University Of Jordan
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INVESTIGATION OF THM'S RESIDUE IN WASTEWATER
AND
THE STUDY OF SELECTED REMOVAL TECHNIQUES

BY

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THESIS

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DEDICATION

TO WHOM I LOVE TO MY FAMILY
AND
* TO MY DEAR LOVELY ANGELS ZEINA AND NOUR *

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I would like to thank every one who helped me doing this study, mainly My two professors Dr. Kamel Qaisi And Dr. Raja Gedeon . Special thanks goes for professor Dr. Abdulah Shanableh For his Brotherly Support . Not forgetting to thank Miss Randa Tuffaha and Mr Ziyad for ther great help.

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ABSTRACT

Trihalomethanes can be formed as a result of a chemical reaction between the organic matter present in the water and chlorine added for disinfection purposes . Trihalomethanes compounds were found in treated water effluent of Abunusier treatment plant and albaqa treatment plant . Chloroform was the predominant compound . Chloroform concentration was found to be more that 95 % of the total trihalomethanes (TTHM). Because of this reason chloroform was considered as trihalomethane indicator .

Certain removal processes were tried to achieve chloroform removal . Air stripping , (surface and diffused) , and adsorption (using Antracite Coal , Activated carbon and Jordanian zeolite) . Two different sizes were studied of each adsorber . The adsorption was tested under three different pH value for each type and size . Air stripping gave an excellent removal percent in both (mechanical and surface) which was near (98 %) . Most of the removal occurred within the first 10 minutes . Antracite , although it is considered to be a filter media , showed an excellent removal efficiency (powdered size 97.5 %) while a good removal efficiency was achieved in the granular size (pH3 67 %) . Both sizes of Activated carbon showed an excellent removal efficiency and with all pH values (98 %) removal percent was accomplished . On the other hand Jordanian Zeolite failed

to accomplish any removal percent what so ever , (zero % removal) . This was the results for the two sizes (granular and powdered) and with the three deferent pH values (3 8 11) . Only batch reactor was used , because of the high volatility of trihalomethanes (mainly chloroform) .

CHAPTER ONE

INTRODUCTION

1.1 General

When people started using surface water for their domestic purposes , they needed a certain procedure to disinfect the water supply . Chlorination was the conventional method of water treatment and easiest procedure for disinfection . It was used in both water and waste water treatment plants , since chlorine is a strong oxidizing agent and cost effective .

Chlorination was used without having the slightest doubt whether this treatment process is unsafe under any prevailing conditions . Because of that it is used at certain stage in the water treatment plants for the sake of disinfection . Engineers start using it , having in mind , that they are producing safe water , without realizing , in certain cases , the possible adverse impacts upon the human health in the long term . It was found that the chlorination process, under certain conditions , will react with certain organic precursors in the water leading to the formation of what is called [halogenated hydro - carbons] , mainly Trihalomethanes (T H M) . Among the main adverse effects of the Trihalomethanes according to the US EPA (Environmental Protection Agency) is that the chloroform (one of the THM's components) is a potential carcinogen when tested on rats and mice (1)(2).

The THM 's were recently discovered since the detection of the THM compounds are not possible without using highly sophisticated instruments such as the gas chromatography meter , with an electron capture detectors (E C D) . No other direct and reproducible procedure is available as yet , for the detection of the THM's.

It is very essential from environmental perspective to study the Trihalomethanes residue in water since its carcinogenicity is considered a matter of concern to human environment . In general chlorinated organics have the same effect but THM demonstrated higher toxicity (2) . It is expected to have a high concentration of THM in the chlorinated surface water , since surface water in general contains adequate amounts of organic material . The chlorinated wastewater from treatment plants is also expected to produce high THM concentration in the effluent (2) . However it is not expected to have THM in chlorinated ground water supplies unless it was contaminated with source of pollution such as sanitary landfills and other non-point sources of organic pollution.

In recent years the environmental effects have shown ever - increasing concern of chlorinated hydrocarbons largely , due to the extensive use of organic compounds in the production of pesticides such as DDT and chemicals used as solvents and as an intermediate stage in chemical industry . Many experiments (3) showed that most of these compounds have a fatal effect upon insects, but at the same time it proved to be harmful for humans too , and could eventually cause major health diseases . Many of these compounds are considered carcinogenic . These compounds are relatively stable and persistent , and need long period of time to dissociate . Many studies were carried out to find out the dissipate potential environmental impact of chlorinated hydrocarbons that are manufactured on a large scale . The following factors were taken into consideration in most of these studies(3) :-

1- What quantities of these compounds are produced , how they are produced , where , and in what form these materials are released into the environment .

2- How they are distributed , and in what concentrations they occur in the atmosphere , in fresh and marine waters , and in soil sediments .

3- At what level , or concentrations they are considered to be toxic to human body or other environment elements .

4- Where do these compounds ends , do they accumulate in living organisms , do they become concentrated in our food chains .

5- how stable these compounds are , and what is the degree of degradation of these compounds , and whether any of these products of degradation considered to be toxic or not .

Studying all of these factors , is considered to be almost impossible because these is a great number of chlorinated hydrocarbons , and the formation mechanisms of these compounds is not clear . And these compounds need long periods of time to dissociate too .

1.2 Emission and distribution pathways

The world production capacities for all major chlorinated hydrocarbons are shown in table (1.1) below , the florochloromethanes are extensively used as aerosol propellants , and are therefore almost completely lost to the atmosphere after use . Other chlorinated hydrocarbons are employed principally as solvents in industrial or domestic applications (3).

Table (1.1)

Estimated world production capacities (1973)
of major chlorinated hydrocarbons 10E3 tons /year

COMPOUND	ESTIMATED WORLD PRODUCTION
trichloroethylene	1010
Perchloroethlyene	1050
mono,die,trichloroeth	480
Methylene cholride	400
trichlorofluormethane	485
Dichlorodiflourometha	570
Vinychloride	10500
mono,dichloroethane	19500
Carbon tetrachloride	1000
Chloroform	245
Methylchloride	150

1.3 Occurrences Of Chlorinated Hydrocarbons In Human tissue

Occurrences of chlorinated hydrocarbons carbons in human tissues was tested by many researchers , due to the major adverse effects of these compounds over the human health . Many experiments proved that these compounds are present in our tissues . And it is not clear weather it is related to age or not . But most of the studies proved that these compounds are stored in deferent parts of the body , mainly body fat . Table (1.3) represent the concentration of chlorinated hydrocarbon in deferent parts of the human tissue . The importance of this kind of research , help in understanding the human behavior towards exposure to such compounds , and can answer certain questions such as , do such compounds accomplish up in our human tissue after being exposed to them without affecting us . Like in fish tissue . Are they being formed in some stages of food or blood metabolism ....etc. In what limits do they become dangerous .

Table (1.3)
Occurrences of chlorinated hydrocarbons in human tissue

[concentrations in microgram per kilogram]
[after G.McConnell , á.M Frequsen 1973]

age of subject	sex	tissue	chloroform	carbon tetrachloride
76 yrs	F	body fat	19	24
		kidney	2	1
		liver	5	1
		brain	4	1
82 yrs	F	body fat	67	1.6
		liver	8.7	1.5
48 yrs	M	Body fat	67	2.1
		liver	9.5	3.5
65 yrs	M	body fat	64	11
		liver	8.8	3.5
66 yrs	M	body fat	68	1.6
		liver	10	5.1
75 yrs	M	body fat	65	5.1
		liver	10	5.1
74 yrs	F	body fat	52	5.2

1.4 Occurrences Of Chlorinated Hydrocarbons in food staff

Studying the formation or the presence of chlorinated hydrocarbons in food staff such as vegetables and fruits was done by many researchers mainly in agriculture field . The main aim was to study weather there is any residual chlorinated hydrocarbons in fruits and vegetables , in order to study the application of pesticides over these fruits and vegetables . Since pesticides consists mainly of chlorinated hydrocarbons. Table (1.4) shows that residual chlorinated hydrocarbons found in some food staff (3).

Table (1.4)

Chlorinated hydrocarbons in foodstuffs
[concentrations in microgram / kilogram]

foodstuff	chloroform	carbon tetrachloride	trichloro-ethylene
Diary produc fresh milk	5	0.2	0.3
cheshisre cheese	33	5	0.3
English butter	22	14	10
Hens eggs	1.4	0.5	0.6
Meat products Steak (beef)	4	7	16
beef fat	3.	8	12
Margarine	3.	18	6
vegetable oil	10	16	7
Beverages canned fruit drink	2	0.0	5
instant cofee	2	0.0	4
tea (packet)	18	4	60
fruits & vegetable Potatoes	18	0.0	0.0
apples	5	3	5
fresh bread .	2	5	7

1.3 Objectives of this study :-

The objectives of this study can be summarized in the following points :-

1- Investigate the presence of chloroform (trihalomethanes) in treated water for different treatment plants .

2- Find out the location on which these compounds are formed .

3- Find out the major reason(s) , Which causes the formation of (THMs) .

4- Studying the following removal techniques :-

a- Adsorption , using the following materials :-

i- Antracite . Granular and powdered sizes .

ii- Activated Carbon . Granular and powdered .

iii- Jordanian Zeolite . Granular and powdered .

b- Aeration , using the surface and diffused principal .

5- The following factors were studied regarding the removal processes .

i- pH

ii- size of Adsorber .

iii- aeration time .

CHAPTER TWO

BACK GROUND
AND
RELATED STUDIES

CHAPTER TWO

BACK GROUND AND RELATED STUDIES

2.1 INTRODUCTION

The maximum contamination level , which was permitted by the Environmental Protection Agency (EPA) , is 0.1 mg per litter of these compounds which are chloroform ($CHCl_3$) , bromoform ($CHBr_3$) , and the two intermediate bromochloroforms ($CHBrCl_2$) , ($CHBr_2Cl$). The two major reasons for setting this maximum permissible level are the ubiquity of measurable concentrations of (THM) compounds , and the second reason is the concern for toxicity and mutagenicity of chlorinated organic compounds (5) . Another permissible limit was assigned by (WHO) for chloroform concentration only for about 30 parts per billion , due to its major toxical , and carcinogenic effects .

Trihalomethanes are easily quantified by gas chromatographic procedures , unfortunately no simple and accurate method exists for the identification and quantification of the major individual nonvolatile chlorinated organic compounds , which are also formed as a result of water chlorination . The principle method used for their identification and quantification has been extraction , derivitization and gas chromatography and mass spectrometry . Even this sophisticated method is not able to measure the higher molecular weight , polar compounds (5) . The compound that proved to have direct health hazards , and widely present in drinking water is chloroform . Chloroform has been shown to be toxic and carcinogenic in rats and mice at high concentration , for this reason the EPA recommended the 0.1 mg/l of TTHM as the maximum contaminations levels (MCL) in chlorinated water supplies . When chlorine is added to the water for disinfection purposes , the THM is not the only product that is formed , but also higher levels of nonvolatile chlorinated organic compounds can be formed due to chlorination of the organic compounds found in natural water . But unfortunately attempts to separate and identify the specific by-product of chlorination formed in natural waters which are responsible for the mutagenicity of the water have in general not been successful (5).

In comparing the total amount of organic halogen (TOX) , produced in drinking water treatment to level of trihalomethanes , (THM) , OLIVER (16) found slightly larger TOX values than THM values . Glaze et. al found five to six times higher amounts of TOX formation potential than THM formation potential using several procedures for this comparison . In view of the fact the mutagenic character of chlorinated drinking water is more closely associated with the nonvolatile higher molecular weight fraction of chlorinated organic compounds . A great deal of attention has been focused recently on the problem of trihalomethane formation . And since the trihalomethane is a portion of total compounds (5) . The compound that proved to have direct health hazards , and widely present in drinking water is chloroform . Chloroform has been shown to be toxic and carcinogenic in rats and mice at high concentration , for this reason the EPA recommended the 0.1 mg/l of TTHM as the maximum contaminations levels (MCL) in chlorinated water supplies . When chlorine is added to the water for disinfection purposes , the THM is not the only product that is formed , but also higher levels of nonvolatile chlorinated organic compounds can be formed due to chlorination of the organic compounds found in natural water . But unfortunately attempts to separate and identify the specific by-product of chlorination formed in natural waters which are responsible for the mutagenicity of the water have in general not been successful (5).

