds

All, benzene, methylene chloride, tetrach-
loroethylene, toluene and tetrachloroethylene were of
analytical grade or better. Stock solutions of 100 mg/L of
each of the chemicals were prepared in one liter volumetric
flasks. The solution was mixed overnight to ensure all the
compounds were fully dissolved. This solution was stored at
4° C in brown colored bottles with a zero head space.

Standard solutions with concentrations of 100, 200,
400, 600, 800, and 1000 ug/L were prepared by diluting the
primary stock solution. These solutions were stored in 15

mL vials capped with teflon-faced septums and sealed tightly
with open top closures (Dietz and Singley 1979). This pro-
cedure allowed the vials to be stable for at least 28 days.
Due to limitations in the number of vials available, all the
standard solutions were used up within 15 days and a new set
was prepared after that.

3.3.6 Heavy Metals

A stock solution containing 100 mg/L of each of the
following metals, nickel, Ni, cadmium, Cd, copper, Cu, zinc,
Zn and lead, Pb was prepared. This solution was stored at
4° C until required. From this solution 8 mL was added to 8
L of wastewater to provide 100 ug/L concentration of each
heavy metal in the sample. This ensured that sufficient
metal concentration existed for detection purposes.

3.4 Procedure

Once the wastewater was collected from the treatment
plant, the following steps were followed for the jar test
experiments:

1. The volume of the wastewater in the collection bottle
was reduced to approximately 8 L.

2. From the metal stock solution a volume of 8 mL was
added to the wastewater bottle. This assured a minimum of
approximately 100 ug/L of each heavy metal in the was-
tewater.

3. Eighty milliliters of the organics stock solution was
added as quickly and gently as possible to avoid any loss of

the volatiles. This provided a concentration of approximately 1000 ug/L of each of the five compounds in addition to any organics already present in the wastewater. Having the exact concentration for either the metals or the organics was not very critical as long as the actual concentrations were analyzed just prior to testing. In this study, only the difference in concentrations before and after treatment was required.

4. The bottle was sealed with a cap covered in aluminum foil and mixed for five minutes.

5. The spiked wastewater was then transferred to the six beakers of the jar test assembly and to a seventh beaker for obtaining the raw water parameters. The beakers were filled in four stages of approximately 250 mL each to the 1000 mL mark. This ensured a more uniform mixture among all the beakers.

6. From the seventh beaker, separate samples were withdrawn to perform all the required analyses. Appropriate volumes were removed from the beaker roughly 50 mm below the surface using pipets. In all cases the samples were taken in the following order: VOCs, heavy metals, phosphorus, BOD, suspended solids, alkalinity and pH. For the VOCs, three 15 mL Kimble vials were filled and sealed with teflon-faced septums. Each vial was then inverted to check for air bubbles. If any were found the vial was emptied and filled again. The vials were stored at 4° C until analysis.

7. Once the jar test assembly was set up and all the beakers were filled with the spiked wastewater, the jar

tests were started and operated as described earlier. In each set of jar tests, one of the six beakers was used as a blank in which coagulants, polymers, and activated carbon were not added (Batchelor and Yang 1982). The percentage removal of all the coagulants were taken relative to the blank. Thus the percentage removals obtained using any coagulant are not actual removals but additional removals to those obtained in the blank by volatilization, sedimentation and by formation of chemical complexes. This was necessary since the efficiency of different coagulants in VOCs removal was one of the primary objectives of this study.

8. After sedimentation, samples were removed from each beaker and handled as described above. The removal efficiency for the VOCs was determined by comparing the equilibrium solute concentration with that of the blank.

3.5 Analysis

The analytical procedures followed in this study are listed in Table 9. All tests except for the VOCs were performed according to Standard Methods (APHA-AWWA-WPCF 1985).

3.5.1 Analysis of VOCs

The analysis of volatile organic compounds in the parts per billion range can be accomplished using gas chromatography. This is a relatively simple technique allowing the determination of organic compounds in a sample for a wide range of concentrations. Standards of known amounts of organics are required to correlate the compound

TABLE 9

Analytical Tests

Parameter	Instrument Used	Standard Methods Number[1]
pH	pH meter	423
Alkalinity	titration	403
Suspended solids	dry at 105 C	209C
BOD	membrane electrode	507
Phosphorus	spectrophotometer Bausch and Lomb Spectronic 20	424D
Heavy Metals	plasma emission spectrometer Beckman Spectra Span V	300
VOCs	gas chromatography Hewlett Packard 5890A	**

1 (APHA-AWWA-WPCF, 1985)

** (Dietz and Singly, 1984)

to their retention times and integrated areas which are derivatives of the technique.

In a gas chromatograph, GC, a liquid or gas aliquot of a sample is injected into a stream of carrier gas as shown in Figure 2. The carrier gas carries the sample through a coiled column in which the organics are slowed down due to physical and chemical reactions . Each compound reacts differently depending .on its properties and thus travel through the column at different speeds. Depending on the properties of the column and the operating conditions of the gas chromatograph each compound exits the column as a triangular peak at a time which is a characteristic of that compound.

A detector at the end of the column monitors the duration and the quantity of each compound. A Flame Ionization Detector, FID, the most common GC detector, burns the organics to produce ions which are related to the concentration of the compound. The output from the detector can be plotted as a chromatogram with the aid of a recorder. The qualitative identifications can be done either by the use of mass spectrometry or comparing retention times of known reference compounds.

Before analyzing a sample with gas chromatography, the sample must be prepared specifically for the compounds to be analyzed. For volatile organic contaminants, the most common and widely accepted technique is the purge and trap method based on work done by Bellar and Lichlenberg, 1974. This method involves the bubbling of helium through the
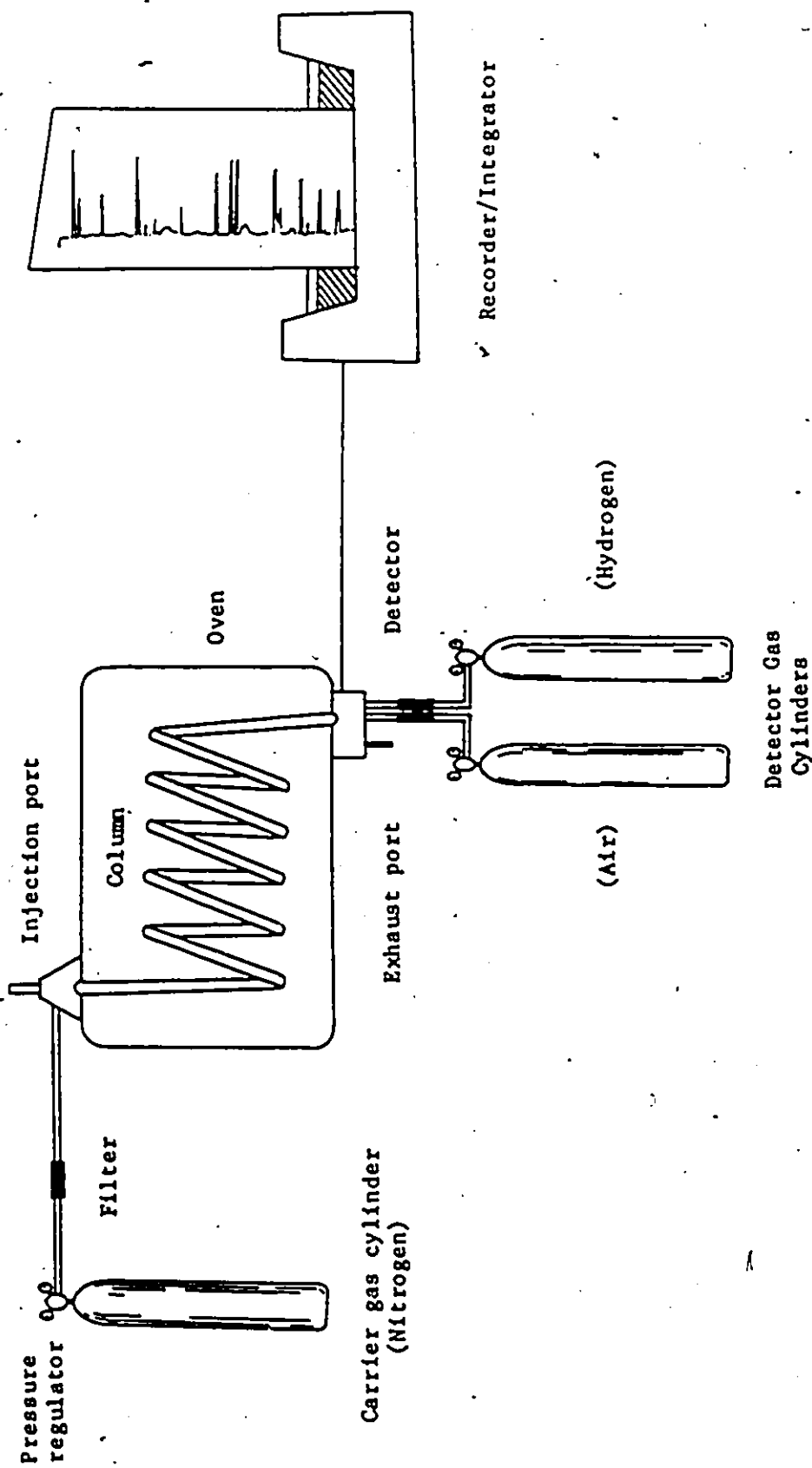
FIGURE 2. Schematic Representation of a Gas Chromatograph

sample causing the volatile organics to leave solution and disperse in the gas phase. The gas is then diverted into an adsorbent filled column in which the volatiles are retained. This trap is then connected to the injector port of the GC and the contents are backflushed with helium at high temperatures. Before injecting another sample, the trap must be conditioned at high temperatures for 7-10 minutes to remove any residue which may interfere with subsequent analysis.

The purge and trap method is very effective in analyzing volatile organic chemicals and is recommended by the United States Environmental Protection Agency, EPA, for GC analysis of VOCs (Thomas and Lammert 1980). The major disadvantage in using this method is the time required to prepare each sample for injection. About 30 minutes are needed from the time of purging to the end of conditioning of the trap. This length of time would have severely restricted the number of tests in this study. A literature search revealed another method which was more suited for this research. This method, known as the static headspace technique, can be used to analyze VOCs in ppb concentrations with only a fraction of the time needed by the purge and trap technique (Dietz and Singly 1984, Tonkeoka and Jennings 1984 and Kaiser and Oliver 1976).

The headspace method is based upon the considerable vapor pressures of volatile organics. In a sealed container the volatile compounds will equilibrate between the water surface and the headspace. Partitioning of the compounds

between the two phases depends mainly on the vapor pressure of the chemicals which in turn is dependent on temperature. The ratio of the headspace volume to the liquid volume in the container also effects the distribution (Dietz and Singly 1979).

In addition to saving time, this method posses a number of significant advantages over the purge and trap technique. The headspace method does not contaminate the injection port or the column with non-volatile organics or inorganics such as that which develops in the trap. Instead, the headspace process provides a form of sample cleanup since only relatively volatile compounds tend to partition into the headspace. Also, one does not have to worry about the adsorbent column clogging up and having to clean or replace it from time to time. The only disadvantage associated with this method is its sensitivity. Accuracy is very easily affected by slight variations in temperature, injection volume, headspace volume and time taken to inject a sample. However, consistency and practice can insure a high level of quality control.

3.5.2 Operating Conditions

The gas chromatograph used in this study was a Hewlett Packard model number 5890A, equipped with a flame ionization detector, FID. A megabore column five meters long was found adequate for this study. The following operating conditions were established based on a literature survey and trials and runs.

Column temperature	40° C
Injection temperature	225° C
Detector temperature	250° C
Detector gas flow rates: Air	390 mL/min.
Hydrogen	50 mL/min.
Carrier gas flow rate: Nitrogen	25 mL/min.
Injection volume	400 uL

A chromatogram from a typical run using this program is illustrated in Figure 3. All five compounds were adequately separated and developed good peaks. The approximate retention time for each of the compounds were as follows:

Methylene Chloride	0.1 min.
Benzene	0.3 min.
Trichloroethylene	0.4 min.
Toluene	0.7 min.
Tetrachloroethylene	1.0 min.

These retention times varied slightly from day to day due to slight variations in sample preparation.

After a certain number of samples have been injected some of the volatile organics and other material accumulated on the walls of the column. This is a common problem with gas chromatography and is usually solved by raising the oven temperature to allow the pollutants to burn off. After injecting approximately 10 to 15 samples, an identical blank sample containing only deionized water was injected. If the chromatogram showed no peaks, sample injections were continued until a second blank was tested. This checking procedure continued until small peaks appeared on the blank
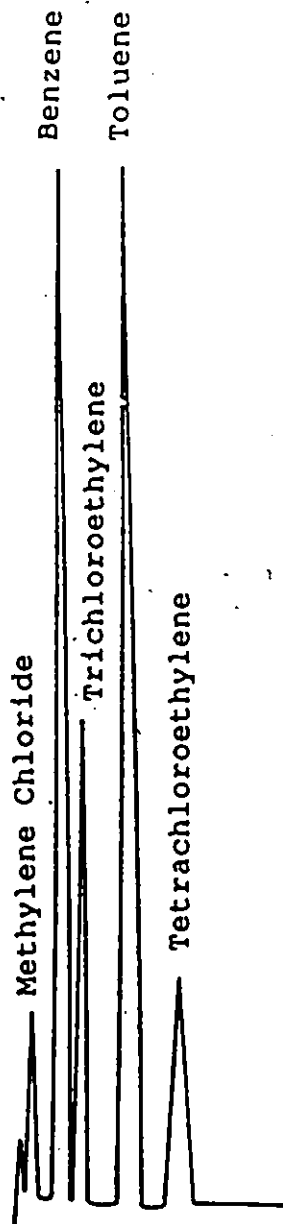
Figure 3. Typical Chromatogram for the Selected Volatile Organics

chromatogram indicating column contamination. At this point the oven temperature was increased to 150° C for 15 minutes to burn off the residue. After the temperature was returned to 40° C, another blank was injected to ensure that all the contaminants had been removed. The process was repeated if contamination was detected. This procedure, although seemingly inefficient, eliminates the use of a program involving automatic oven temperature increase after each run which takes approximately 5 minutes. The comparison of results by both procedures showed no significant differences.

3.5.3 Sample Preparation

The analysis of volatile organics, in the range of concentrations associated with this study, required the use of organic free glassware. Therefore, all glassware used for handling the organic compounds were cleaned using the following sequence: detergent wash, distilled water rinse, methanol rinse, deionized water rinse (twice), and oven drying at 150° C overnight (Dietz and Singly 1979, Paulason and Whitlock 1982, Cook and Hartz 1983).

The water used for preparing standards and blanks was purified deionized water. This was achieved by passing deionized water through an activated carbon filter. Occasionally random vials along with the purified water were tested for contamination.

Samples to be analyzed were taken from storage along with previously prepared standards. From each vial 5 mL, of solution was removed using a constant volume pipet. The

vial was quickly resealed and vigorously shaken by hand for one minute. It was then placed in a water bath kept constant at 30° C. Neither the volume removed, nor the incubator temperature are major factors as long as all samples tested at that time were treated identically. The samples were kept in the water bath for at least 30 minutes. Although subsequent studies showed that only a 7-8 minute period was required for the organics to reach equilibrium between the two phases, 30 minutes was used in all cases to ensure complete partitioning.

The vials were removed from the incubator, towel dried and shaken for 15 seconds before injecting the gas sample into the GC. The gas samples were injected using a 500 uL gas tight syringe supplied by Chromatographic Specialists. After the injection of each sample, the syringe plunger was removed and the barrel flushed with ultrapure nitrogen for one minute. This was to ensure that all the organics were removed from the walls of the syringe before the next sample was injected.

Each time a set of samples was analyzed on the GC, standards of known concentrations were also injected. This was necessary to develop a relationship between the integrated area and the concentrations of each of the volatile organics. A typical plot of the integrated area versus concentration for each of the five compounds is presented in Figure 4. The correlation coefficient, R^2, for all of these curves is given in Table 10. It can be seen that the correlation ranged between 0.9623 for methylene chloride to

0.9977 for trichloroethylene for a concentration range of 100 to 1000 ug/L. These excellent correlation coefficients are representative of all the standard curves developed. In addition, as can be seen from the variance values given in Table 10 that three different samples from the same batch gave very close results.

Since this study dealt with percentage removal and not the actual amount of organics present, simply taking the difference of the integrated area of the blank and the treated samples would have been sufficient. However, the relationships developed for each set of data ensured the proper operation of the system.
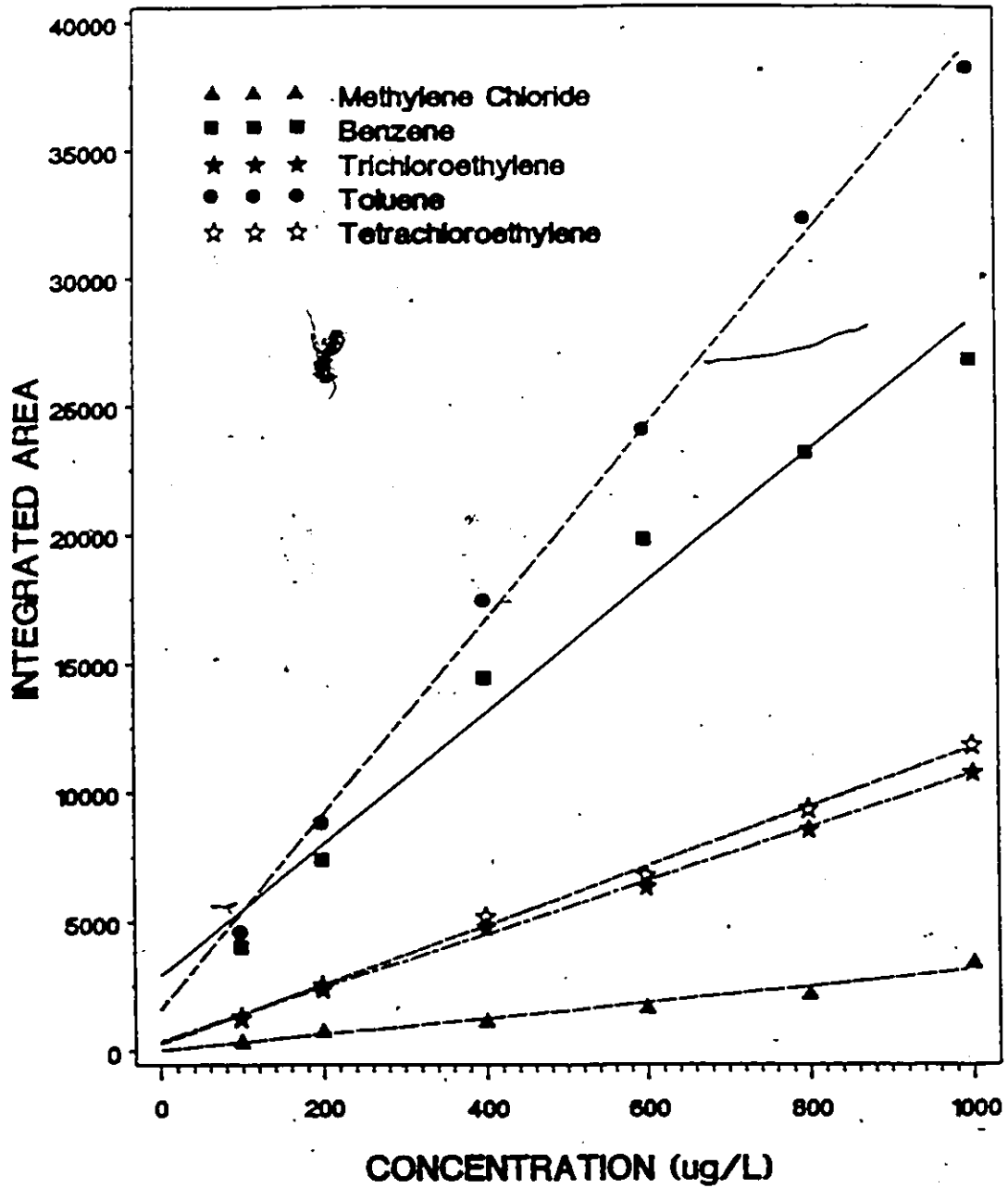
Figure 4. Calibration Curves for the Selected Volatile Organics

TABLE 10

GC Calibration Characteristics of the Five Organics

Chemical	Detention Time (min.)	R^2	Variance (%)
Methylene chloride	0.1	0.9623	1.5
Benzene	0.3	0.9766	2.9
Trichloroethylene	0.4	0.9977	1.3
Toluene	0.7	0.9970	1.5
Tetrachloroethylene	1.0	0.9968	1.9

IV. RESULTS AND DISCUSSION

4.1 Coagulant Dosage

In analyzing the efficiency of any coagulants, it is important to consider the influence of coagulant dosage. In the case of the cationic polymers, both polymers 8103 and 603 clearly indicated a point of optimum dosage. It can be seen from Figure 5 that polymer 8103 had one peak at which the volatile organics were best removed.. The percentage removals for all five organics are removals obtained using polymer 8103 in addition to the removals achieved in the blank. The percentage removals of the volatile organics observed in the blanks for all the jar test experiments are presented in Appendix A. Benzene, the least affected chemical, did not behave in the same fashion. Nevertheless, the optimum dosage for polymer 8103 can easily be marked at just under 40 mg/L. Beyond that point a form of polymer overdosing appears to occur. The second incline in Figure 5 could represent the increase in adsorption as more adsorbing sites are created with the addition of more polymer. A second experiment using polymer 8103 revealed the same pattern as obtained in Figure 5. The percentage removals at each coagulant dosage were within plus or minus three percent. Polymer 603 also showed an optimum dosage of approximately 40 mg/L; the relationship between percentage removal and coagulant dosage of polymer 603 can be seen in Figure 6.
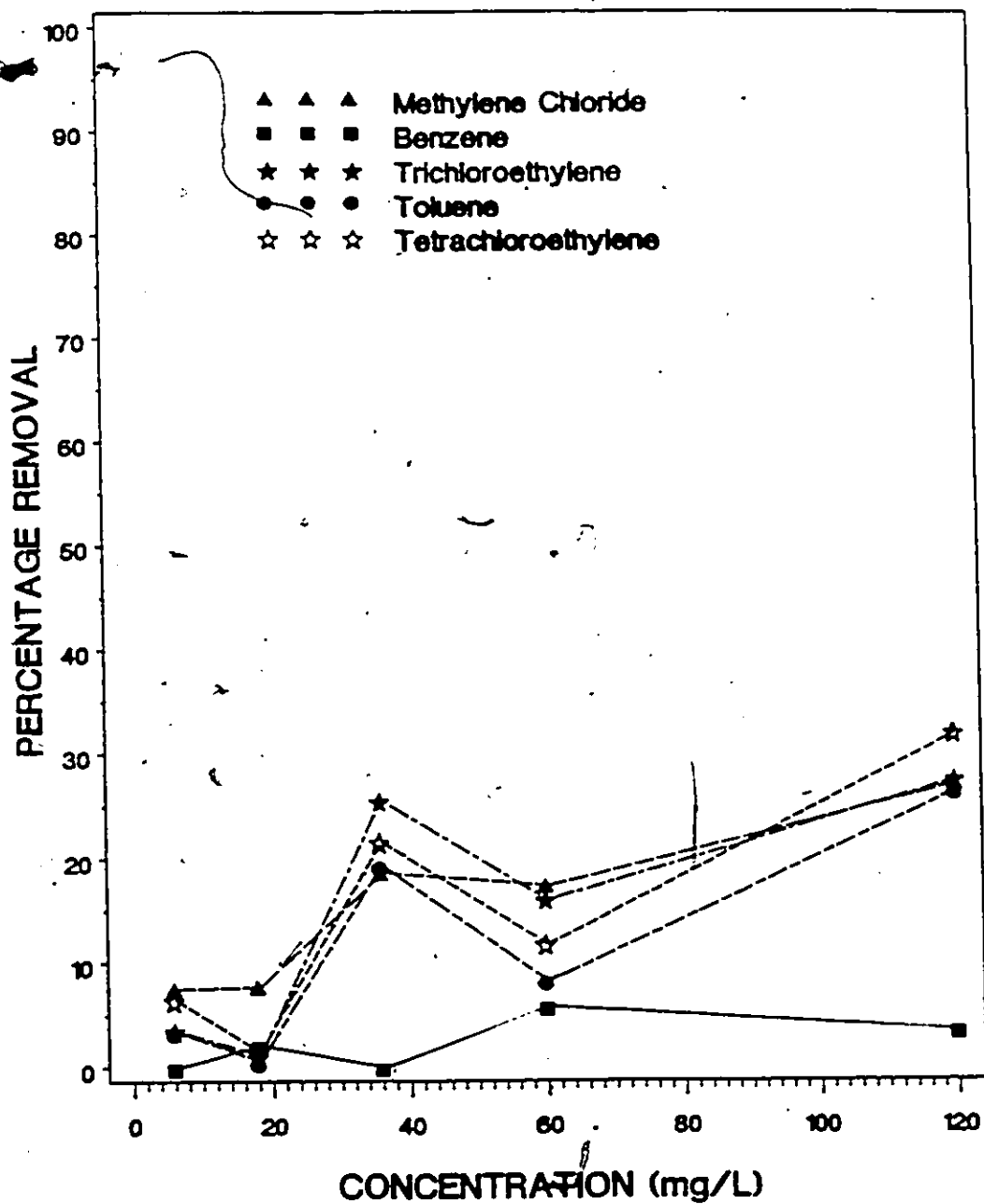
Figure 5. Percentage Removal of VOCs using Polymer 8103
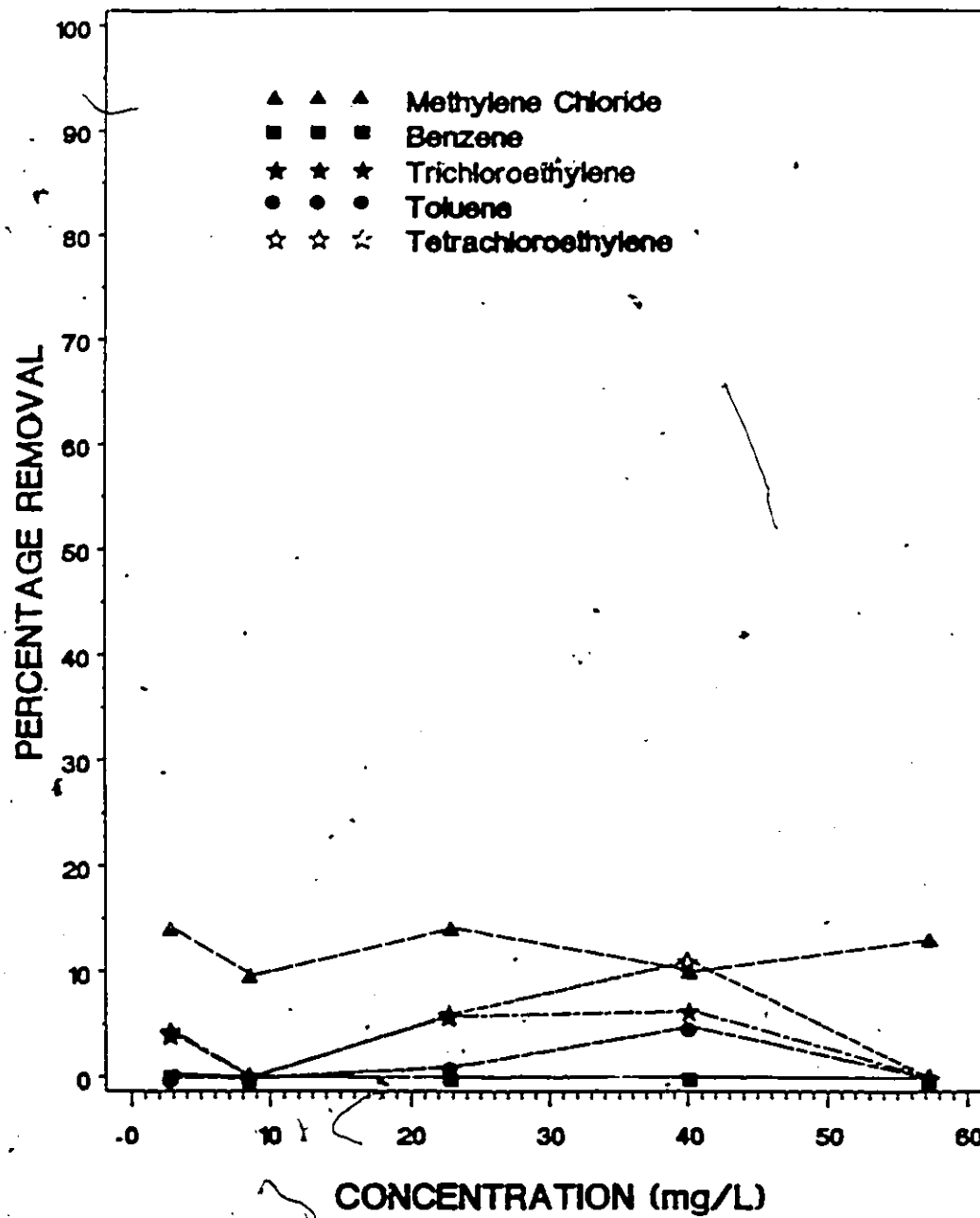
Figure 6. Percentage Removal of VOCs using Polymer 603