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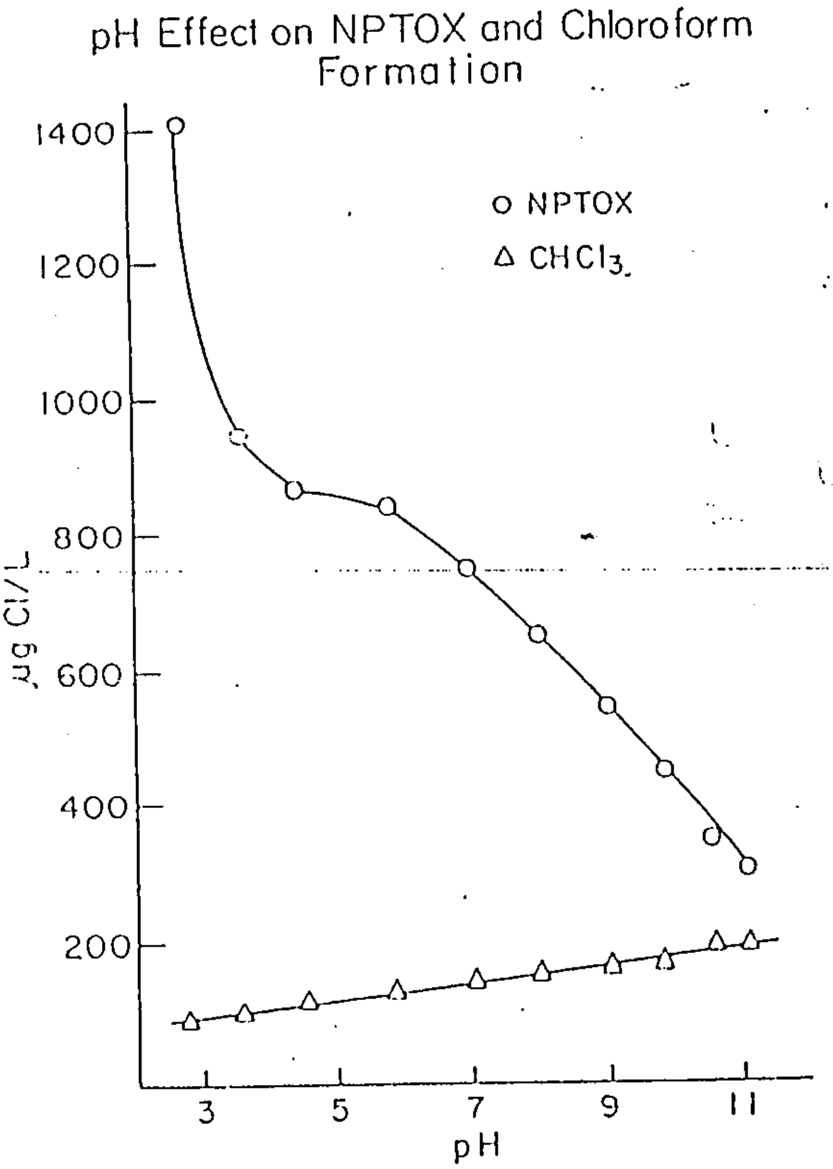
Both the THM and TOX formation is strongly affected by the pH and the temperature of the water that are formed in , but the formation of TOX , and THM have different response to the temperature and the pH , when the pH is reduced the THM levels decreases while the TOX was even increased to a greater extent. Thus decreasing the pH would reduce the THM formation and will increase the concentration of the TOX , besides the formation of complicated compounds of the TOX , which are represented in the symbol (NPTOX) , this is represented in figure (2.1) below . Thus , at low pH . chlorine would be a good choice , and chlorine substitution becomes very important , even though THM's are currently regulated , and because of this , if the formation mechanism and behavior of chlorine was clearly understood THM's in general can be controllable . Because of that before chlorination is applied it preferable to check this alternative of applying chlorine in certain stages in order to control the formation of THM , and before chlorination process is applied one should understand the effect of chlorination over the applied water , because each water would have its own characteristics .



Adopted from: Fleischacker and Randtke, J. AWWA, 75, 132, 1983.

FIGURE (2.1) TOX and THM Formation with pH.

2.2 Occurrences in the environment.

Techniques for the isolation , identification and measurements of chlorinated hydrocarbons have been extensively studied and described . Almost all depend on solvent extraction before being analyzed using the gas chromatography with an electron capture detectors . The response of the electron capture detectors varies widely according to to the number of chlorine atoms in the molecules , this would play a certain roll in the sensitivity of the results and determination of different compounds , fortunately these problems now are overcome by new devices .

Initial observations of the occurrences of chlorinated hydrocarbon in the atmosphere have been made by J.P. Riley , J.E. Lovelock . All the authors agree that fluorochlormethanes , Perchloroethlyene , chloroform and carbon tetrachloride are found universally in the atmosphere at concentrations normally in the range between 1 and 10 microgram /litter . The concentrations of chloroforms and carbon tetrachloride , which are chemicals intermediates with limited losses , are surprisingly high , even some authors such as Lovelock suggested that they may arise naturally by reaction between chlorine and methanes in the atmosphere (4).

Analysis of rain water , rivers , municipal water supplies , and sea water again showed that perchloroethylene , trichloroethene , chloroform , and tetrachloride are widely distributed at micro grams per kilograms . In addition some samples of sea water from Liver-pool Bay , which receives large volumes of industrial and domestic effluents , contains traces (less than 1 micro grams /kg) of some chlorinated hydrocarbons. Samples of marine sediment from Liver-pool Bay contained the same compounds as the overlying waters , but there was no correlation between the chloro-organic content of sediments and that of mid depth water . It appears that coarse gravels have little adsorptive capacity for these compounds , whereas sediments rich in organic detritus have much higher adsorptive capacity . Averaged over all , the concentrations of chlorinated compounds in sediments were similar to those in the water (10). From this we conclude that these compounds may be adsorbed in natural organic substances , and though these compounds can be controlled or removed using the adsorption process . Table (2.1) describes some of the chlorinated hydrocarbon characteristics .

Table (2.1)

Characteristics Of Haloginated Hydrocarbons (4)

compound	B.P Bioling Point	vapour pressure mm Hg / 20	solubility In water ppm w /w
methylchloride	24.2	3756	7250
methylene chloride	40.1	362.4 (25)	13200
chloroform	61.3	150.5	8200
carbon tetra-chloride	76.8	90.0	785
trichloro ethylene	87.0	57.9	1100

2.3 EFFECTS OF CHLORINE DOSES OVER THE FORMATION OF THM 'S

2.3.1 General

The basic principle of wastewater disinfection , which many people are familiar with , is to feed as much chlorine as practical , and as early as possible in the treatment process . In order to reduce the value of the biological oxygen demand [B O D] and the chemical oxygen demand [C O D] . And if anything goes wrong in the treatment process , such as , having taste odor and color ...etc , the direct solution was / is to add more chlorine . Every one thought that this would be the perfect solution , because of the fast response towards error correction.

Unfortunately this technique was solving small problems and at the same time creating major one . The discovery that free chlorine residuals reaction with natural organics to produce trihalomethanes [THM s] proved to people that this disinfection process is not necessarily safe. And it could never be the right solution for any problem , and chorine added for disinfection should be added with certain type of water and in specific point of application . And though any problem which may take place after chlorination should be studied well in order to find out the practical solution for these problems (6).

Chlorine can exists in several chemical forms in water. In water treatment , it is usually added as chlorine gas as (Cl_2 , when chlorine is added to the water for disinfection purposes , chlorine is rapidly and completely converted to hypochlorus acid (HOCL) , and this acid will break to to hydrogen ion and OCl^- . This is represented in the following two formulas (6) :-

$$Cl_2 + HCO_3 \Longleftrightarrow HOCl + CO_2 + Cl^- \quad (1)$$

$$HOCl \Longleftrightarrow {}^+H + OCL^- \quad (2)$$

The acid ionization constant for this equilibrium at 20 degree is 2.62 E -8 . This produces an equal concentration of the two chemical forms of free chlorine as shown in figures (2.3.1) and (2.3.2) . When ammonia presence in water is in excess , monocloramines (NH_2ClO)

, is formed in less than a second at pH of 7 to 10 , at higher chlorine concentration and lower pH chlorine adds to monochloramines to form dichloramine , ($NHCl_2$) , a slow reaction would start taking place , which is the reaction of monocloramines with the dichloramines to form the nitrogen gas , these reactions are summarized as follows (4) (6):-

$$HOCl + NH_3 \longrightarrow NH_2Cl + H_2O \qquad (3)$$

$$HOCl + NH_2Cl \longrightarrow NHCL_2 + H_2O \qquad (4)$$

$$NH_2Cl + NHCl_2 \longrightarrow N_2 + 3H^+ + Cl^- \qquad (5)$$

These equations also represent the breakpoint chlorination.

As the chlorine dose increases the free chlorine added to a water neutral pH with a fixed concentration of ammonia present is converted first to stable monochloramines , when more than 0.5 mg/l of Cl_2 is added per 0.1 mg of NH_3 , dichloramines begins to form slowly and reacts with the monochloramine which is already present to give chloride and nitrogen gas with the loss of the combined chlorine residual continues as more chlorine is added from (5 : 1) weight ratio , chlorine to nitrogen until the breakpoint is reached at an 8 : 1 ratio . Combined chlorine residual disappears as the added chlorine oxidizes the ammonia in monochloramines (equation 5). Then finally free chlorine residual appears

, this residual is very important , since using chlorine for disinfection purposes , this chlorine residual would be carried out throughout the distribution systems till it reach the consumer this is represented in figure (2.3.1)

2.3.2 Disinfection Efficiency :

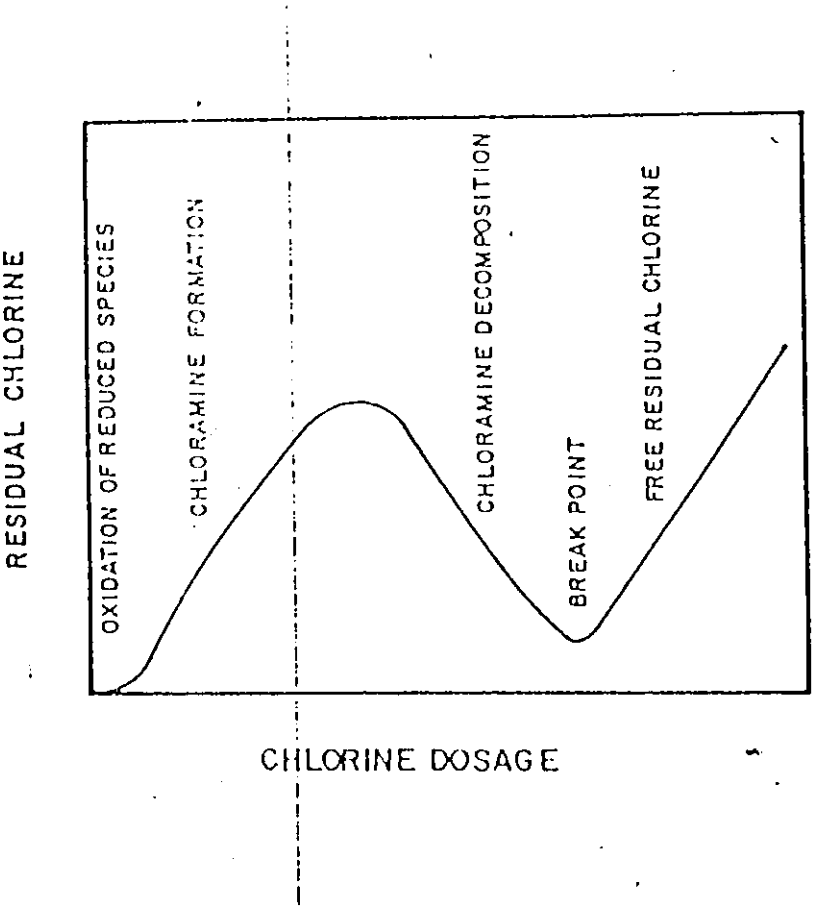
All of this chemistry is important because ech chemical species differs graetly in its ability to disinfect , and in its ability to react further to produce by- products . The relative germicidal effeciencies of several forms of chlorine and some other disinfectants are compared in the table (2.3.1)(6).

Table (2.3.1)

relative disinfectant with species

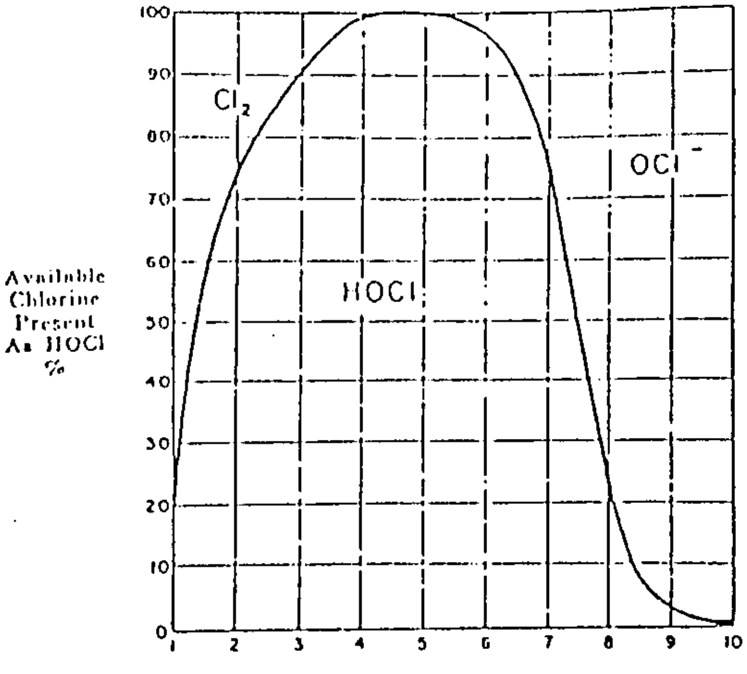
:PECIES	RELATVE DISINFECTANT Poliovirus
HOCl	1
ClO2	1 / 3
OCL	1 / 7
NHCl2	1 / 8900
NH2Cl	1 / 570

The previous table was complied by the Safe Drinking Water Commitee of the National Reasearch Council , National Academy of Science . Table(2.3.1) shows germicidal efficiency as the relative germicidal dose (



Breakpoint Reaction of Chlorine with Ammonia.