Again, benzene was poorly removed by polymer 603. The third cationic polymer, 7607, indicated no relationship between percentage removal and coagulant dosage. As can be seen in Figure 7, only methylene chloride showed any response to this polymer at all dosages.

The behaviour of the anionic polymers was slightly different than what was observed for the cationic polymers. Anionic polymers when used as sole coagulants do not generally enhance the removal of any contaminants. The negative charge of the polymer opposes the negatively charged particles thus preventing floc formation. Figure 8 confirms such a behaviour of polymer CX-617. However, as can be seen from Figure 9, polymer 2790 was capable of removing some of the VOCs. With the exception of benzene, the removal of the remaining VOCs increased with increase in polymer dosage. This indicates the possibility of direct polymer adsorption. The possibility of chemical entrapment can easily be ruled out since the floc formation was similar to that of the blank. Perhaps greater concentrations of either anionic polymer would have provided more adsorption sites and hence greater removals.

The optimum dosage for the metal coagulants were different than those observed for the polymers. Both alum and ferric sulfate, Figures 10 and 11, indicate a peak removal of the majority of the chemicals at dosages of 10 mg/L and a minimum removal at dosage of 30 mg/L. For ferric sulfate, VOCs removal peaked again at dosage of approximately 80 mg/L. As the dosage increased to 250 mg/L,

61
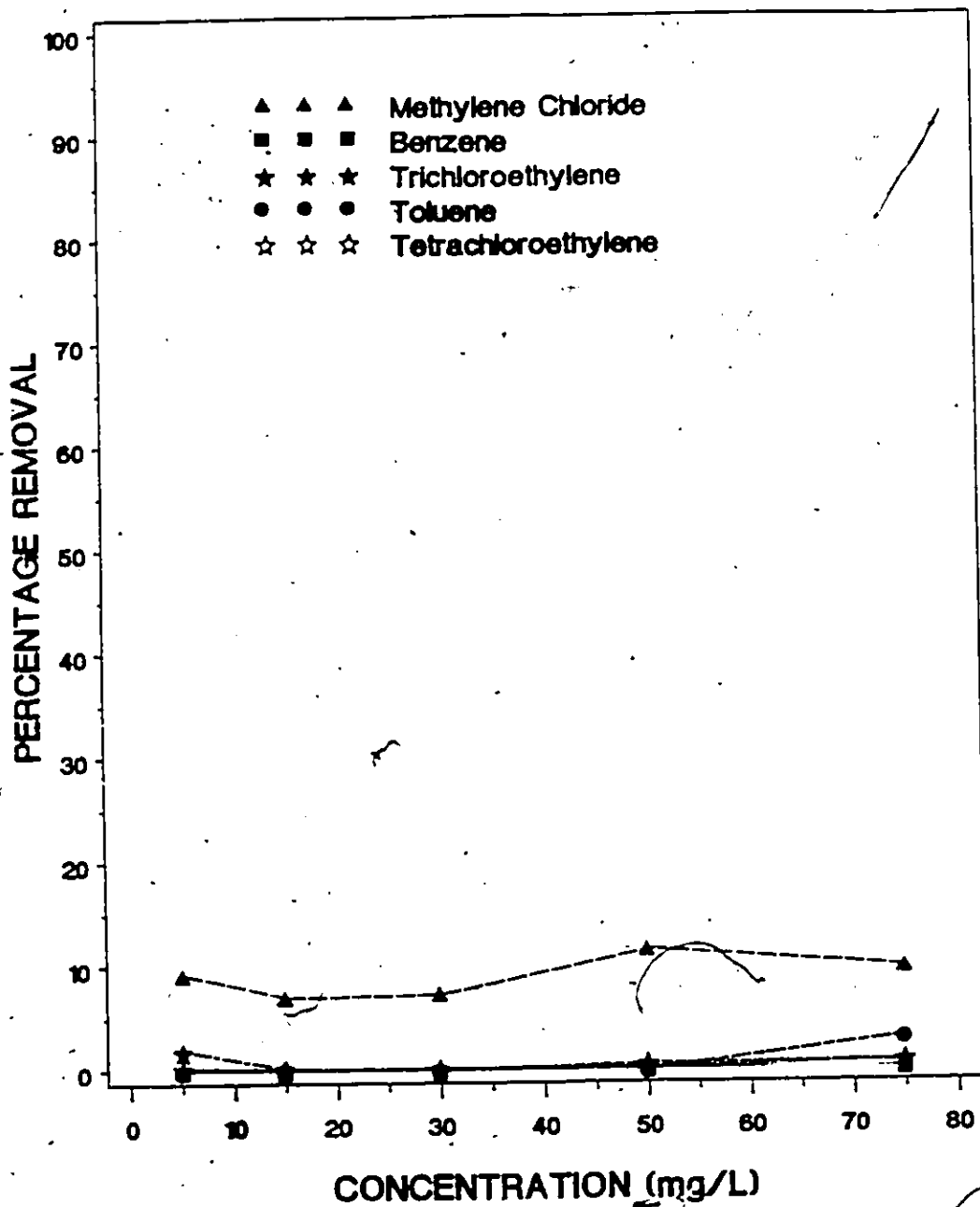
Figure 7. Percentage Removal of VOCs using Polymer 7607
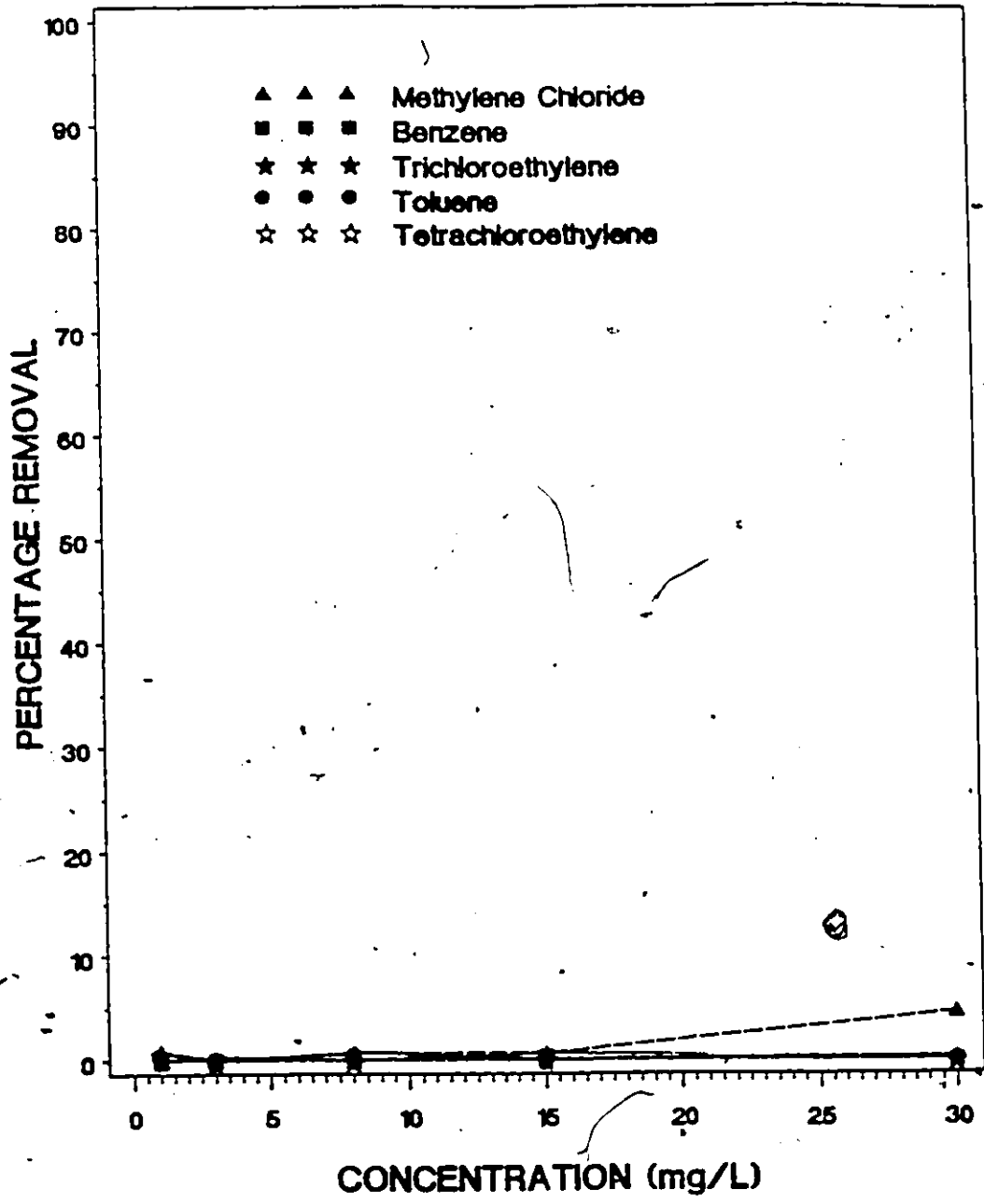
Figure 8. Percentage Removal of VOCs using Polymer CX-617
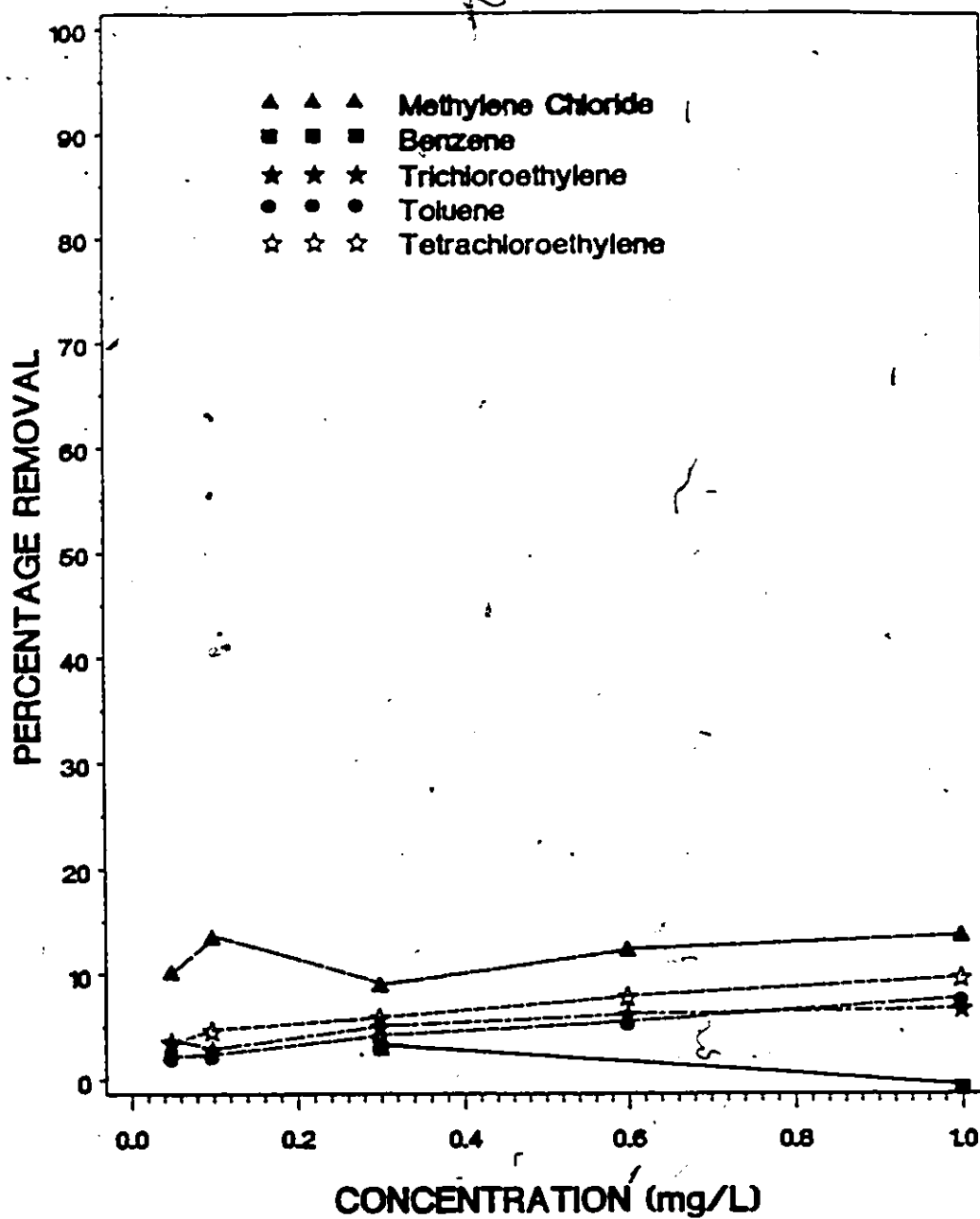
Figure 9. Percentage Removal of VOCs using Polymer 2790
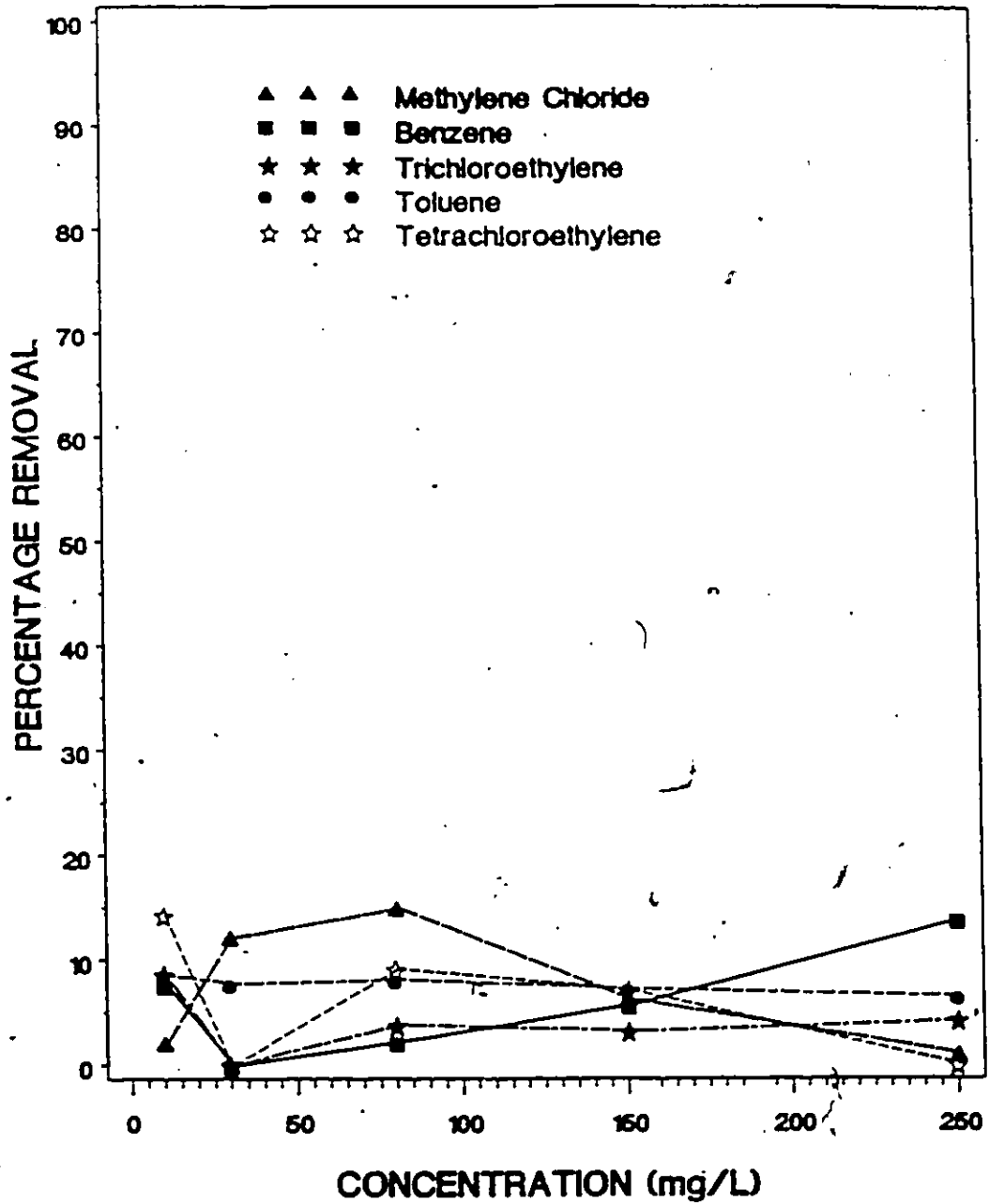
Figure 10. Percentage Removal of VOCs using Ferric Sulfate
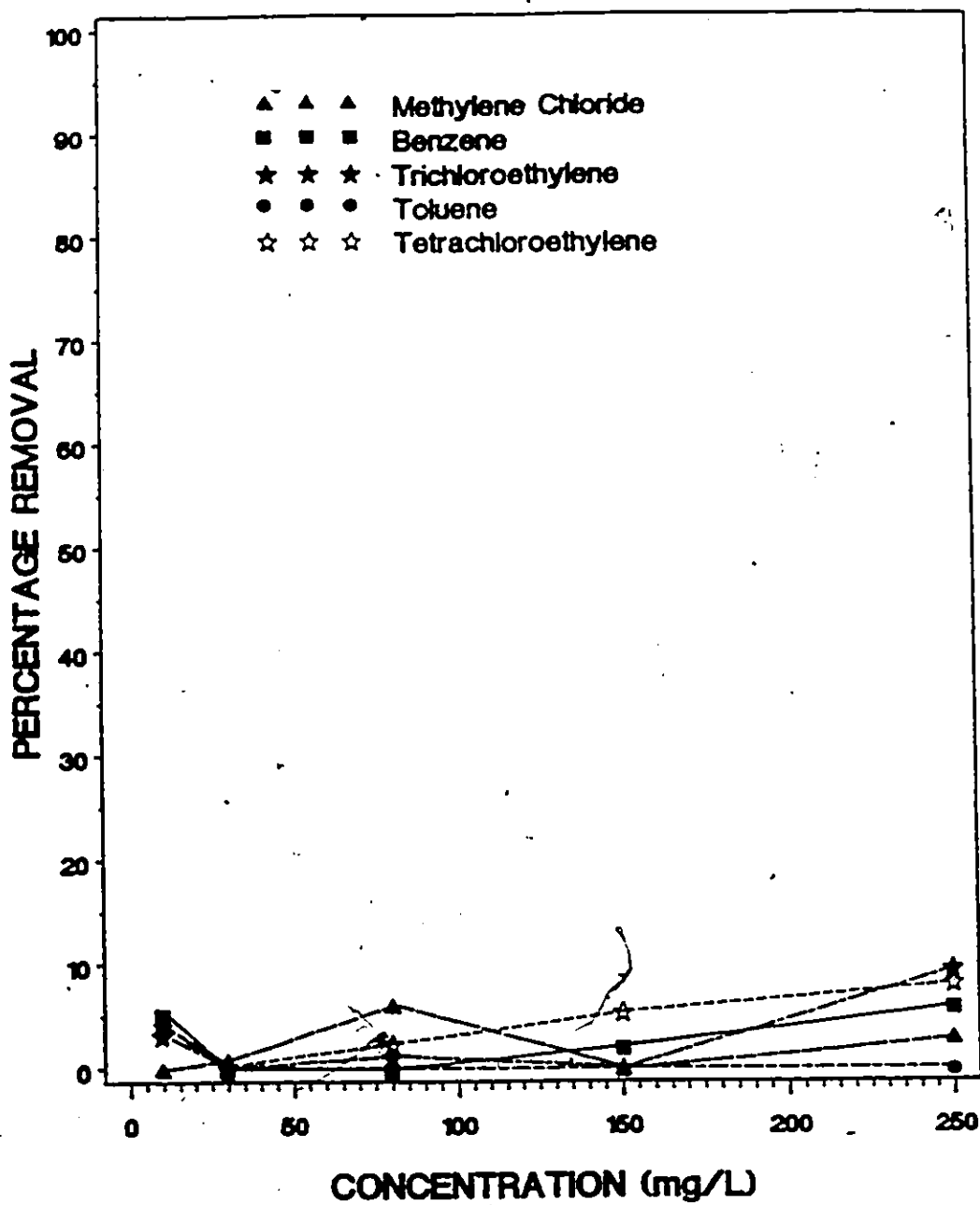
Figure 11. Percentage Removal of VOCs using Alum

the removal of benzene increased while the removal for other chemicals either slightly decreased or remained constant. In the case of alum, removal efficiencies behaved similar to what was observed by previous researchers (Semmens and Ayers 1985, Semmens and Field 1980, Hubel and Edzwald 1987). The VOCs removal was enhanced with increase in coagulant dosage. The optimum dosages of metal coagulants for suspended solids removal is usually between 20-40 mg/L.

4.1.1 Efficiency of the Coagulants

The percentage removals of each of the five organics by all seven coagulants are summarized in Table 11. The average removal of all the VOCs by each coagulant are also calculated in Table 11. The percentage removal values are at the coagulant dosage that gave optimum VOCs removal. The efficiency of polyelectrolytes and the two metal coagulants in removal of VOCs were generally very poor. The best VOCs removal was achieved with polymer 8103 among all seven coagulants and it was only 18 percent on an average for the five chemicals. The least effective was polymer CX-617, the long chained anionic polymer. It showed an effect on methylene chloride and none of the other chemicals was removed. In fact polymer CX-617 retained a certain portion of the four volatile organics thus allowing the blank to show better removals. The remaining three polymers as well as alum and ferric sulfate salts demonstrated results that ranged between those obtained for polymers 8103 and CX-617.

The average removals of each volatile organic by all

TABLE 11

Percentage Removal of the VOCs by each Coagulant

Coagulant	Dosage (mg/L)	Percent Removal					
		H_2Cl_2	C_6H_6	C_2HCl_3	C_7H_8	C_2Cl_4	Average for 5 VOCs
8103	40	18	5	26	19	22	18
603	40	10	13	7	5	12	9
7607	50	10	0	0	0	0	2
2790	1	14	0	8	10	11	11
CX-617	30	5	0	0	0	0	1
Alum	250	4	6	10	0	9	6
Ferric Sulfate	80	15	3	4	7	8	7
Average for Seven Coagulants		11	3	8	6	9	--

seven coagulants are also tabulated in Table 11. Methylene chloride was the most readily removed chemical. It was the only chemical that was partially removed by every coagulant. The average removal of methylene chloride by all the coagulants was only 11 percent. Trichloroethylene and tetrachloroethylene were reduced by 8 and 9 percent respectively. Toluene had an average of 6 percent removal. Finally, benzene which was the least removed was reduced by only 3 percent. Overall, any removal of the VOCs by any of the coagulants can be considered insignificant.

4.1.2 Polymer Charge

The search for any relationship between the charge on the polymer and VOCs removal was very limited in this study. Only the cationic polymers need be considered since they are capable of destabilizing particles most commonly found in the wastewater. The three cationic polymers used in this study had a range of cationic charges. The performance of these polymers indicated no influence of the charge on VOCs removal. This was expected since the total cationic charge required is a function of the net negative charge on the impurities in the wastewater. The charge then becomes a function of the the coagulant dosage. The influence of the polymer charge was considered mainly in terms of effects on the adsorption process. The results of this study showed that the cationic charge plays no role in VOCs removal.

4.1.3 Polymer Molecular Weights

The molecular weights of the cationic polymers

showed no relationship to the removal of volatile organics. All three cationic polymers had different molecular weights. Polymer 7607, with a molecular weight of 600,000 was not at all effective in removing any of the VOCs with the exception of methylene chloride. Polymer 603, which has a molecular weight of 30,000, performed slightly better. But the polymer that performed best was polymer 8103. This had a molecular weight of 100,000. Although no linear relationship can be made from this study, it is clear that cationic polymers with very high molecular weight are least effective in volatile organics removal.