FIGURE (2.3.1) b



$HOCl - OCl^-$ Distribution with pH.

FIGURE (2.3.1) a

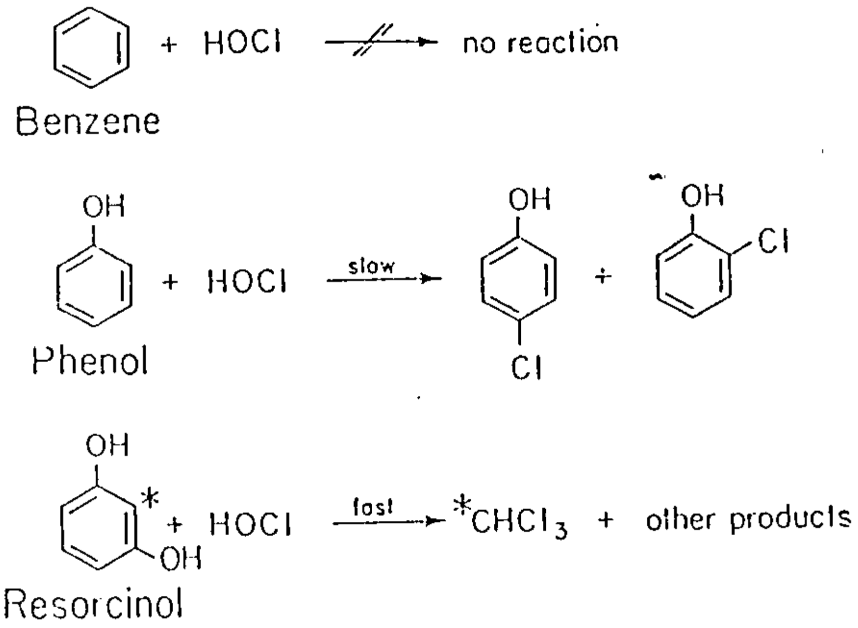
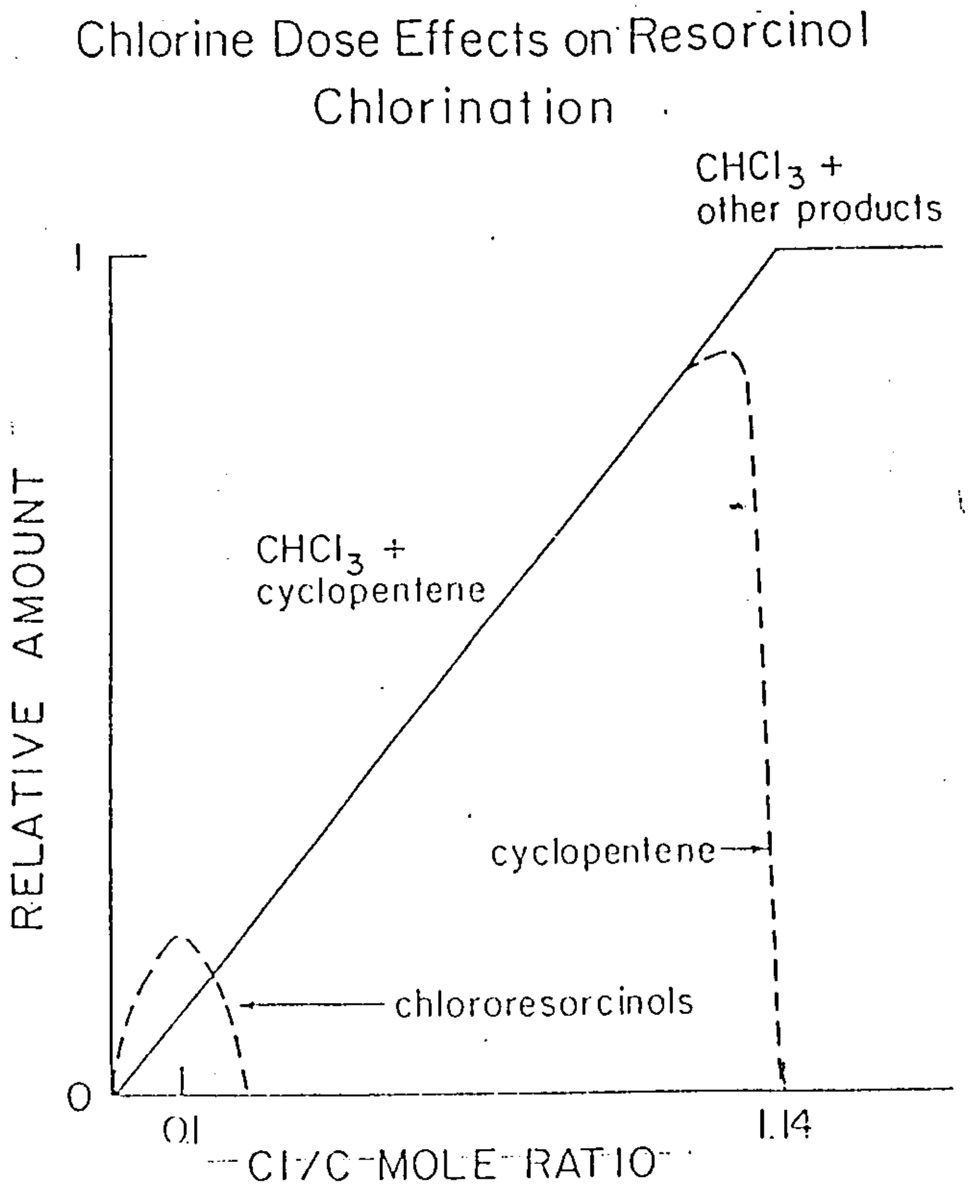


FIGURE (2.3.3) Substitution of HOCl on Phenol and Resorcinol.



Adopted from: Christman et al, Water Chlorination and Health Effects, Vol. 2, Jolley et al ed., 1978.

Resorcinol Chlorination Products with Increasing Chlorine Dose.

FIGURE (2.3.3)a

percent of the chlorine consumed as chlorine demand actually substitutes onto organic chlorine compounds . Fortunately the large majority is simply reduced to chloride.

Chlorine dose also affects the distribution between THM's and TOX . At low chlorine doses , substitution products dominate . At higher chlorine doses , oxidation and cleavage products (and ultimately THM 's) become more important . This is illustrated in figure (2.3.3) , using the resorcinol as an example , this would be a very good example for substitute products , (on which chloroform is one of these substitutes) , chlororesorcinols at low chlorine to carbon ratios , and the dominance of oxidation and cleavage products (chloroform) at higher chlorine doses , this then , is another example in which the change of operating conditions to reduce one part of the TOX (that is to reduce the formation of THM 'S) , but n general the concentration of TOX 'S will increase . In other words the elimination of the THM products would result in the increase of the (TOX) in the water, on which the phase of the problem is being changed and cured . This discussion points out the importance of (TOX) (6) .

2.4 Routes to THM and TOX :

2.4.1 General

In general , the distribution of products within the THM AND TOX fractions is a function of the extent of the reaction of chlorine with organic compounds . As previously noted , THM s are the principal volatile fraction of TOX . The TOX is often separated into purgeable (purgeable total organic halogen [PTOX]) , mainly THM and nonpurgeable (NPTOX) fractions. It is important to realize that THMs and TOX are the end products of many fast complicated reactions .

2.4.2 THM AND TOX Precursors .

Plants decomposition products are leached into unpolutted water and form the majority of the organic carbon present. These compounds are generally classed as aquatic humic materials and are presumed to be the major precursors of THM and TOX formed in the chlorination process. Table (2.4.1) below summarizes the sources of organic compounds in water supplies that proved to be precursors of THM s and TOX (6).

Table (2.4.1)

Trihalomethanes precursors (6)

Source	Examples
plants	Fluvic Acids . Humic Acid Degradation products such as resorcinol,vanillic acid, plants pigments
Algae	Algal biomass and pyrimidines (proline,uracil)
Industry	Effluents of used waters , which is mainly polluted with phenols and other compounds .

2.5 Formation of trihalomethane compounds

2.5.1 General

Chlorinated organic compounds can form as a result of water treatment process . Independent investigations by (Rook and Bellar et al demonstrated for the first time the presence of selected trihalomethanes [THM s] , primarily chloroform , in finished waters . Additional research demonstrated an increase in the concentration of THMs in sewage treatment plants effluent following chlorination . The national Organics _ Reconnaissance Survey (NORS) demonstrated the presence of haloginated organics in the drinking waters of each of 80 cities surveyed . Various haloginated organic compounds , such as chloroforms , bromodichloromethane , dibromochloromethane ,and bromoform were identified in different demonstrations (4) (5) (6).

There are an infinite number of organic materials commonly contained in the natural waters and waste water that may react with free chlorine . The reaction mechanism is not well understood , and the most part of this mechanisms for theses reactions have not been studied because rapid and precise analytical methods capable of monitoring the reaction products have not been available . Kleopfer and Fairless , Novak el al , FRiloux , Grob and others , reported that the presence of organohalides but no direct conclusion was drawn to explain the source of theses organohalides materials . So this study was not able to show out how do organohalides form neither the formation mechanism , besides the fact that this study couldn't find the source or origin of these materials , most probably because of the flash speed of these reactions , and not using cromatographic analyzing equipments on which can detect these compounds . Another methods developed by Dev. and Qual Assurance Lab of the Natl. Environ. Res. Crt in Cincinnati has developed a certain procedure for isolating and measuring nanograms of volatile and semi-volatile organic materials in water and waste water . Preliminary observations made during the development of this technique showed the presence of organochlorine compounds in the laboratory distilled and tap water . Further observations also indicated the presence of some brominated hydrocarbons in tap waters . Raw river water , which is the source of tap water , contained non or much lower concentrations of the organohalides and since the presence of these compounds in water have a possible health hazard , this experiment was done to find out the source of these compounds and how do they form . This experiment done can be summarized as follows , samples were collected in 125 or 500 ml ground-glass , stopperd bottles . The bottles were carefully filled , no bubbles were allowed to pass through the sample as the bottle filled , also no air space was allowed in too , then these samples were analyzed as soon as possible .from the collection time , to prevent these compounds from degradation or even having them evaporaized . The analysis was carried using the Gas Chromatograhy (purge method) , this procedure provides a method capable of analyzing for organic materials that are less than 2 per cent soluble and that boil below 150 C. An average detection limit of 1 micro gram was achieved , the detector used was the Flame Ioniaation detectors the (F I D) with the microcolumetric - gas chromatography (M C T) . Initial gas cromatographic analysis were conducted on the lab. tap water with the use of the (F I D) and the (M C T) these analysis showed that unequivocal qualitative identification of ethyl alcohol , chloroform , bromodiechloro-methane , and dibromochoromethan were made with the use of the GC. After these results were achieved analysis were carried out on other finished waters and these results are summarized in tables (2.5.1) , after taking into consideration that these samples have no possible lab contamination (4) .

In other words these results that the river waters and even the tap water have certain concentration of the organohalides compounds and that the trihalomethanes were also present in these waters . After having this ideas Scientist doing these analysis wanted to find out how do they form in the water and what was there origin . A second series of analyses was performed an raw river water that had been treated with alumn and chlorine , then the GC analysis was used the results summarized in table 33 showed a tremendous increase in the haloginated hydrocarbons , and that the addition of free chlorine formed the trihalogenated - methane compounds , the concentration of these compounds increased with the increase of chlorine contact time which was about 15 hrs . then this concentration form a state of equilibrium since little or no change in the concentration was noticed . This observation and previous ones proved that the trihalogenated methanes compounds were not introduced as impurities contained in the water itself nor it was introduced by the addition of alumn and chlorine , **it is apparent that a chemical reaction was taking place between the free chlorine and organic compounds present in the water** . The mechanism of these reactions was not accurately explained nor the formation mechanism of these compounds because of the complicated measures used for detection and also because of the reaction itself which is very fast too. One possible mechanism for the formation of chloroform ,(which is believed to have the worst health hazards effects), is suggested by the compounds detected in the tap water - tap water and ethanol and tri haloginated methanes (no mono nor dihalogenated compounds were found in tap water) . The ethanol oxidizes to acetaldehyde , then the acetaldehyde reacts with free chlorine to form chloral , then the chloral reacts with water to form chloral hydrate , then the chloral-hydrates decomposes to form chloroform .