Molecular weights usually plays a more important role with anionic and nonionic polymers. In this study both anionic polymers had very high molecular weights. Polymer 2790 had a molecular weight in excess of 10,000,000 while polymer CX-617 is considered to have an infinite molecular weight in water. No conclusion can be drawn regarding VOCs removal based on the molecular weights of these two anionic polymers.

4.2   Coagulants and Coagulant Aids

The next phase of the study was to observe the effectivness of coagulants and coagulant aids in combination to remove VOCs. This was required since none of the polymers or the metal salts showed any potential in removing VOCs when used alone. Based on the previous results, it was decided to use the metal salts as primary coagulants and the polymers as coagulant aids for the remaining tests. The or-

der of addition of cationic polymers and alum was not very critical since they both serve the same general purpose of particle destabilization. However, the reduction of pH by the metal coagulants prior to the addition of the polymers was assumed to enhance the polymer's efficiency. As for the anionic polymers, they usually perform better when they are added after particle destabilization.

The primary coagulant dosage was held constant for all the tests at 80 mg/L while the coagulant aid dosage was varied based on the results of phase one. These dosages were determined based on the optimum dosages obtained in the previous phase of this study. In addition, preliminary tests using 80 and 40 mg/L of alum as a primary coagulant along with polymer 2790 as a coagulant aid showed that an alum dosage of 80 mg/L was slightly better than 40 mg/L. Based on these results the primary coagulant dosage was fixed at 80 mg/L.

4.2.1 Alum plus Polymer

Table 12 summarizes the VOCs removal obtained using alum as the primary coagulant and the polymers as coagulant aids. It shows that when alum was used in conjunction with the polymers, VOCs removals were not affected significantly. The polymers enhanced the efficiency of alum but the average VOCs removal decreased from what was obtained with the two cationic polymers in phase one.

The use of the combination of coagulant and coagulant aid was expected to significantly improve the

TABLE 12

Percentage Removal of the VOCs Using Alum Plus Polymer

Coagulant Aid	Dosage (mg/L)	Percent Removal					
		H_2Cl_2	C_6H_6	C_2HCl_3	C_7H_8	C_2Cl_4	Average for 5 VOCs
8103	32	3	2	14	14	15	10
603	20	4	4	7	8	9	6
7607	45	3	6	9	9	9	7
2790	0.2	18	10	8	10	10	11
CX-617	30	17	3	11	10	7	10
Average for Five Polymers		9	5	10	10	10	--

removals but this was not the case. The efficiency of polymer 8103 fell from 18 percent when used alone to only 10 percent when used with alum. This was still greater removal than was obtained by alum alone. Methylene chloride removal decreased considerably. relative to its removal by polymer 8103 alone. Similarly, polymer 603 fell from an average removal of 9 percent to only 6 percent. This change may be small but the fact that VOCs removal had decreased instead of being increased is important. Toluene behaved oppositely to the other volatiles. With polymer 603 and alum, an 8 percent removal of toluene was observed. This is an increase from the 5 percent observed from the polymer alone and the zero percent from alum alone. The third cationic polymer, polymer 7607, which had no effect on four of the chemicals when used alone actually improved when used with alum. Even though four of the chemicals showed the same percentage removal as observed with alum alone, toluene experienced a 9 percent removal. Neither coagulant nor polymer had removed any amount of toluene when used alone. Overall, the use of polymers as coagulant aids along with alum slighlty enhanced the removal of VOCs. But in most cases the efficiency of the polymers as coagulant aids was much poorer than their efficiency when used as primary coagulants.

The anionic polymers also did not show much suscess in removing VOCs from wastewater when used as coagulant aids. Polymer 2790 helped alum to increase it's performance but the overall removal was still less than what was ob-

tained with the polymer alone. The second anionic polymer presented different results. The combination of the alum and polymer CX-617 was slightly better than either coagulant alone. Here again toluene was reduced by 10 percent. It was not effected by either coagulant during phase one of the study. Nevertheless, the removal of VOCs was insignificant by both combinations.

The reason for the poor results obtained by the addition of cationic polymers to alum can be explained. Since both coagulants carry a positive charge they were capable of destabilizing the colloids. This was evident from the formation of good flocs. This improves the chances of possible entrapment of volatile compounds within the flocs. The removal of VOCs becomes a function of polymer adsorption, formation of complexes with the coagulants, and floc entrapment. The adsorption of VOCs onto the polymer explains the enhancement of VOCs removal relative to the alum. Also, the decrease in floc formation due to overdosing with cationic charges decreases the VOCs removal experienced with the polymer alone. Thus, the use of polymers as primary coagulants produced excellent flocs which allowed VOCs removal by floc entrapment as well as adsorption.

The reasons for poor results obtained by the anionic polymers when used as coagulant aids are not as clear. In both cases, floc-formation was intensified. This possibly explains the performance of polymer CX-617. For polymer 2790, there are several possibilities that could be involved such as poor adsorption of the polymer or the development

of certain chemical reactions?

4.2.2   Ferric Sulfate plus Polymer

Ferric sulfate performed slightly better than alum as a primary coagulant to the polymers. The results of this portion of the study can seen in Table 13. Volatile organic removal increased for some polymers and decreased for others. The average removal of all VOCs using polymer 603 was 21 percent. This is greater than the removals obtained by the sum of both ferric sulfate and polymer 603 when used alone. As can be seen from Table 13, only the benzene removal did not improve. The average removal of benzene had decreased with polymer 8103. This polymer as a coagulant aid did not influence the removal of either toluene or tetrachloroethylene. Benzene was also poorly removed. Both polymers 8103 and 603 aided ferric sulfate in achieving approximately 30 percent removal of methylene chloride. Polymer 7607 in combination with ferric sulfate performed similar to its performance with alum. The VOCs removal virtually remained the same as obtained with ferric sulfate alone. Here again, the toluene which was not removed by either polymer 7607 or ferric sulfate, showed a 7 percent removal with the combined coagulants. The anionic polymers behaved the same with ferric sulfate as they did with alum.

The results of phase two were poorer than what were expected. As coagulant aids, the anionic polymers were expected to outperform the cationic polymers. However, the cationic polymers aided alum and ferric sulfate in removing

TABLE 13

Percentage Removal of the VOCs Using Ferric Sulfate Plus Polymer

Coagulant	Dosage (mg/L)	Percent Removal					
		H_2Cl_2	C_6H_6	C_2HCl_3	C_7H_8	C_2Cl_4	Average for 5 VOCs
8103	32	32	3	17	6	8	13
603	20	29	5	16	23	30	21
7607	25	24	7	4	7	5	5
2790	2	9	6	3	4	4	5
CX-617	30	12	4	8	10	9	9
Average for Five Polymers		17	5	10	10	11	--

more VOCs. It is possible that these anionic polymers were not representative of the coagulant aids required for these VOCs. Many more polymers, cationic and anionic should be studied in order to statistically evaluate their performance.

4.2.3   Effects of Cationic Charge

The possibility of the cationic charge influencing the removal of VOCs was again considered. Polymer 603 which has the highest positive charge performed best when used as a coagulant aid with ferric sulfate. The same polymer produced the worst results when added with alum. Polymer 8103 which carries a charge of 1.1 meg/gm outperformed polymer 7607 which has a charge of 3.1 meg/gm. When used as a coagulant aid, the polymer charge indicate no connection with VOCs removal.

4.2.4   Effects of Molecular Weights

By examining the performance of polymer 7607, when used both as a primary coagulant and a coagulant aid, a general trend can be established regarding molecular weights. Cationic polymers with very high molecular weights are not as effective in VOCs removal as the ones with relatively low molecular weights. A molecular weight of 600,000 for polymer 7607 is considered very high for a cationic polymer. It's performance was very poor in all three cases in which it was used. Polymer 603, which has the lowest molecular weight, achieved the best overall removal when

used with ferric sulfate. Polymer 8103 with a molecular weight of 100,000 gave a total VOCs removal in between those of polymers 603 and 7607. As coagulant aids for ferric sulfate the lower the molecular weight of the polymers the better was the VOCs removal. Therefore, it can be concluded from this study that the high molecular weight cationic polymers are not effective in VOCs removal. Again this conclusion is based only on the results of one long-chained polymer. Additional tests using a larger number of polymers are needed to prove if the results of this study reflect the behaviour of all high molecular weight cationic polymers.

4.3   Effects of Powdered Activated Carbon

Powdered activated carbon, PAC, was used as an adsorbing agent with the coagulant-combinations showing the most promising results. In this phase of the study, 500 mg/L of pretreated PAC was used in conjunction with ferric sulfate and polymer 603. This study was conducted on two different VOCs concentrations. The first set had the same VOCs concentrations of 1000 ug/L of each of the five organics as in phases one and two. The second set was spiked with only 100 ug/L of each of the VOCs. As expected the actual concentration of the five VOCs was greater than what was added initially by spiking because the wastewater already contained some VOCs.

4.3.1 High VOCs Content

By adding the PAC, the average VOCs removal in-

creased from 21 percent to 50 percent. Table 14 lists the new percentage removals obtained when the PAC was added. The benzene was the least removed by the ferric sulfate and polymer 603 combination. It still remained the least removed when the PAC was added. The removal of the other four volatiles almost doubled due to the addition of the PAC. This enhancement is no doubt due to the high adsorbing capacity of the activated carbon. However, 500 mg/L of PAC has a capacity to adsorb almost all the VOCs that were added to the wastewater provided sufficient time is allowed for equilibrium, which most likely is not the case in the jar tests.

4.3.2   Low VOCs Content

In this part of the study, all aspects of the test were kept the same as for the first test of phase three except that the wastewater was spiked with only 100 ug/L of VOCs. With a lower amount of VOCs in the wastewater, a greater percentage removal of VOCs was expected because the ratio of volatile organics to activated carbon was much less. The actual results of this part of the study, Table 15, are contrary to what was expected. The average removal of all five organics was only 35 percent. This was considerably lower than the 50 percent obtained when the VOCs contents were ten times higher.

4.3.3   Influence of Total Organic Carbons

There are several reasons that can be given to ex-

TABLE 14

Percentage Removal of the VOCs Using Ferric Sulfate,
Polymer 603 and PAC From Wastewater Spiked
With 1000 ug/L of the VOCs.

Volatile Organic	Percent Removal
Methylene Chloride	47
Benzene	40
Trichloroethylene	52
Toluene	56
Tetrachloroethylene	51
Average	50

TABLE 15

Percentage Removal of the VOCs Using Ferric Sulfate,
Polymer 603 and PAC From Wastewater Spiked
With 100 ug/L of the VOCs

Volatile Organic	Percent Removal
Methylene Chloride	37
Benzene	31
Trichloroethylene	19
Toluene	39
Tetrachloroethylene	49
Average	35

plain the results of the first two experiments of phase three. First, the raw water quality could have played an important role in the removal process. Any VOCs initially present in the wastewater would have had a much greater impact on the concentrations of the lesser spiked wastewater. Although the blank should compensate for any chemicals already present, becouse the VOCs removal is reported relative to the blank, still the impact on the lower spiked solution will be much greater. This perhaps explains the larger drop in trichloroethylene removal which experienced a 52 percent removal in the first experiment and only 19 percent in the second. The other four chemicals showed lesser change. Another explanation for the reduction in the VOCs removal could be the interference of other organic material in the wastewater. Activated carbon has long been used for removing colour and odour from the wastewater which is caused mostly by the organic matter. Since the VOCs represent only a small percentage of the total organic carbon ,TOC, the VOCs contents of both spiked solutions were virtually insignificant in competing for adsorption sites on the activated carbon.

4.3.4   Behaviour with Other Polymers

Before moving to the next phase of this study, the results of the initial experiments in phase three needed to be verified. The experiments were repeated with polymer 603 and the results were very similar. Greater percentage removal of VOCs was achieved from the wastewater with the

higher VOCs content. The next step was to repeat the experiments with polymer 8103. Again two more experiments were conducted. This time polymer 603 was replaced with polymer 8103, and all other aspects of the experiment were kept the same. The results of this part of the study are summarized in Table 16. It is clearly seen that this phenomenon is not only a function of a polymer but also of a physical aspect of the coagulation process. Polymer 8103, in conjunction with ferric sulfate and PAC, produced results similar to those obtained with polymer 603. The removal of trichloroethylene was most affected and methylene chloride was the only substance that bucked the trend. A greater percentage removal was observed for methylene chloride in the solution of lower concentration. But the overall removal for the higher spiked solution was 47 percent compared with 42 percent for the lower spiked solution.

4.3.5 VOCs Removal from Deionized Water

At this point it has become clear that the smaller the VOCs content in the wastewater the lower the percentage removal can be expected during coagulation processess. This may not be true with concentrations largely different from what were used in this study. The next step in this study was to confirm the explanation given earlier that other organic materials present in the wastewater were competing for adsorption sites on the activated carbon. It was decided to run the same coagulant combination on deionized water spiked with the two sets of concentrations. The same rapid mix

TABLE 16

Percentage Removal of the VOCs Using Ferric Sulfate,
Polymer 8103 and PAC From Wastewater Spiked
With 1000 and 100 ug/L of the VOCs.

Volatile Organic	Percent Removal	
	With High VOCs	With Low VOCs
Methylene Chloride	32	45
Benzene	40	39
Trichloroethylene	52	27
Toluene	55	50
Tetrachloroethylene	54	49
Average	47	42

time, flocculation time and sedimentation time were used. This test·acted as a datum representing the adsorption capacity of the coagulants in adsorbing VOCs for the particular operating conditions used throughout this study.

The results of these two additional experiments are listed in Table 17. The average percentile removal of the VOCs was 62 percent for the lower spiked sample and was only 44.percent for the higher spiked sample. This is opposite to the results obtained when using the wastewater. Another observation that can be made from Table 17 is that the average removal of 44 percent for the higher spiked solution was less than the 50 percent obtained from the wastewater. Toluene and tetrachloroethylene were removed approximately by the same amount; but the other chemicals were removed better in the presence of other organic matter.

4.3.6 Process of Coagulation

4.3.6.1 Carbon Adsorption

The results of all the above tests can be explained partly by the process of carbon adsorption. As discussed earlier, the presence of other organic matter in the wastewater greatly affects the carbon's adsorption capacity. In the deionized water, the only organic matter present was the VOCs added. Therefore, one beaker of the deionized water contained a total mass of 5000 ug of organic material and the second beaker contained only 500 ug. When the PAC was added, the organic molecules began to adsorb onto the carbon. After a specific period, the mass adsorbed in the

TABLE 17

Percentage Removal of the VOCs Using Ferric Sulfate,
Polymer 603 and PAC From Deionized Water Spiked
With 1000 and 100 ug/L of the VOCs.

Volatile Organic	Percent Removal	
	With High VOCs	With Low VOCs
Methylene Chloride	39	--
Benzene	25	47
Trichloroethylene	45	49
Toluene	58	75
Tetrachloroethylene	63	78
Average	44	62

first beaker was greater than that in the second beaker. The percentage removal, however, was not proportionally greater. The activated carbon is capable of adsorbing all the organic molecules in either beaker if enough time is provided to reach equilibrium. As time passes more and more organics become adsorbed thus leaving less adsorption sites available. In the case with only 500 ug/L of organics open sites are easier to find. For this reason a larger percentage of VOCs were removed from the second beaker during the same period in the deionized water tests.

. In the experiments with the wastewater, the opposite behaviour can be explained by the same analogy. Since the VOCs content in the wastewater represents a small percentage of the TOC, the TOC in both cases can be assumed equal. When the PAC is added the massive bulk of organic particles will quickly fill the adsorption sites available on the PAC. In the beaker with the higher VOCs, more of these trace organics are able to compete for adsorption sites. In this case, time is a more important factor since the mass of the PAC is not large enough to adsorb all the organic material. This phenomenon could partially cause greater percentage removal in the beaker with the higher content of VOCs.

4.3.6.2   Role of Coagulation

Another reason for greater removals from the solution with the larger VOCs mass in the wastewater is the better performance of the coagulation process. It has been suggested by a number of researchers that some trace or-

ganics are removed by floc entrapment. The higher the VOCs content in the solution, the greater is the chance for adsorption on other suspended material and entrapment within the flocs formed. These parameters seem to overcome the loss in the carbons adsorption power to the other organics when the VOCs content is high.

4.3.7 Filtered Wastewater

In order to verify the explanation given above, one additional set of experiments was conducted. The wastewater was filtered in order to remove all the suspended solids which play an important role in floc formation. Once again all other aspect of the experiment were held constant. The ferric sulfate, polymer 603 and the PAC were added in the same manner. The results of this final set of experiments can be seen in Table 18. An average removal of 46 percent for the 1000 ug/L solution and a 52 percent removal for the 100 ug/L solution were observed. These results fall in between the results obtained with the wastewater and the deionized water. This is what was expected with the wastewater in which most of the suspended matter and the organic particles were removed by filtration. The little amount that passed through the filter managed to form some flocs and aided in the removal of some VOCs. On the other hand the decrease in the TOC allowed more VOCs to be adsorbed onto the activated carbon. The combination of these two effects gave the results reported in Table 18. These results confirm the explanations given for the behaviour of

TABLE 18

Percentage Removal of the VOCs Using Ferric Sulfate,
Polymer   603 and PAC From Filtered Wastewater
Spiked With 1000 and 100 ug/L of the VOCs.

Volatile Organic	Percent Removal	
	With High VOCs	With Low VOCs
Methylene Chloride	36	--
Benzene	34	46
Trichloroethylene	50	50
Toluene	53	54
Tetrachloroethylene	57	56
Average	46	52

VOCs removal.

4.4 Relation of Conventional Parameters

The discussion of the overall performance of the
coagulation process in VOCs removal cannot be complete
without considering their relationship to the behaviour in
terms of the conventional parameters. As mentioned earlier,
most primary clarifiers are operated on the basis of optimum
removal of suspended solids. Also, alkalinity, BOD, phos-
phorous and heavy metals play an important role in coagula-
tion and flocculation basins and therefore must be con-
sidered.

4.4.1 Effects of Single Coagulants

In the removal of suspended solids and BOD, all five
polymers and the two metal salts performed as expected. The
cationic polymers showed definite improvements in removing
these pollutants relative to the blank.   The metal
coagulants performed very similar to their traditional ex-
pectations.   Although the anionic polymers were slightly
better than the blank, they still functioned similar to most
-anionic polymers.

The percentage removals of suspended solids and BOD
and the change in alkalinity with polymers 8103, 603 and
7607 are shown in Figures 12, 13 and 14 respectively. All
three cationic polymers performed very well in reducing
suspended solids and BOD. This is because these polymers
are capable of particle destabilization which, in turn
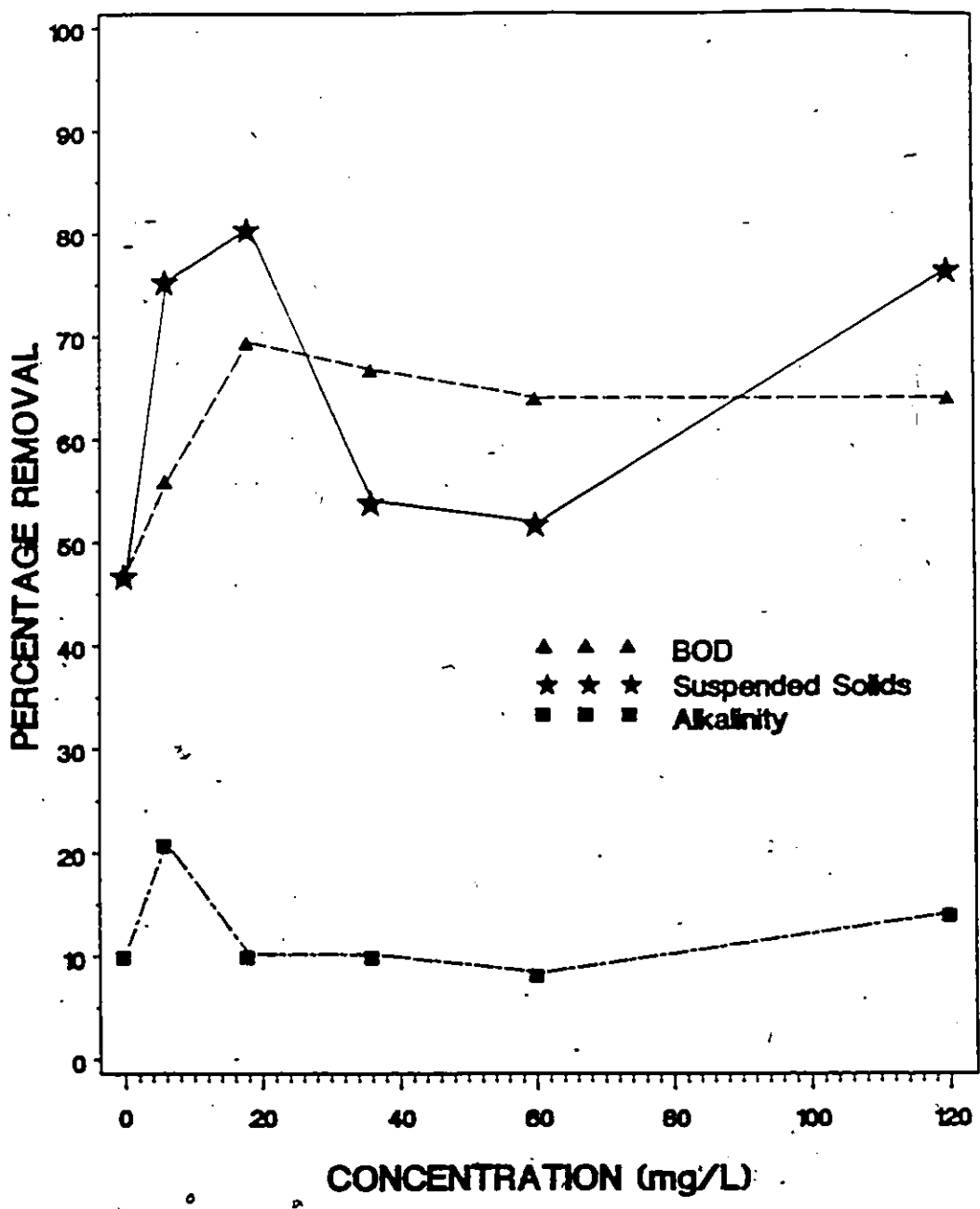
Figure 12. Removal Efficiency of Conventional Parameters
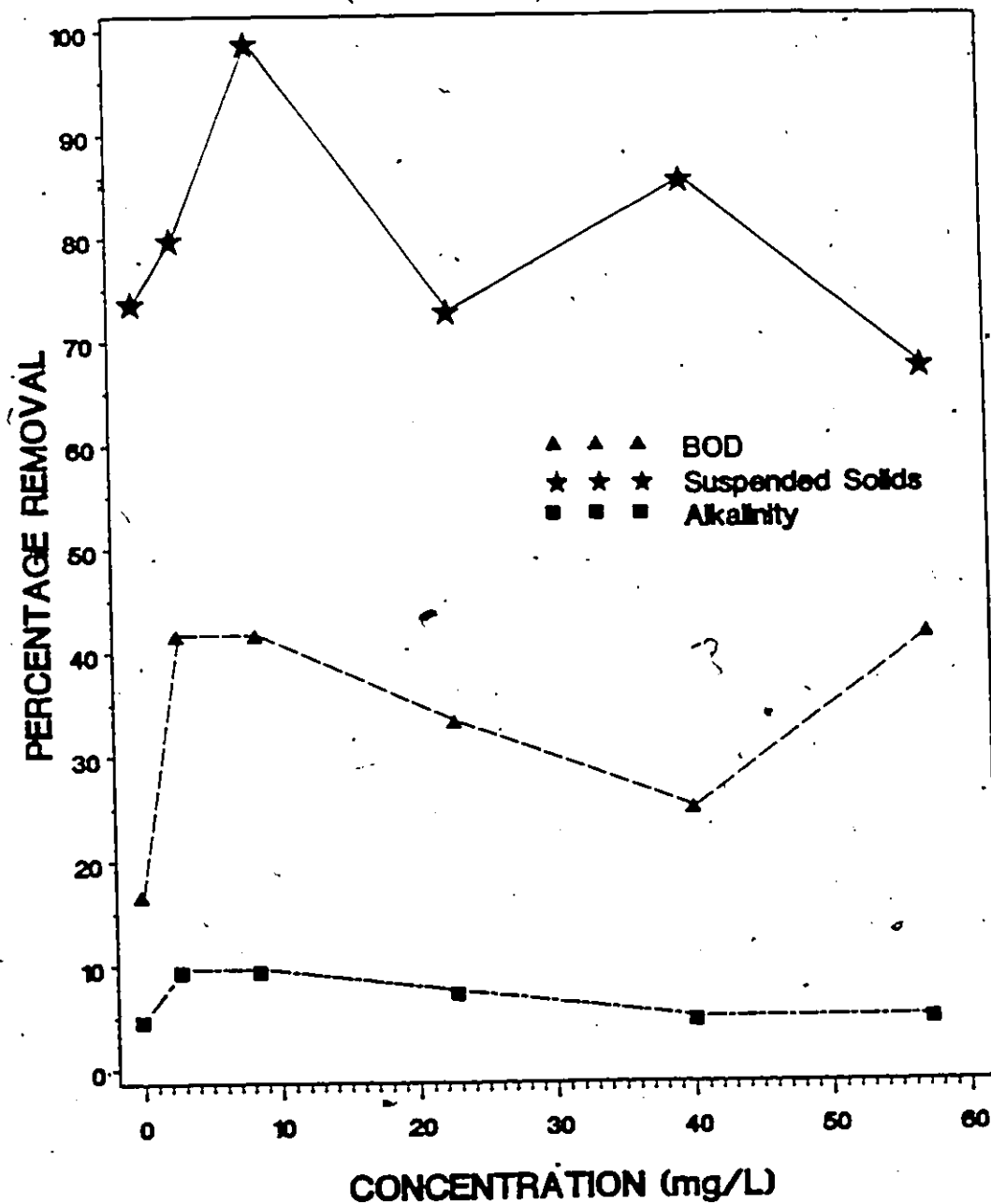Using Polymer 8103