As for the formation of the brominated compounds that are present in the water probably results from bromine impurities contained in the chlorine or in the water itself , the bromine would react in the same manner as chlorine to form the brominated compounds . The concentration of the tribrominated compounds was - if present - was below the detection limit o the method used , that is most probably because of the use FID detectors , but the results would differ if the mass spectrum , or the capillary column system was used , but still since these compounds were below the detection limit there environmental impact could be neglected .

2.6 Degradation in the environment :-

2.6.1 Biochemical degradation .

As the major chlorinated hydrocarbons are so widely distributed in the environment , they are exposed to a wide range of potential degradation routs . Although there is evidence that they can be metabolized by mammalian tissues , it is not known how other phyla have this ability . It is generally accepted that micro-organisms whether aerobic or anaerobic do not have it . Microbiological degradation , which is so important for the destruction of many organic compounds , dose not have any significant direct part to play in this case (3). In mammals , the metabolic pathways most of the compounds, lead to the formation of chlorinated accetic acids , either directly or via chloroethanaols . Chlorinated accetic acids have all been shown to be susceptible to further degradation by micro-organism in sea water .[Pearson ,G. R.and McConnel].

On the other hand , it has been suggested that low concentrations of chlorinated solvents could , however , inhibit microbial degradation process in general , especially in aerobic environments . Particular concern has been expressed over the effects on sewage treatment . The observations showed that concentration in raw sewage are normally less than 0.1 mg/l , some of this chlorinated hydrocarbons is adsorbed on primary sludge , while most of it is lost to the atmosphere during biological oxidation , either by activated sludge or trickling filters (3) . This was the case in this study since in Abu-Nusier treatment plant the Chloroform concentration was almost zero after coming out of the oxidation ditch due to excessive aeration (for oxidation purposes) . But it had a sudden rise once before the chlorination process , and that may be due to the chlorinated environment in the water channels . And the great jump in the chloroform concentration was in the effluent which after the chlorination process , which lead to the formation of chloroform again (one of the chlorinated hydrocarbons).

Experiments showed that the concentration of chlorinated hydrocarbons that could inhibit the aerobic oxidation does not occur at concentrations below 10 mg/l , which fortunately can not occur in normal conditions . This concentration will not be found in any sewage works especially the domestic ones , but it could be found in certain local industrial treatment plants . An extensive investigation of effects on anaerobic digestion in sewage works , particularly by Chlorofom was investigated by Swanwick , J. D and Foulkers [1971], but the results obtained could not prove that the presence of the chlorinated hydrocarbons such as chloroform may inhibit the microbial degradation (3).

2.6.2 Physio - chemical degradation .

There is evidence that chlorinated hydrocarbons , could have chemical breakdown in water . But in general these reaction are very slow . The estimated half-life of some compounds in general would be about six years . But this cant be considered as a rule , since few compounds may have faster degradation , but most of the chlorinated hydrocarbons are very stable in the environment . Exceptions are also present so some compounds that are easily dehydrochlorinated , the reaction rate in such cases would be pH dependent . For example the trichloroethene , would have a chemical half-life in sea water (at pH 8 and 10 deg. tem.) bout nine months . However rapid degradation may occur in aqueous system in the presence of metalic iron , But unfortunately the whole degradation compounds have not been identified (3).

2.7 CONTROLLING THE FORMATION OF TRIHALOMETHANE

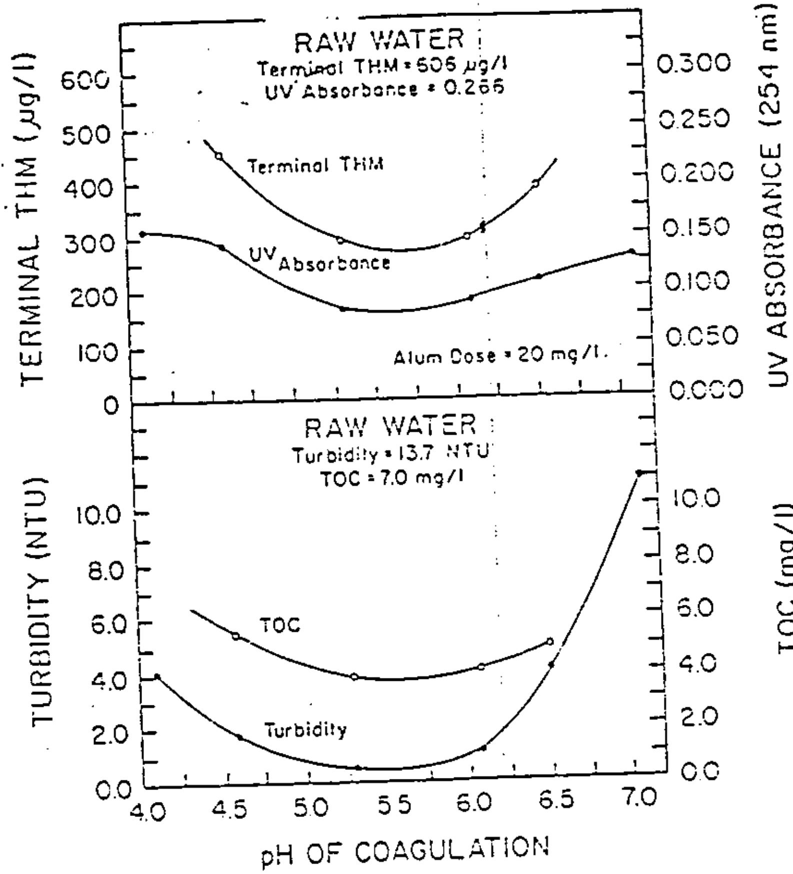
2.7.1 General

The formation of trihalomethanes in water problem can be handled from different points of views , and that would be based upon the way desired for treatments , and this can only be achieved if the formation process of THM's is clearly understood, THM's control in water can be in two different ways ; First , by preventing the formation of these compounds ,which require an understanding of formation process , or the treatment processes . Secondly , by removing these compounds after being formed in water . One way to achieve this is by removing precursors , which in fact are the organic substances that are present in water which have the potential to form THM . To do so the source of these organic compounds must be verified . Expected sources of such organic compounds may be plants , algae , and of course the humans sources . The plants would give , the , fluvic and humic acids while the degradation products of these acids would be , resorcinol , vanillic acid , syrigic acids and 3,5 dihydroxy-bezonicacid (Rook , 1977 . Christman , el al ., 1978) , also plants pigments such as Chlorophyll and phlorocetophenone , (Morris & baum , 1978) . While the algae would produce the algae biomass itself , plus the Amino acids , trypotphan , proline , and uracil , (Morris & baum , 1978) . While the human source as expected , would be though the industrial activities , and the chemicals presence in the effluents of industries such as phenols . (Norwood , el al ., 1980. Boyce & Hornig 1983). After knowing the sources of the organic compounds we can control the THM's in water in an indirect way , that is by eliminating these compounds from water before the chlorination process . Another indirect method is not to use chlorine for disinfection , and to use alternative disinfectant, such as ozone , ultraviolet radiation , or chloramines ...etc, as to prevent the formation of the trihalomethanes in the water , rather than removing these products from waters after being formed . But unfortunately using other disinfectant is not safe 100 % , since each method have its own advantages and disadvantages in the treatment process . For example using ozone as a disinfectant would have the problem that no residual disinfectant will remain in the water , which means if the distribution system has a certain locations on which infiltration is taking place , the water would not be considered safe afterwards . Ultraviolet light and ozone are both excellent disinfectants which have been shown to produce minimal problems , ie by-product production . However , neither one is widely used for drinking water disinfection in the United States of America because of the lack of measurable residual . In these cases chemistry is very important because each chemical species differ greatly in its ability to produce disinfection compounds

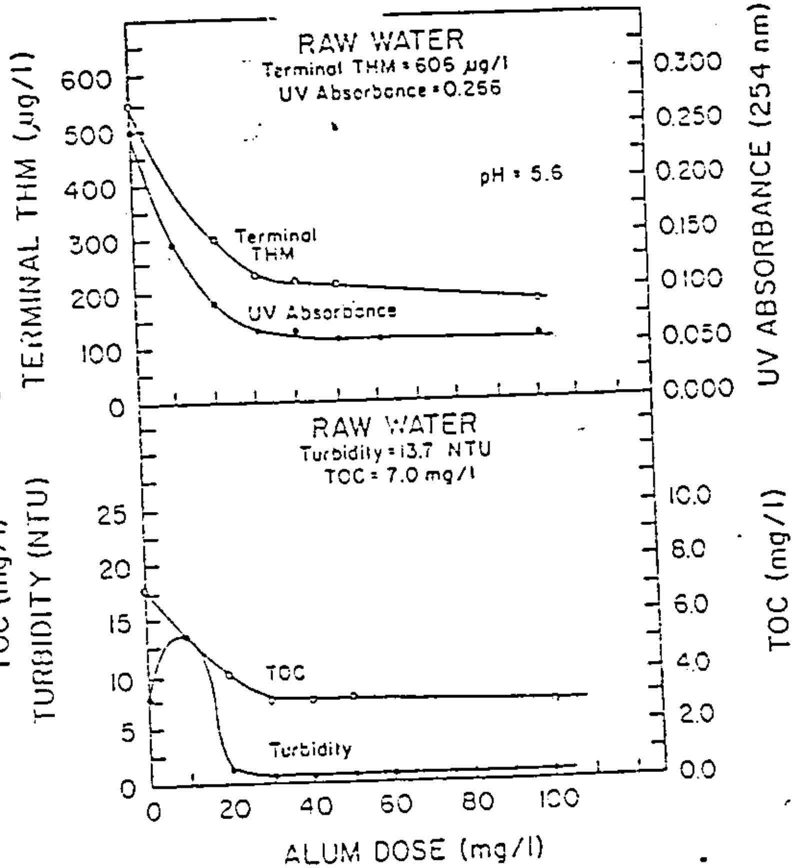
, and in its ability to react further to produce the so called , by products , on which problems may start to rise . To find out the chemical by-products in water would be difficult , since these chemical by products may vary a lot , and totally dependent over the water chemical characteristics . This means that these chemical by-products might differ from case to case for the same water or , might be completely different if compared to other type of water . Because of this reason no simple straight forward method was used to remove all the so called precursors of the THM 's , or simply because they are not all well identified for example ,if organic compounds were taken into consideration , there is an infinite number of these compounds , are they all considered to be the THM's precursor ? . It is difficult to answer this question because these compounds are not well understood . However , some scientist showed that the removal of known THM's precursors would prevent the formation of the THM's in these treated waters. The EPA has recommended five - generally available - treatment techniques for achieving compliance with the maximum contamination level (MCL) for the total trihalomethanes (TTHM) , four of these methods involved in improving the clarification processes for removing the (THM) precursors , or the use of alternative disinfectants .One of the additional treatment methods that the EPA considered was the usage of ozone as an disinfectant alternative .Another method that proved to be excellent in removing the THM's precursors was the coagulation process as it is explained below (9).

2.7.2 APPLICABILITY OF COAGULANTS FOR CONTROLLING THM FORMATION

Coagulants such as AL (III) , and Fe (III) have been shown to be capable of removing significant concentrations of the total organic carbon (TOC) , and the THM precursors from aquatic systems . These reductions have been demonstrated for both synthetic solution of humic extraction (Babcock and Singer , 1979 ; Edzwald , 1979 ; Glaser and Edzwald , 1979 ; Scheuch and Edzwald , 1981 ; Johnson and Randtke , 1983) , and in actual water treatment plant situations (Young and Singer , 1979 ; Kavanaugh , 1978 , gong and Edzwald , 1981). In the coagulation of raw water in actual practice , removals of (TOC) and (THM) formation potential tend to range between 40 % to 70 % ; the reduction in (THMFP) concentration tends to be higher than the corresponding reductions in (TOC) . The key to the successful application of coagulation for the (TOC) and (THMFP) removal is the pH control , as the effectiveness of the coagulates is very much dependent over the pH of the water . Experiments showed that for Al (III) the optimal pH ranged between (5 - 6) , while the optimal pH for Fe (III) ranged between (3.5 - 5) , these results are well represented in figures (2.7.2) (10) . With the regard to the use of alternative oxidants and / or disinfectants for controlling the THM formation , there coagulation process should be carefully understood , and , the whole process should be dealt with as a single procedure . For example if , prechlorination is eliminated when the coagulation process was applied , and a post chlorination is adopted in order to take advantage of the use of coagulant , settling and / or filtration process must be applied for the removing of the THM precursors coagulated , and here the need of for an alternative pretreatment oxidant for the control of iron and manganese , taste and odor , in this regard potassium permanganate , or a strong oxidation agent is added to remove these problems (odor , taste ,... etc.). The question then, what is the effect of these oxidants on the THM precursors , and what is the effect of using these oxidants over the coagulation process . Unfortunately no single answer is available , since each oxidant used would have a unique effect over the whole process , and each case should be studied in a separate way . For example (Colthrust and Singer 1982) , showed that the solid manganese dioxide produced from the reduction of permanganate could also serve as adsorbent of humic substances (organic compounds) and provide an additional effective removal mechanism for THM



Effect of pH on Coagulation with Alum (Sample 1).

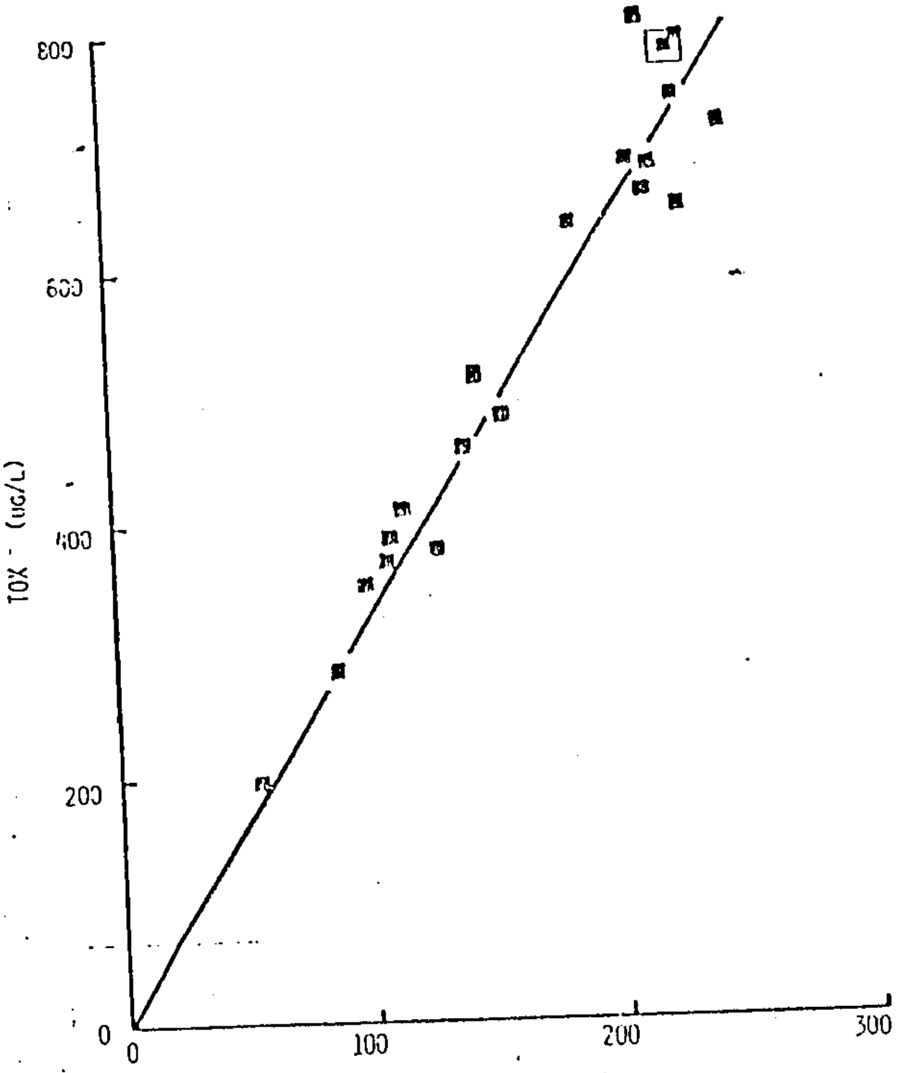


Effect of Alum Dose on Water Quality (Sample 1).

Singer, et al., Trihalomethane Formation in Water Treatment Plants in North Carolina, Report No. 179, Water Resources Research Institute of the University of North Carolina, Raleigh, N.C. April 1982.

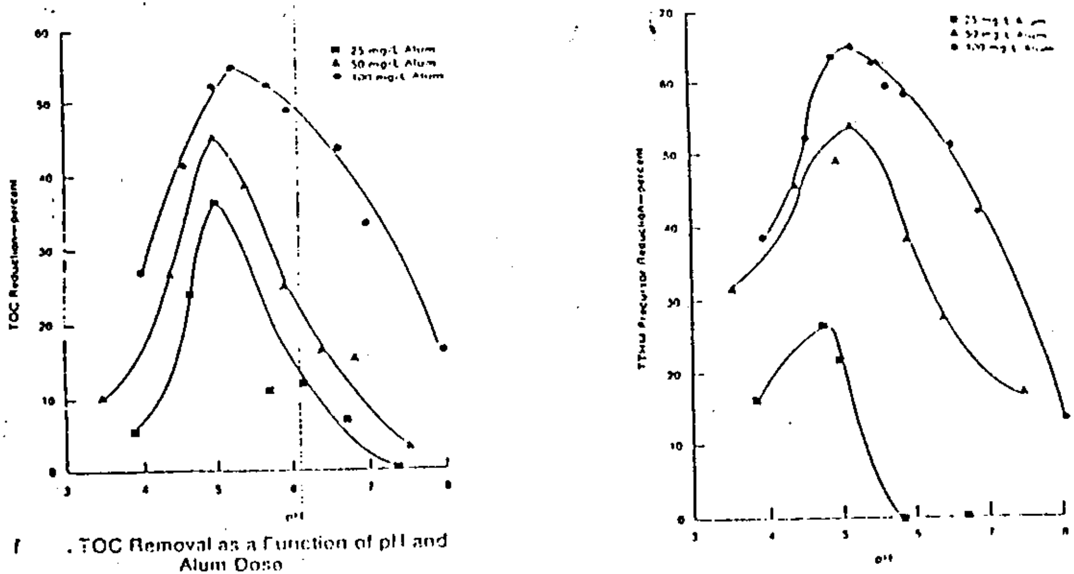
FIGURE (2.7.2) a

TOX FORMATION POTENTIAL VS CHLOROFORM FORMATION POTENTIAL IN ALUM COAGULATED AND FILTERED BLACK LAKE FULVIC ACID



Reckhow and Singer, "Removal of Organic Halide Precursors by Preozonation and Alum Coagulation," presented at AWWA Annual Conf. Las Vegas, NV, June, 1983.

FIGURE (2.7.2) b



. TOC Removal as a Function of pH and Alum Dose

TTHM Precursor Removal as a Function of pH and Alum Dose

Semmens and Field, "Coagulation: Experiences in Organics Removal," JAWWA, Vol. 72, No. 8, p. 476 (1980).

FIGURE (2.7.2) c

precursors .

2.8 Prechlorination with chloramines to reduce THFP

Using prechlorination in water treatment plants showed that this process could reduce the formation of THMs directly by affecting the THM precursors . And many studies proved that prechlorination with chloramines rather than prechlorination with free chlorine , showed that THM s compounds may be reduced if applied correctly (8) (9).

In order to figure out the effect of prechlorination , in controlling the formation of Trihalomethanes the following experiment was carried out . Two units (unit 1) and (unit 2) were prepared ,unit one was prechlorinated with chloramines and unit 2 was prechlorination with free chlorine . The two units were not equally effective in removing and controlling trihalomethane (THM) . Precursors in parallel pilot systems that varied only in the method of prechlorination . As expected , the THM levels in the prechlorination process with chloramines (unit 1) were low and those using free chlorine (unit 2) were high. Control of the bacterial population (as determined by standard plate count) in unit 1 was more consistent than that in (unit 2) (8). This experiment showed that THM can Be controlled by prechlorination , and at the same time maintain a remarkable disinfection power .

Regulations to control trihalomethanes (THM s) and other synthetic compounds in drinking water have resulted in numerous studies of formation reactions and of various removal methods. Trihalomethanes are commonly formed during chlorination,which is used principally to control microbial growth . One method suggested for controlling THM s was to eliminate chlorination. However , water treatment managers were concerned that the elimination of chlorination would lead to a problem with microbial growths within the treatment units. Disinfection by means of chloramines was proposed as an alternative to chlorination because (Brodtmann and Russo) had found that chloramines effectively killed bacteria with little formation of THM s. However , concern was also ex-pressed as to the long term control of bacterial population in a continuous flow system such as a treatment plant . The prechlorination process is described for a pilot - plant , system that was used to compare the effects of two pre-disinfection schemes - free chlorine and chloramines on THM precursor (trihalomethane formation potential) (8).

There are certain methods that are capable of removing the THM's precursors , and THM compounds themselves , such as using adsorption , and , stripping (air stripping) , and these two methods are discussed bellow .

2.9 AIR STRIPPING OF TRIHALOMETHANE

2.9.1 General

Air stripping is a promising way of controlling volatile organic solutes , such as trihalomethanes , from water supplies. There are various means of promoting air - water contact to enhance mass transfer between water and air , such as mechanical surface aeration , diffused aeration , spray or tray towers , open channel cascades , and packed tower aeration . With a sufficiency high air - water flow ratio , substantial removal of trihalomethane can be achieved by means of diffused aeration , or countercurrent packed - column air stripping . With sufficient energy input , substantial trihalomethane removal can be also accomplished mechanical surface aeration. Previous experiments showed that packed tower procedure is less costly than the diffused aeration processes and have high efficiency too . The poor economy of the diffused aeration process for trihalomethane removal can be explained by the rapid saturation of the air bubbles with the trihalomethanes as the bubble rise through the column , the energy required to compress air to a pressure sufficient for aerating certain basin (example 4 meters deep) is largely wasted if the are bubbles become saturated in the first few centimeters of their rise through the liquid column . for the same reason the spray towers , which have been shown to be effective . Since a long period surface aeration have been improperly neglected as an alternative , perhaps because of the use of diffused aeration from the economical point of view , both surface and diffused aeration are generally achieved in open basin , and their cost effectiveness for oxygen transfer is approximately equal . However , there is an important difference between oxygen and trihalomethane , and gas transfer here will vary completely , since the Henry's constant differ greatly . The Henry's constant for oxygen is approximately 100 times than chloroform ($CHCl_3$) , and almost 1000 times than bromoform ($CHBr_3$) . The consequences is that air bubbles in diffused aeration become saturated with chloroform ($CHCl_3$) and bromoform ($CHBr_3$) , so rapidly that great quantities of air are required to achieve effective transfer rates . Whereas the air has much greater capacity for oxygen . While in surface aeration , there is direct transfer to the atmospheric boundary layers , which provides much larger volume and much greater range for equilibrium capacity than the gas bubbles in the diffused aeration . This problem by the diffused aeration could be overcome by using larger number of diffusers , or have the diffusers distribution all over the tank depth to provide sufficient aeration to the whole tank , and not to fix the diffusers on the bottom of the tank .On the other hand surface aeration , would loose its effectiveness , if the depth of the tank was increased , actually state the depth to width ratio of the aeration tank would be difficult , since , it is dependent on characteristics of the mechanical equipment used for aeration , and the effectiveness of the way on which the air is exposed to the water , actually , to have sufficient removal , the above questions must be answered through actual experiments , to provide the actual conditions and figure out the removal efficiency , depending on the mechanical characteristics beside the physical and shape characteristics of the tank or basin used for treatment .

2.9.2 Calculations related to air stripping

- basic rate equation

the following equation is considered the basic equation for mass transfer.

$$\frac{1}{V}\frac{dm}{dt} = -K_L a \, (C_L^* - C_L)$$ where

- m = mass of solute (kg) .
- V = liquid volume (m^3) .
- t = time (s) .
- K_L = overall mass transfer coefficient (m / s) .
- a = specific interfacial area (m^2/m^3) .
- C_L^* = bulk average concentration in the liquid phase (kg/m^3) .
- C_L = liquid concentration in equilibrium with the gas phase concentration C_G (kg/m^3)
- K_La = IS EQUIVALENT TO A FIRST ORDER TRANSFER RATE CONSTANT

2.9.2.1 Equilibrium :-

For dilute solution of nondissociating organic compounds in water the value of C_L^* is approximately proportional to CG , according to Henry's law (11) .

$$CL^* = CG/Hc$$

where :-

Hc = Henry's constant (dimensionless) which is the ratio of the concentration in the gas phase to that in the liquid phase at equilibrium .The Henry's constant is a property of the solute - solvent system and the temperature T (k) , and is independent of pressure and hydrodynamic conditions . The Henry's constant can be expressed in other units such as atm . m^3/mol , but using the dimensionless unit is more simple .