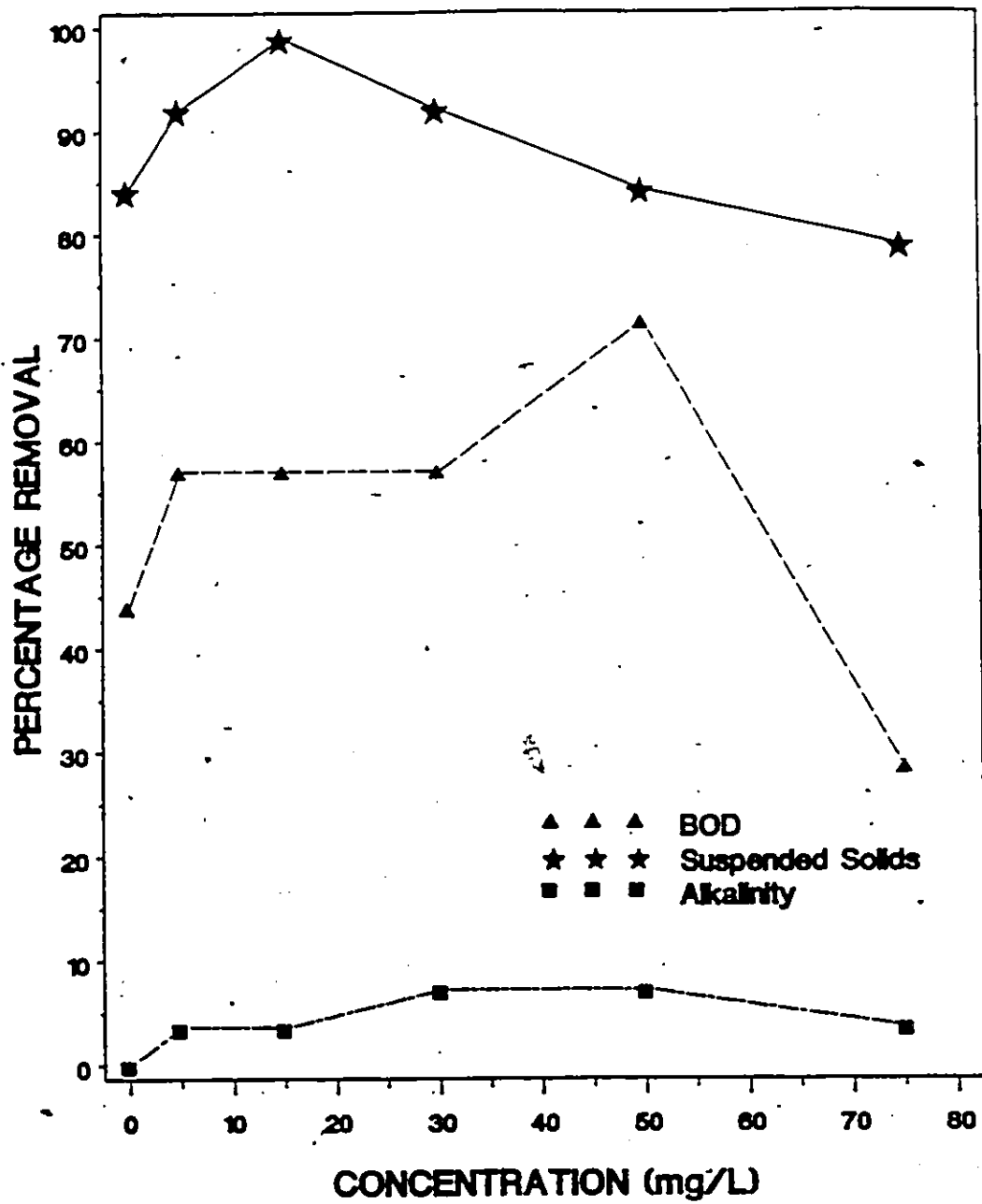Figure 13. Removal Efficiency of Conventional Parameters Using Polymer 603

Figure 14. Removal Efficiency of Conventional Parameters
Using Polymer 7607

results in improved floc formation. The negligible effect on alkalinity by all three polymers is no surprise. Most polymers are not capable of chemically reacting with alkalinity in the wastewater. Thus any decrease in alkalinity can be attributed to adsorption or floc entrapment. An important observation made from Figures 12 to 14 is the coagulant dosages required for optimum removal of BOD and suspended solids. In all three cases much lower dosages are required for these conventional parameters than those observed for optimum VOCs removal.

The two anionic polymers did not respond to the removal of the conventional parameters in similar fashions. Polymer 2790 was not any more effective than the blank in removing either BOD or suspended solids. This can be seen from a plot of percentage removal versus polymer dosage in Figure 15. The of BOD and suspended solids removal efficiencies by polymer CX-617 were much better than those of the other anionic polymer. As shown in Figure 16, the removal of all three parameters at an optimum dosage of approximately 3 mg/L are better than what was observed for the blank. Even the alkalinity was reduced by 20 percent at that dosage. This behavior of polymer CX-617 can be attributed to the massive length of the polymer itself. Colloids can become trapped within the polymer and get removed. This is possible since polymer CX-617 had produce some flocs.

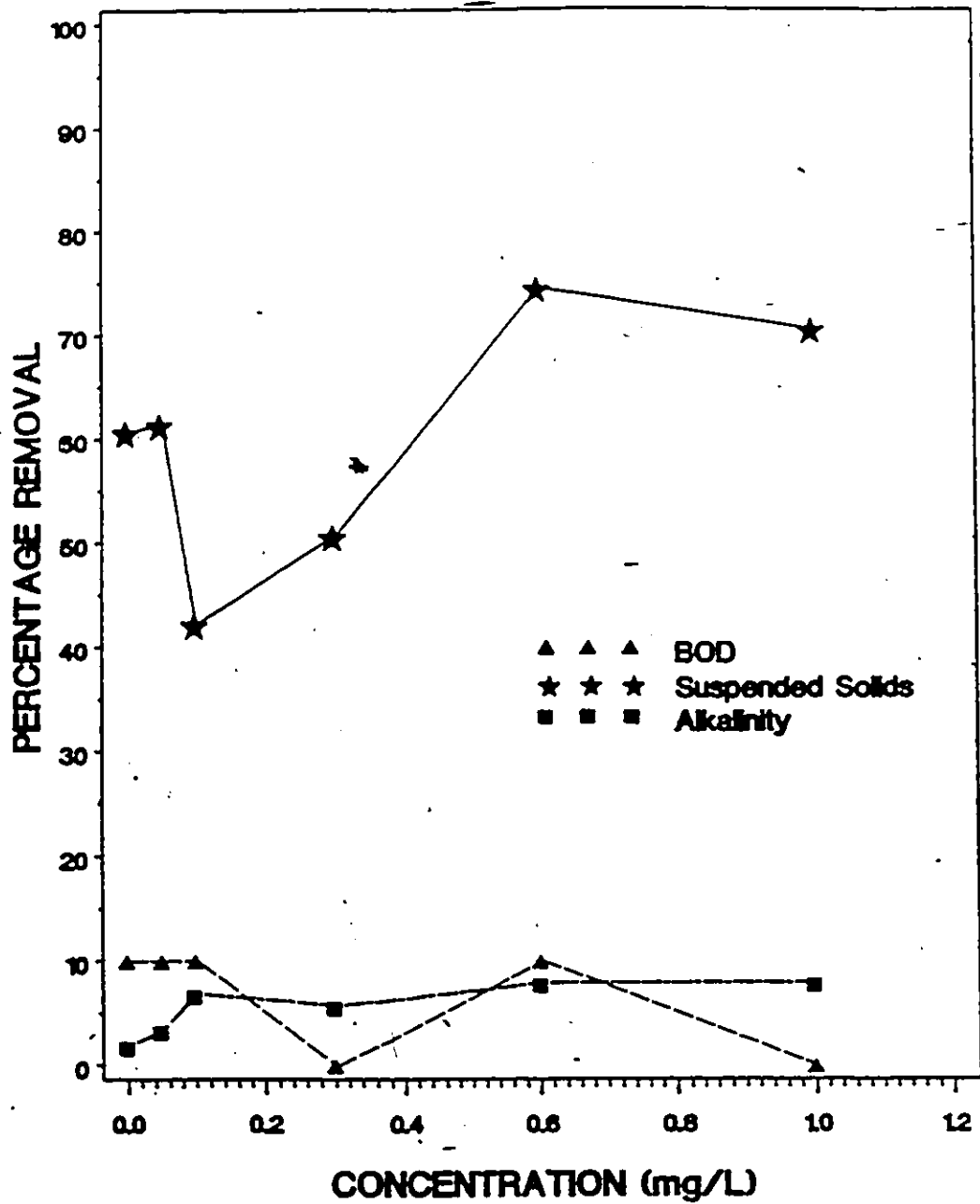The results of the two metal coagulants were typical of there historical performance in treating conventional

Figure 15. Removal Efficiency of Conventional Parameters
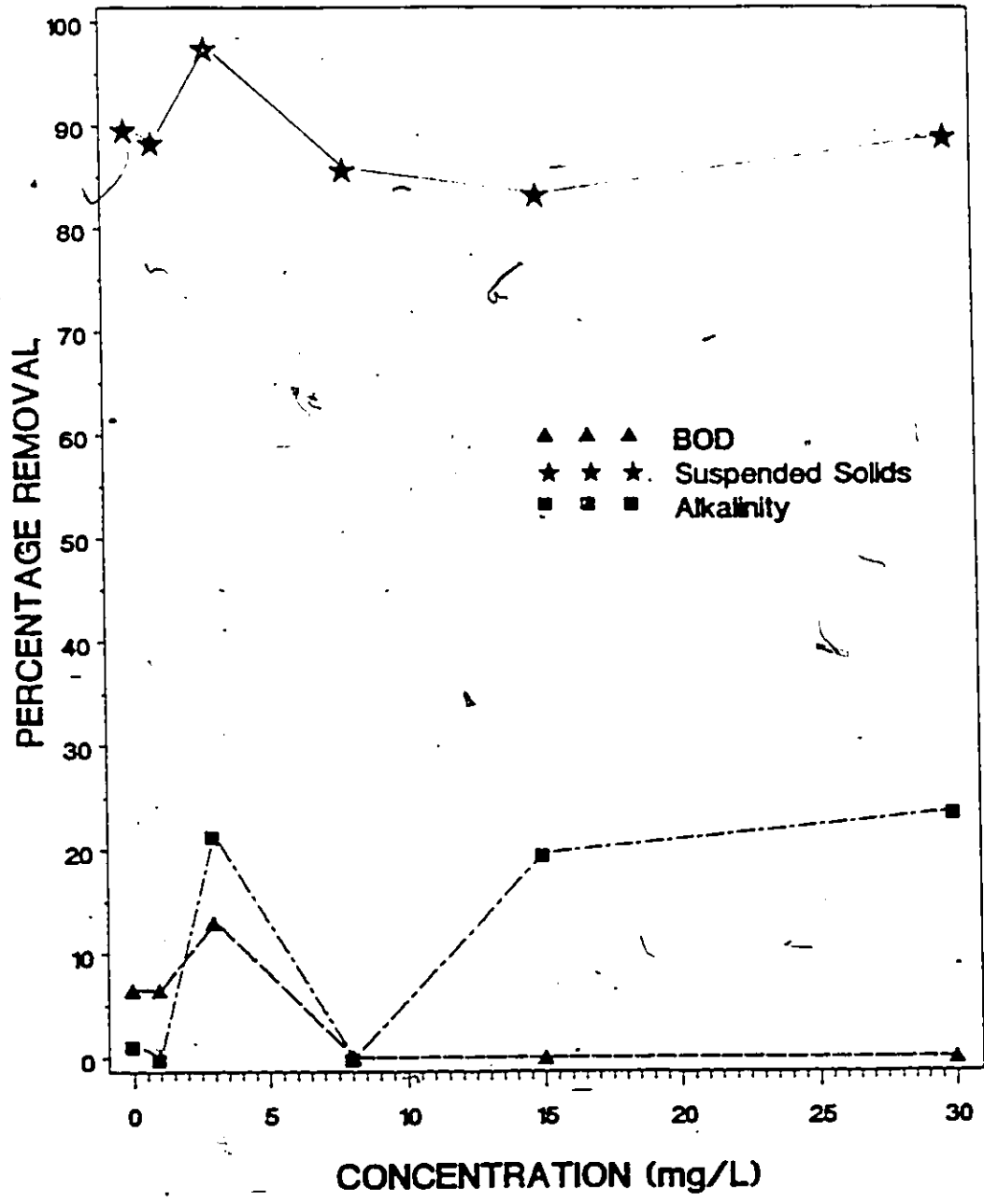Using Polymer 2790

Figure 16. Removal Efficiency of Conventional Parameters Using Polymer CX-617

-pollutants. The plots of removal efficiency for alum and ferric sulfate can be seen in Figures 17 and 18 respectively. Both coagulants greatly improved the removal of BOD and suspended solids. The change in alkalinity is also noticeable. This is because alum and ferric sulfate chemically react with alkalinity causing substances to form precipitates which settle out of the solution. Again, as observed with the cationic polymers, the optimum dosage required for the removal of conventional parameters is much less than that required for removal of VOCs.

4.4.2   Coagulant Aids

In all the jar tests of phases two and three, removals of all the conventional parameters were high. The percentage removals for these parameters can be seen in Table 19 for alum plus coagulant aids and in Table 20 for ferric sulfate plus coagulant aids. It should be noted that these percentage removals are at the polymer dosages giving maximum VOCs removal. The final pH values after tratment are also included in Tables 19 and 20. The pH of the raw wastewater varied from 6.9 to 7.8. The reduction in pH in the treated water is attributed to the addition of the metal salts, alum and ferric sulfate. Of all five polymers, only polymer CX-617 decreased the pH. For polymer 603, when combined with ferric sulfate and PAC, the removal of phosphorous and five heavy metals were analyzed. The results of these tests can be seen in Table 21. With ferric sulfate and polymer 603, 45 percent of the phosphorous was removed. When the activated carbon was added the phosphorous removal
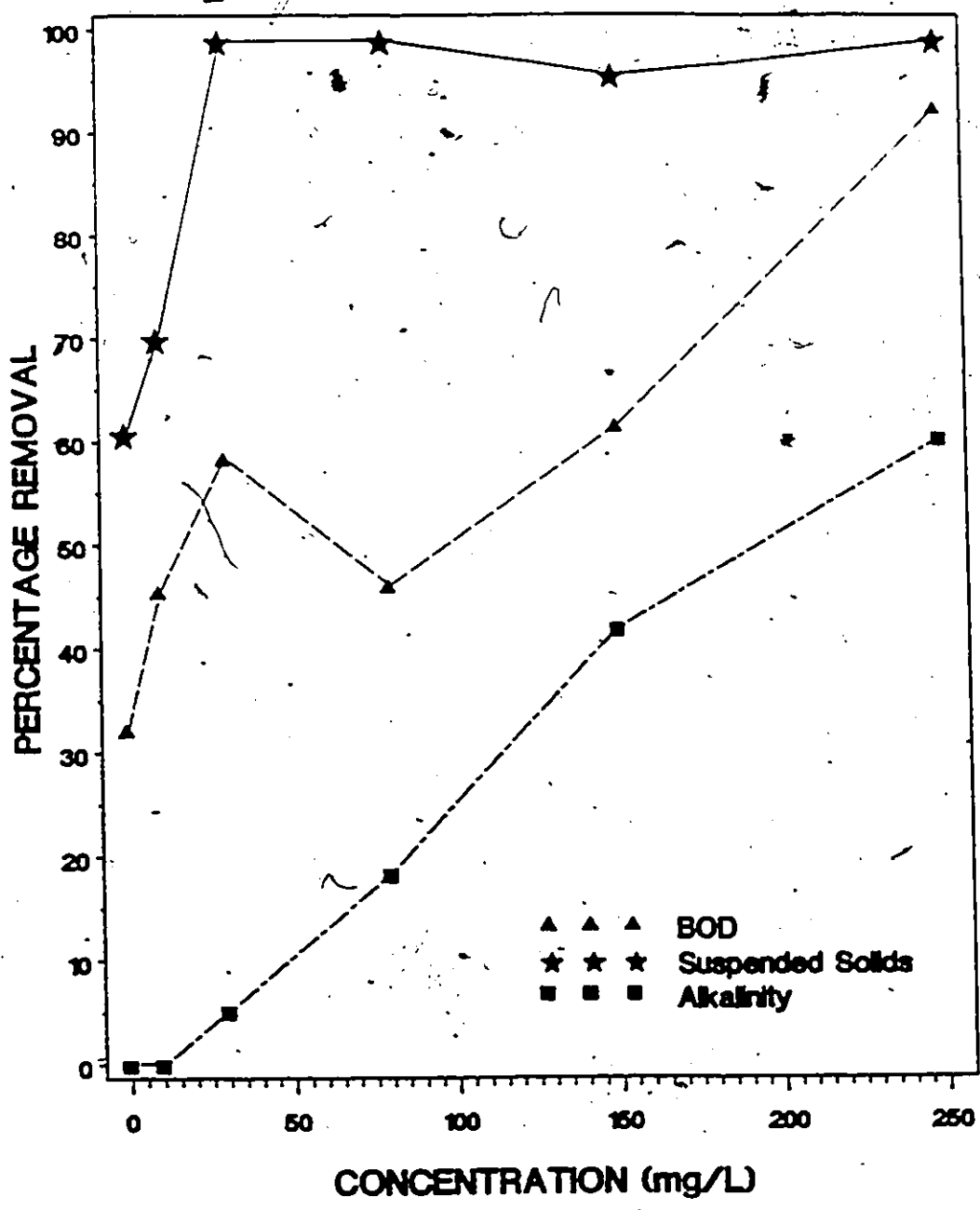
Figure 17. Removal Efficiency of Conventional Parameters Using Alum
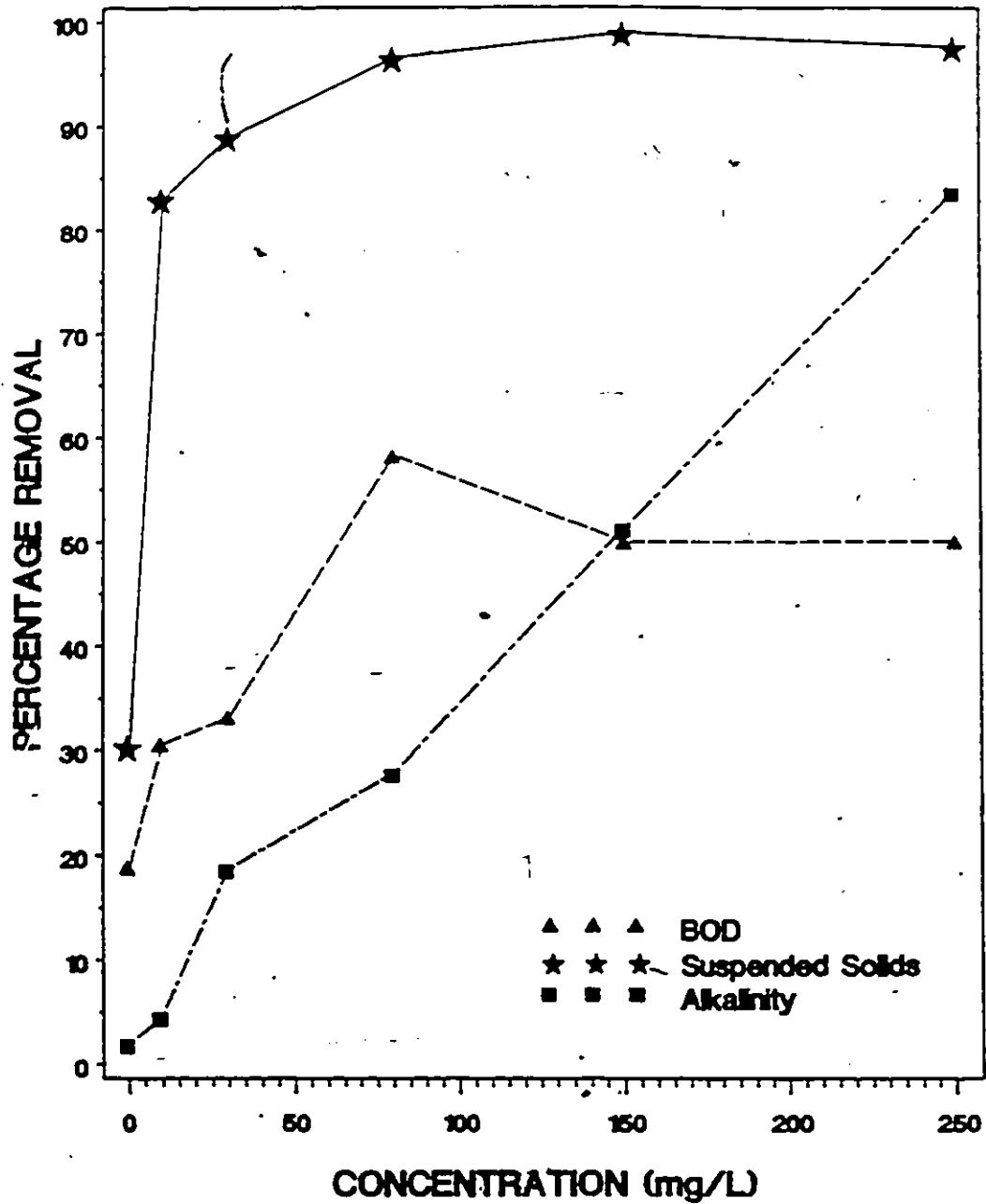
**Figure 18. Removal Efficiency of Conventional Parameters
Using Ferric Sulfate**

TABLE 19

Percentage Removal of the Conventional Parameters
Using Alum plus polymers.

Coagulant	Dosage (mg/L)	Percent Removal		Alkalinity Reduction (%)	Final pH
		BOD	Suspended Solids		
8103	32	86	99	26	7.2
603	20	80	99	19	7.3
7607	25	81	99	21	7.2
2790	2	--	99	21	7.0
CX-617	30	--	99	32	6.9

Alum Dosage = 80 mg/L

TABLE 20

Percentage Removal of the Conventional Parameters
Using Ferric Sulfate plus Polymers.

Coagulant	Dosage (mg/L)	Percent Removal		Alkalinity Reduction (%)	Final pH
		BOD	Suspended Solids		
8103	32	81	93	28	6.7
603	20	80	86	30	6.7
7607	25	85	99	30	7.2
2790	2	88	97	33	7.2
CX-617	30	73	99	32	7.2

Ferric Sulfate Dosage = 80 mg/L

TABLE 21

Percentage Removal of the Heavy Metals and Phosphorous Using Ferric Sulfate plus Polymers 603, With and Without PAC

	Percent Removal						
	Heavy Metals						Phosphorous
Coagulants	Ni	Cd	Zn	Pb	Cu	Average	
Ferric Sulfate & Polymer 603	0	94	38	61	78	54	45
Ferric Sulfate & Polymer 603 & PAC	35	99	0	75	97	61	49

Ferric Sulfate Dosage = 80 mg/L
Polymer 603 Dosage = 20 mg/L

increased to 49 percent. Also, the PAC slightly increased the removal of the heavy metals, cadmium, lead and copper. Nickel, which was not removed by ferric sulfate and polymer 603, showed a reduction of 35 percent when the PAC was added. On the other hand, zinc which showed 38 percent removal with the two coagulants, was not removed at all when the PAC was added. There could be some analysis error since the metal concentrations were very low. Nevertheless, the removal of all the pollutants considered in this study was good at the coagulant dosages providing optimum VOCs removal.

From the results of this study the overall performance of the coagulation process can be summarized. The application of the coagulants for optimum removal of conventional contaminants generally gave poor removal of the VOCs. However, the coagulant dosage giving maximum VOCs removal showed good removal of the raditional parameters.

V.   CONCLUSIONS AND RECOMMENDATIONS

5.1   Conclusions

Based on this study the following conclusions can be drawn regarding the removal of volatile organic compounds during the coagulation process:

1. The coagulation/flocculation process was not effective in removing VOCs from wastewater.

2. All coagulants, cationic and anionic polymers and alum and ferric sulfate, were generally poor in VOCs removal when used individually. Using the polymers as coagulant aids along with alum and ferric sulfate did not improve the performance. Coagulant dosages higher than those used conventionally were required for maximum VOCs removal.

3. The higher the molecular weight of the cationic polymers, the less effective they were in removing VOCs when used both as primary coagulants and coagulant aids.

4. The addition of powdered activated carbon increased the overall removal of VOCs. However, the enhancement in removal was limited to approximately half the original VOCs concentrations due to limited carbon contact time. The removal of the volatile organics can be attributed largely to carbon adsorption and

also partly to floc entrapment. The total amount of organic matter ,TOC, in the wastewater greatly effects the efficiency of the activated carbon.

5. Volatile organic compounds did not behave similar to the other organic matter in wastewater treatment.

5.2   Recommendations

The results of this study indicate the need for more research in this increasingly important field. The following studies are suggested for future work:

1. Future studies should be conducted with laboratory simulated wastewater of known characteristics. The quality of the wastewater used in this study varied considerably from test to test. This had played a major role in this study since the organic matter in the wastewater effects VOCs removal.

2. The relationship between molecular weights of the cationic polymers and the removal of VOCs should be examined closely.

3. Pilot scale studies should be conducted on the effects of powdered activated carbon in the coagulation process. The physical aspects of mixing and dispersion of the PAC should be examined.

4. Future studies regarding the removal of trace organics must be conducted and evaluated based on specific chemicals and not on the total organic matter such as TOC. Trace organics are only a small fraction of the TOC and their behavior in wastewater

treatment is incongruent.

5. Future studies should include material balance between the VOCs before treatment and VOCs removed by volatilization in the sludge to verify the results of this study.

6. The effects on the solubility, vapor pressure and other properties of VOCs in wastewater with the deferent coagulants should be examined. Changes in these properties could influence the calibration curves of the VOCs which were performed using deionized water.

APPENDIX A

Percentage Removal of VOCs from the Blanks

Percentage Removal of VOCs from the Blanks

Coagulant	Percent Removal				
	H_2Cl_2	C_6H_6	C_2HCl_3	C_7H_8	C^2Cl^4
8103	7.5	6.2	6.6	4.1	6.2
603	4.4	5.3	16.1	8.5	16.2
7607	5.1	---	---	---	---
2790	6.3	26.6	12.0	7.6	11.2
CX-617	10.4	8.5	24.2	---	---
Alum	---	4.5	7.1	9.6	6.2
Ferric Sulfate	16.6	6.5	15.9	6.7	10.2
Alum & 8103	---	8.3	12.5	11.0	11.1
Alum & 603	12.6	11.6	10.8	10.1	12.1
Alum & 7607	11.1	8.3	11.3	9.3	9.6
Alum & 2790	18.1	12.4	15.8	13.1	13.1
Alum & CX-617	11.8	7.9	11.1	9.7	13.3
Ferric Sulfate & 8103	5.4	2.3	3.8	3.3	1.4
Ferric Sulfate & 603	8.3	---	7.6	5.7	3.4
Ferric Sulfate & 7607	22.5	17.7	13.5	16.3	15.5
Ferric Sulfate & 2790	13.8	7.4	9.1	7.0	6.7
Ferric Sulfate & CX-617	---	14.0	13.9	14.8	14.3

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