2.9.3 Two Resistance Theory

The overall rate constant is the resultant of two resistance in series , namely those of the liquid and gas phase boundary layers . According to the two resistance theory the total resistance (RT) , can be estimated by summing the two individual resistances of the liquid and gas phase respectively.

$$RT = 1/KLa = RL + RG$$

If the concentration driving force is expressed in terms of mass concentrations and the Henry's constant as a ratio of mass concentration , the overall transfer rate constant ,KLa 1/s is (11).

represented by

$$KLa = 1 / ((1/ Kla + 1/(KGaHC))$$

where :-

KLa and KGa are individual rate constant (m/s) for the liquid and gas phase respectively .

2.9.4 Mechanical Surface Aeration

It is meant by the mechanical surface aeration , the conventional way of surface aeration which is achieved through direct energy input at the water surface using typical aeration turbines . Such technique is commonly used in wastewater treatment processes rather than in water treatment , but tests showed that it is relevant to water treatment . From standard performance test results with full scale units proved that the oxygen transfer rate constant (KLa)O2 , is proportional to the energy input , and this is represented as follows (11).

$$KLa\ O2 = Kp\ (P/ V)$$

where :-

P = power input (W)

V = aeration basin volume (m^3)

Kp = proportionality constant with units of (m^3.1/w.1/s)

In general the ratio of oxygen transfer rate to power input ranges between 1.2 to 2.4 kg O2 per kWh . To be on the conservative side if the lower value to be taken into consideration the liquid phase rate constant would be :-

$$KLa\ (O2) = (3.6\ E{-}5\ (P/V))$$

The liquid - phase rate constant , Kl a depends on solute's diffusivity in water , however several studies suggested that the liquid phase transfer rate constant for an organic compound is related to that of oxygen by the following formula(11) ,

$$(KLa\ i / KL\ a)\ O2 = \acute{I}i = (Di / Do2)\ \hat{}\ 0.62$$

where :-

(Di / DO2) is the ratio of diffusivity of i and O2 in water and in general this ratio is approximately between 0.5 to 0.7 for trihalomethanes . For chloroform ($CHCl_3$) the laboratical experiments showed that approximately

$$(KG / K\ L) = 25$$

based on mechanical surface aeration , under turbulent mixing conditions .

2.10 Trihalomethane removal by packed- tower aeration

Contamination of portable water by trace organics considered one of the major water quality issue . Several new treatment processes for removing these traces were developed. One of these processes is the packed-tower aeration . The advantages of this principal can be summarized as low cost and simplicity of design and operation . The cost of packed tower aeration is particularly attractive , compared with costs of other processes for removing volatile organics . Adsorption processes using activated carbon or adsorbent resin are considered other alternatives for removing volatile organics . design of and operation of these processes , but these processes are considered expensive and difficult to operate (12) , however to control the formation of Trihalomethane (T H M) there are many alternatives to be used , such as air stripping which provides a high degree of treatment at a reasonably low treatment cost . Table (2.10.1) below summarizes some processes and its approximate cost in the united states , (unfortunately no records of such techniques are available for Jordan).

Table (2.10.1)

Total costs for 80 % reduction of total trihalomethanes (12).

Treatment	Cost $/ 3785 L
Powdered activated carbon	40
Granular activated carbon	16
Ozone	15
Packed - Tower Aeration	3
Chlorine Dioxide	2 - 3
Combined Chlorine	2 - 3

The packed tower aeration is well established in the chemical and air pollution control industry . Its application in removing volatile organic compounds or Trihalomethanes from potable water is new . Currently , commercial design information is not specified related

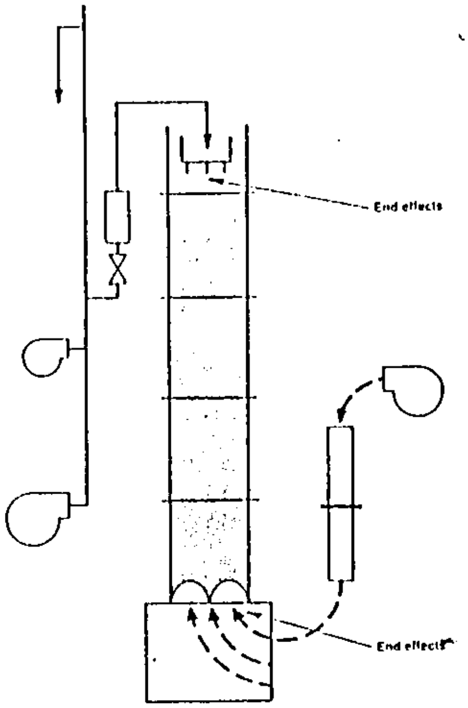
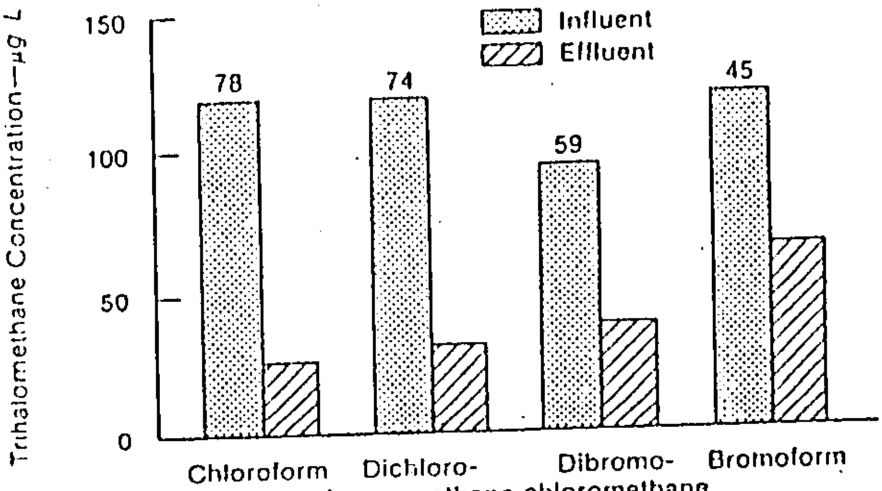


Figure 2. End effects in a countercurrent packed tower

FIGURE (2.10.1) a



Comparison of trihalomethane removals

FIGURE (2.10.1) b

to trace quantities of organic compounds in water . The water utility industry is familiar with similar processes but unfortunately each design is done for a certain case and an not be used as a general design. In other words the design of such processes in a function of the water being treated itself , and though no general design would be accepted to maintain the maximum contamination level of pollutants in water . The design of packed-tower system is generally based on mass transfer for a given organic compound and water loading rate . Tavanaugh and Trussell and Singley et al , have described the design approaches for packed tower aeration as fully dependent upon the mass transfer coefficient for a given volatile organic compound and water loading rate . Singley et al determined constants from mass transfer correlation depending on the hydraulic formulas which are based on the Reynolds number for at least 10 organic compound. The first study on packed-tower aeration was conducted in late spring on 1981 at a lime softening plant . The quality or raw ground water was satisfactory except for the color . The color for this ground water was reduced using lime soda ash followed by a bleaching stage using chlorine . And since the chlorine demand was high , to remove the color and to provide free chlorine residual for disinfection . And because this water contains high concentration of natural aquatic humus trihalomethanes were formed . Packed - tower aeration

, liquid - liquid , gas liquid , gas - solid or liquid - solid interphases . The material being concentrated or adsorbed [matter which is to be removed] is called the adsorbate , and the material used to remove the undesired matter is called the adsorbent (13). The term sorption , which includes both adsorption and absorption , is a general expression for process in which a component moves from one phase to be accumulated in another , particularly for cases in which the second phase is solid . The phenomenological differences between adsorption and absorption are illustrated graphically in figure (2.11) .

2.11.1 Relationship Between Surface Tension And Adsorption

Surface adsorption , is an expression used to describe the extraction of matter from one phase and concentrated at the surface of a second. Here since the surface of the matter is related directly . The surface tension of the liquid must be taken into consideration . Surface tension is defined as the quantitatively equal to the mount of work that would be necessary to compensate the natural reduction in free surface energy (13) . From a molecular point f view . Enlarging a surface requires the breaking of bonds between molecules making up liquid phase , and the forming of bonds between molecules of different phase . Surface tension forces can be illustrated in a drop of water present over a glass plate , this drop of water would try to have a certain spherical out shape .This is due to the cohesion forces between the water molecules which cause the attraction between these molecules . While on the other hand there is a certain force which is trying to dissipate the water drop , these forces are called the adhesion forces . This mechanism explains why the drop of water would not spread . But this spherical shape is because this drop is minimizing the outer surface , and thus minimize its free surface energy . Based on this , any solute which increases the surface tension is negatively adsorbed at the boundaries of the liquid phase that is , the solute would migrates away from the surface towards the center of the liquid phase , and so never be adsorbed . Figure (2.11.1) represent this phenomenon . But on the other hand if this mater have enlarged solid liquid interface this means that there is a certain attraction and the liquid is extracted over the surface of the solid (13).

2.11.2 Types Of Adsorption .

There are three types of adsorption , the physical , the exchange adsorption and chemical adsorption . The physical adsorption or sometimes is called the van der walls adsorption. In this type of adsorption the molecules (pollutant) is attracted to the adsorber due to attraction forces between the molecules . On which the pollutant molecules would be held within the adsorber molecules . For example the intermolecular attractive forces between a solid and gas are greater than those existing between molecules of the gas itself . The gas will condense upon the surface of the solid even though its pressure may be lower than the vapor pressure corresponding to the prevailing temperature . The adsorbed substance does not penetrate within the crytal lattice of the solid and dose not dissolve in it . But remains entirely upon the surface (Ponic , V.,Z Kore , and S. Cerny , 1974). This type of adsorption in most cases would be economical to use , since regeneration of the adsorber would be in a physical matter too. The second type of adsorption is the chemical adsorption , sometimes is called the [chemisorption] or activated adsorption . This type of adsorption is mainly due to chemical interaction between the solids [adsorber] and the adsorbed matter (Clark , A. 1970). In other words the adsorption here would be due to sort of chemical reaction depending on the chemical bonds between molecules of the adsorber and the adsorbed substance . During this type of adsorption the liberated heat during the chemisorption is usually large . Here since these reaction are usually exothermic ones these reactions are expected to be irreversible . And the adsorber is expected to undergo certain chemical reactions , which would make it difficult to regenerate. While the exchange adsorption is as the term implies ,a process in which ions of one substance concentrate at a surface as a result of electrostatic attraction to charged sites at the surface . For two potential ionic adsorbates in like concentrations and in the absence of other specific sorption effect . The charge on the ion is the determining factor for exchange adsorption (6) . The following conditions must be satisfy in order to accomplish the adsorption process (13).

1- The adsorbed molecules must be transferred from the bulk phase of the solution to the surface of the adsorbent particle .

2- The adsorbent molecule must be transferred to an adsorption site on the inside of the pore .

3- The adsorbate must become attracted to the surface of the absorbent .

2.11.3 Causes of adsorption :

Adsorption from solution onto a solid occurs as the result of one of the two characteristics properties for a given solvent - solid system , or a combination . The primary driving force for adsorption may be a consequence of [lyophobic] (solvent - disliking) character of the solute relative to the particular solvent . Or high affinity of the solute for the solid . For the majority of systems encountered in water and wastewater treatment practice , adsorption result from combined action of the two forces . The degree of solubility of a dissolved substance is by far most significant factor in determining the intensity of the first of the two driving forces . The more substance likes the solvent system the more hydrophilic [water liking] , in the case of aqueous solution . the less likely it is to move toward an interface to be adsorbed . Conversely , a [hydrophobic - water disliking] substance will more likely be adsorbed from aqueous solutions.

A large number of organic contaminants , such as sulfonated alkylbenzene , have a molecular structure comprised of both hydrophilic and hydrophobic groups (6).

2.11.4 Factors influencing Adsorption

1- Surface Area

Adsorption is a surface Phenomenon ; therefor the extent adsorption is proportional to specific surface area . Specific surface area can be defined as the amount of adsorption accomplished per unit weight of solid adsorbent (6). The adsorption capacity of a nonporous adsorbent should also vary as the inverse of particle diameter , that is four highly porous adsorbent should be relatively independent of particle diameter . However for porous materials such as activated carbon , the breaking up of large particles to form smaller ones can in some instance serve to open some tiny , sealed channels in the carbon , which then might then become available for adsorption thus possibly yielding dependence of equilibrium capacity on particle size (Werber and Morris 1964a).

2- Nature of the Adsorbate .

The adsorption process is widely affected by the nature of the adsorbate itself . The solubility of the solute for example is considered a major factor in the adsorption equilibria . In general an inverse relationship can be anticipated between the extent of adsorption of a pollutant and its solubility in certain solvents from which adsorption occurs .As mentioned before , adsorption increase with the decreasing solubility of the solute in the solvent . Regarding organic matter , in general , the solubility of any organic compound in water decreases with increasing the cain length which form this organic compound , because this compound [long chain] becomes more hydrocarbon-like as the number of carbon atoms becomes greater. Figure (2.11.2) below shoes the effect of molecular wt. on the adsorption capacity .

3- pH

The pH of the solution will influence the extent of the solution . Because the hydrogen and the hydroxide ions are adsorbed quit strongly , the adsorption of other ions is also influenced by the pH of the solution . pH affects adsorption in that it governs the degree of ionization of the solution . In general , adsorption of typical organic pollutants from water is increased with the decreasing the value of pH [towards the acidic conditions] . In many cases this may result from neutralization of negative charges at the surface of carbon with increasing hydrogen ion concentration

. This effect is expected to vary with different types of carbons , because the charges on the surface of the carbon is not the same all the time . And it depends directly on the way or technique used for activation .

4- Temperature

Adsorption is also directly affected by the temperature of the solution . And since adsorption reactions are considered to be exothermic reaction ,thus the extent of adsorption in general is increased with decreasing temperatures . The changes of enthalpy for adsorption are usually of the order of those for condensation reactions.

5- Type Of Reactor

Batch And continuous - flow Adsorption systems :

It is meant with the bach system is that the treated water is not renewed while treatment , and the whole amount of this treated water is exposed to the adsorber. Or in other words the adsorber is mixed the the polluted water , and through a certain contact period the pollutants are adsorbed from the water . Then after that the adsorber is removed , then It is either discarded or regenerated to be used again . The continuous flow system is the system on which the polluted water is passed through sort of fixed layer of the adsorber . And while the water passes through this layer , the pollutants are removed . This type of adsorption , sometimes is called the column- type continuous flow . Because the fixed layer here is a column , on which the adsorber is placed , while the polluted water enters the column from one side and leave from the other. The column type adsorption appear to have distinct advantage over the batch system , because the rate of adsorption depend on the concentration of solute in the solution being treated. For column type the adsorber is continuously exposed to fresh solution on which the concentration of the pollutants will remain constant . While n the batch system the concentration of the pollutants is decreased . Thereby decreasing the effectiveness of adsorbent for removing solute.

6- Effect Of Agitation

The rate of adsorption is largely affected by the agitation of the system . The degree of agitation is controlled by either film diffusers or pore diffusion . If the agitation was little between the adsorbent particle and the fluid , then the surface film of the liquid around the particle will be thick and film diffusion will likely be rate-limiting step . If good mixing was accomplished this will increase the rate of film diffusion to a point that pore diffusion would become the rate - limiting factor . Pore diffusion is generally rate - limiting factor for batch type reactor systems which will provide a high degree of agitation . Film diffusion will probably be the limiting rate step for continuous - flow systems at flow rate of 10 gal / min per square foot or less (after Weber 1972) .

2.11.5 Adsorption Isotherms :-

The adsorption isotherm is a functional expression for variation of adsorption with concentration of adsorbate in bulk solution at constant temperature . Commonly , the amount of adsorbed material per unit weight of adsorbent increases with increasing concentrations but not indirect proportion (13).

Figure (2.11.1) shows types of adsorption . There are many types of isothermal adsorption . relations witch may occur. The most common relation ships between the quantity of the amount solute adsorbed per unit weight of solid adsorbent (qe) , and the concentration of solute remaining in solution at equilibrium (C) . These expressions of this type is termed as adsorption isotherm as mentioned above .

2.11.5.1 The Langmuir and Bet

The Langmuir adsorption model is valid only for mono (single) layer adsortion , Whereas the Brunauer , Emmentt , Teller (B E T) model represents isotherms reflecting multilayer adsorption . Both equations are limited by the assumption of uniform energies on the surface the difference can be noticed in figure (2.11.5.1).

The Langmuir Isotherm equations are based on the following assumptions :- (6).

- a- The adsorption is considered to be reversible and equilibrium conditions can be achieved .
- b- The adsorbed matter is assumed to be adsorbed on the surface of the of the adsorbent , and forms a thickness of one molecule .
- c- The area available for adsorption is limited .
- d- The presence of adsorbed molecules at one site will not affect the adsorption of molecules at the adjacent site (13) .

Two convenient linear forms of the Langmuir equation are represented as follows :-

$$C/qe = 1/bQ + C/Q \quad \ldots\ldots\ldots\ldots 1$$

$$1/qe = 1/Q + (1/bQ) * (1/C) \quad \ldots . 2$$

where :-

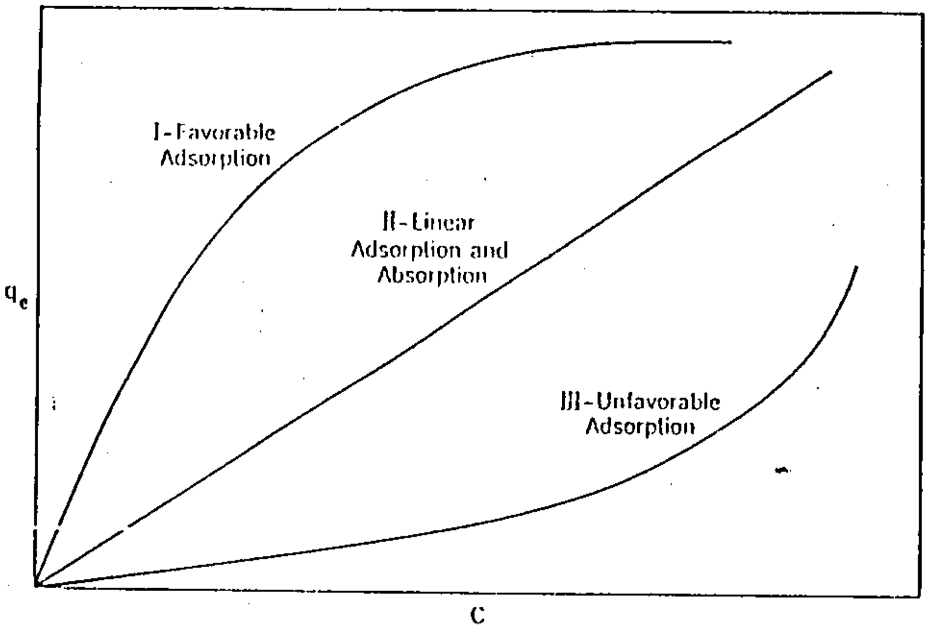
C = is the measured concentration in solution at equilibrium .

qe = the number of moles of solute adsorbed per unit weight at concentration [C]

Q = is the number of moles of solute absorbed per unit weight of adsorbent in forming a complete monolayer on the surface.

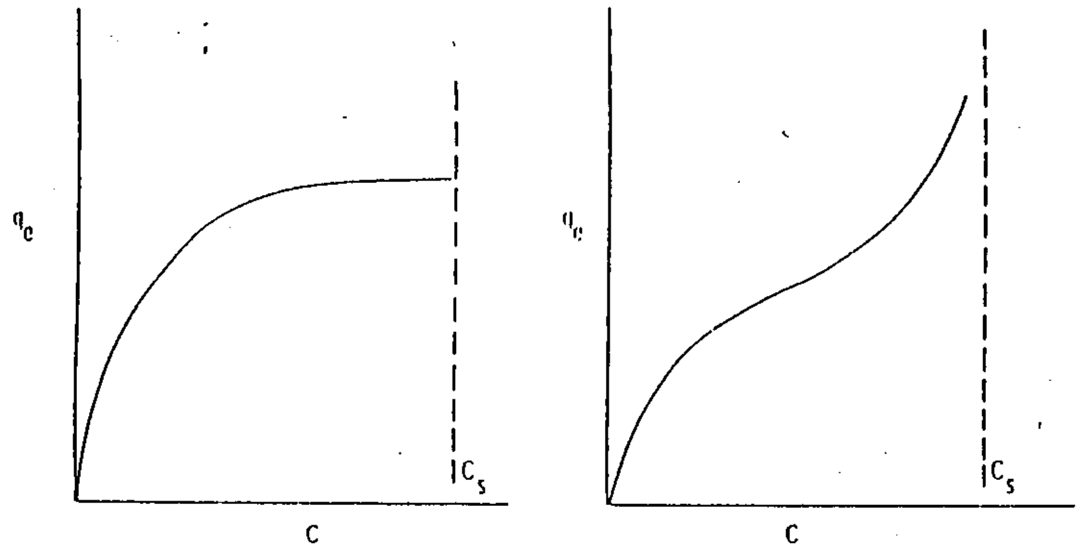
Or in much easier formula , the Langmuir equation (1918) can be written as follows :-

$$x / m = abc / (1 + ac) \quad \ldots\ldots\ldots 3$$



Types of sorption separations.

FIGURE (2.11)

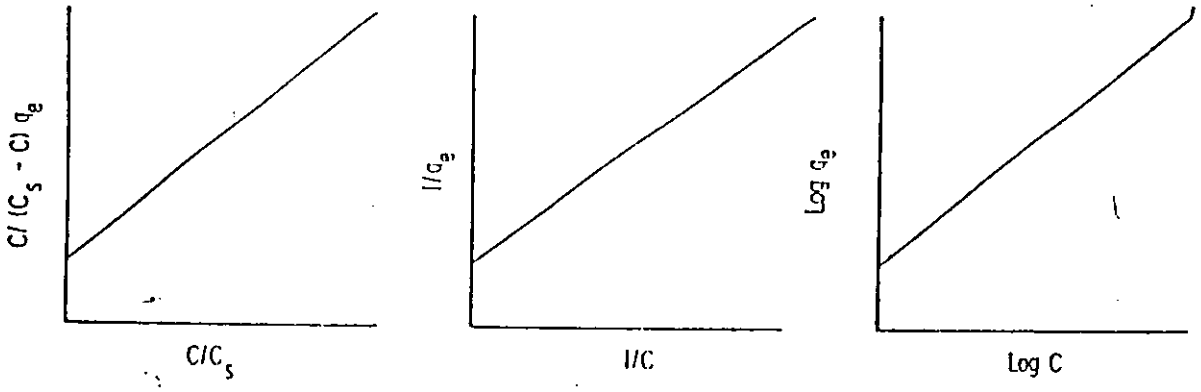


a. - LANGMUIR

b. - B. E. T.

Typical isotherms for Langmuir and BET adsorption patterns.

FIGURE (2.11.5.1)



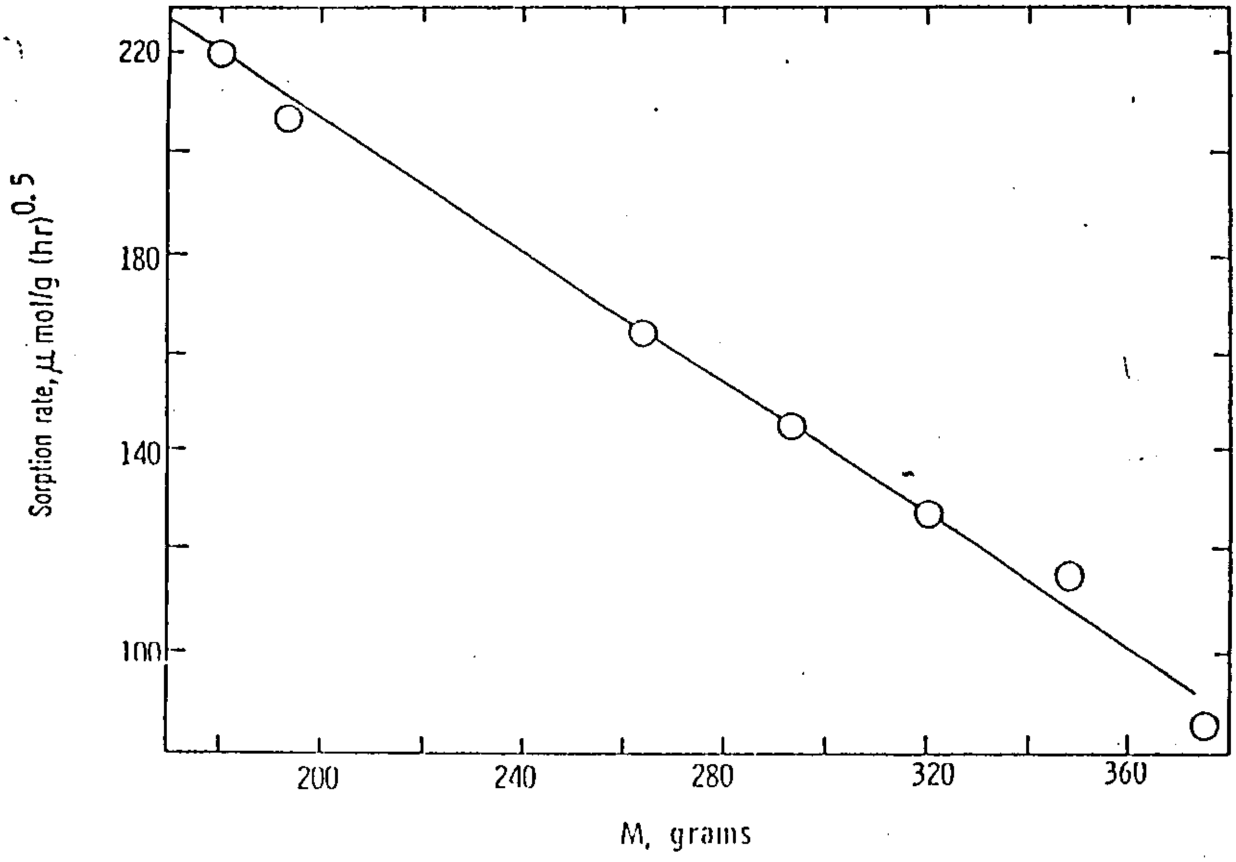
a. - B. E. T.

b. - LANGMUIR

c. - FREUNDLICH

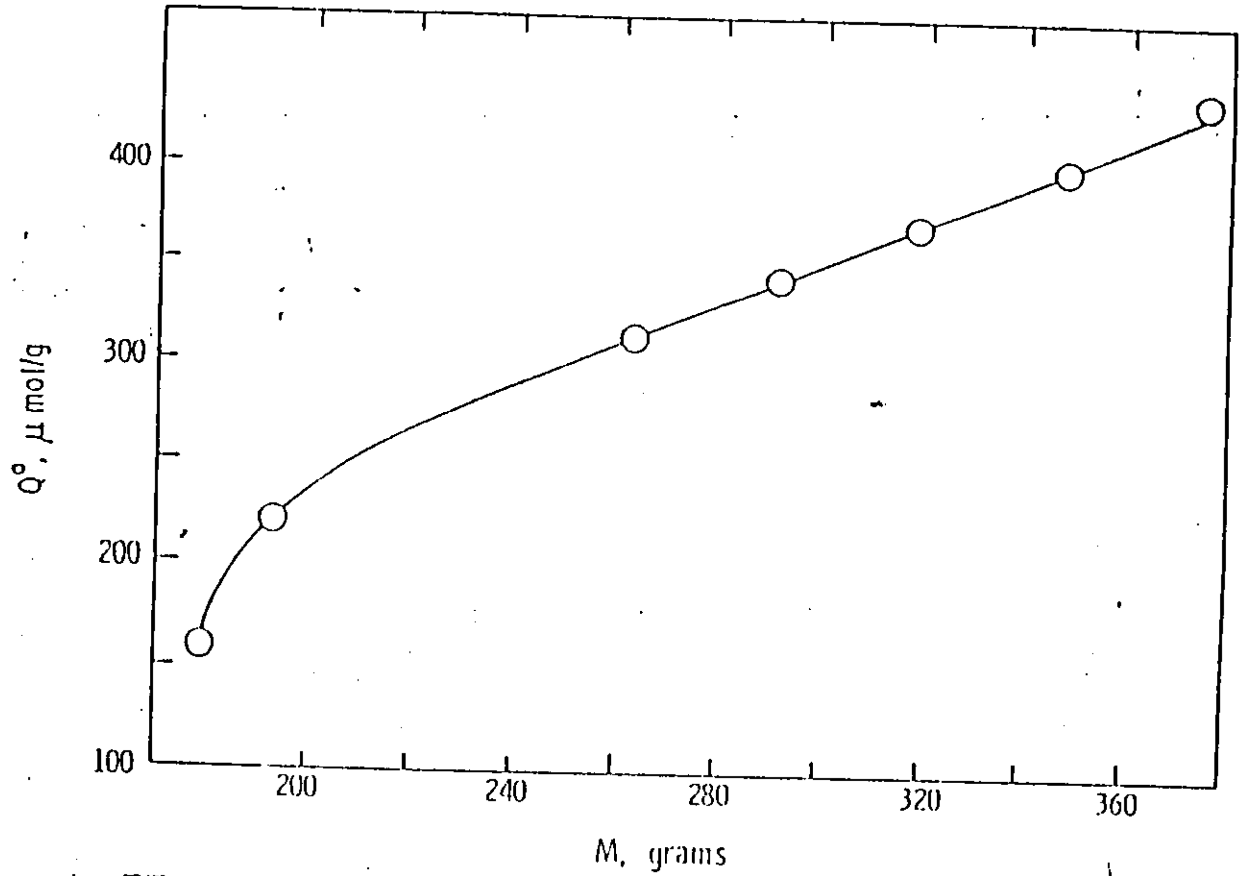
Linear forms for graphical representation of adsorption equations.

FIGURE (2.11.5.2)



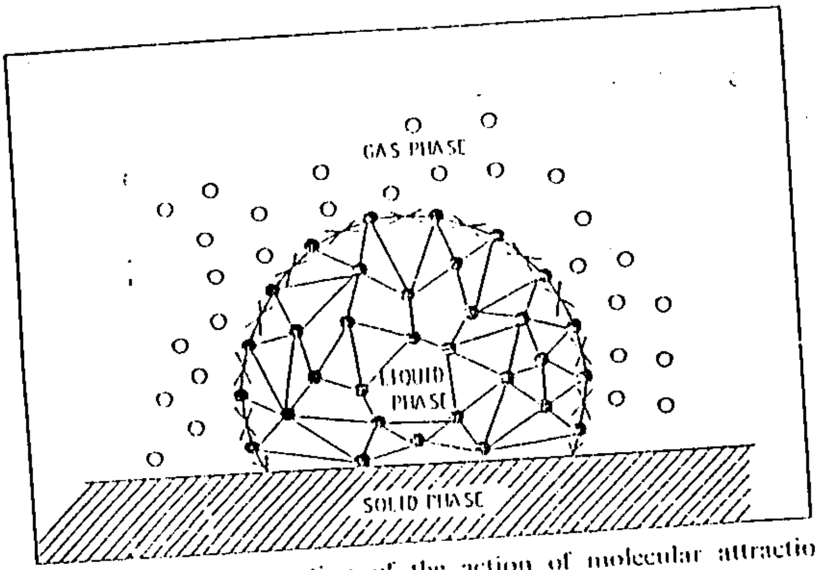
Effect of molecular weight on molar rate of adsorption. (After Weber and Morris, 1963*a*.)

FIGURE (2.11.2) a



Effect of molecular weight on capacity for adsorption. (After Weber and Morris

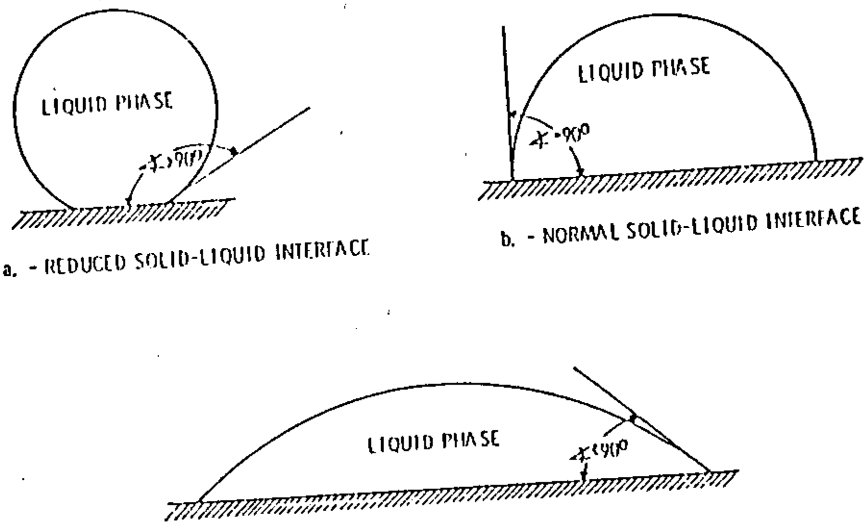
FIGURE (2.11.2) b



Schematic representation of the action of molecular attraction forces to produce surface tension.

FIGURE (2.11.1) a

Adsorption



a. - REDUCED SOLID-LIQUID INTERFACE

b. - NORMAL SOLID-LIQUID INTERFACE

c. - ENLARGED SOLID-LIQUID INTERFACE

Schematic representation of the effects of surface tension on the interface between a liquid and a solid.

FIGURE (2.11.1) b

where :

x = amount of material adsorbed (mg or gm) .

m = weight of adsorbent (mg or gm) .

c = concentration of material remaining in the solution after the adsorption process .

a = constant .

b = constant .

The Langmuir linearized form , is represented in the figure (2.11.5.2) .

2.11.6 Adsorption Of Chlorinated Methanes

The removal of chloromethanes in general from aqueous solutions by adsorption on plastic materials was studied in a seriees of batch experiments . Each type of plastic material was tested with various initial concentrations of each organic contaminant . The performance of granular activated carbon (GAC) was examined too under the same conditions in order to do certain comparisons between the plastic media and the activated carbon (9). An experiment carried out by (C. CookJr And Kenneth E. Hartz) compared the removal of chlorinated methanes by activated carbon and by the plastc media in order to find out relation between these materials . The removal effeciencies from the batch adsorption experiments are presented in table (2.11.6.1) , the plastic material used were polyethelene (PE) , neoprene (NEO) , and polyvinyl chloride (PVC) , Tubing and polyurethane (PU) , size 8 x 30 mesh were used .

Table (2.11.6.1)
Removal Efeciencies Determined From
Batch Adsorption Experiments (14) .

concentration mg/l	adsorbent material	methylene C. percent	chloroform percent
0.1	PE	0	5.52
	NEO	0	17.18
	PVC	5.66	25.77
	PU	3.77	28.33
	GAC	33.02	68.94
1.0	PE	0	4.96
	NEO	0	25.87
	PVC	14.76	45.58
	PU	3.95	46.78
	GAC	89.29	98.94
10.0	PE	0	9.68
	NEO	0	30.84
	PVC	18.01	50.02
	PU	8.69	53.53
	GAC	91.88	92.03

In general the performance of PVC and PU were approximatley equivalent for each concentration of the two organic contaminants . Neither PE nor NEO aforded Detedtable removal of methylene chloride at any concentration , but both removes chloroform . The GAC provided superior removal in each of the batch experiments.

This study proved that plastic adsorbent materials may be used with arying degrees of efficiency in the removal of cloromethanes , on which trihalomethanes are considered part of them . And since plastic media is used in certain stages in both water and wastewater treatment plants , this technique could be tested for the removal of these compounds . wastewater treatments .Trickling media , or flitration media on which could be modified to act as a double purpose media , for example filtration and at the same time adsorption of THM.

CHAPTER THREE

METHODOLOGY
AND
ANALYSIS

Chapter Three
Methedology And Analysis

3.1 Hazardous Organic Compound Analysis

The assessment of the source source , extent and nature of hazardous waste-contamination relies on sophisticated chemical analysis to identify and quantify a wide range of pollutants. For organic compounds , Which is the case in chloroform , these analyses are most often performed using combined gas chromatography some time with , mass spectroscopy (MS) . these GC data are used by environmental scientists and engineers for site evaluation , design of ongiong monitoring programs , and remedial activities (15) .

Once these data are tabulated in engineering reports or stored in data bases , the data are often reviewed interpretively but rarely checked to determine if the compounds have been accurately identified or quantified . It is usually assumed that this has been done in laboratory by the analyst . In reality GC / MS data are most often produced using highly automated instruments , and the new devices are fully computerized systems with very little intervention by experienced spectroscopists . With the exception of priority pollutants , qualitative and quantitative inaccuracy is a widespread in measurements of such chemicals (15).

3.2 Theory Of Chromatography

The gas chromatography analysis is the major, and the recommended method for organocompound analysis by many international agencies , such as the EPA ,and the WHO . There are many chromatographic analysis such as the the gas chromatography (GC) ,, high performance liquid chromatography (HPLC) ...etc , and many others . These methods have the chromatographic principal , as a common factor and because of that it is important to know what is exactly meant by this word.

A RUSSIAN botanist , Mikhaail Tswett , used the word chromatography to describe his separation of plant pigments , which was effected by passing an extract of the pigments through a column packed with calcium carbonate . The result was a series of colored zones on the column thus the name chromatography from the greek word chromatus and graphein , meaning color and " to write" . And since variety of analysis have nothing to do with color , scientists started calling it chromatography . chromatography now refers to any of a diverse group of techniques that effect a separation through a distribution of sample between two different phases . Further qualification is necessary to distinguish between chromatography from other separation techniques , such as extraction .The method in these processes is that one phase is considered stationary while the second one is the mobile phase and though percolate through the first phase (16).

Particularly , the mobile phase is gas or liquid , while the stationary phase is a liquid or solid . The separation of the component , or solutes , of a sample results from difference in thier rates of adsorption solution, or reaction with the mobile and stationary phases . The nature of mobile and stationary phases , the type of interaction between the two phases and the solute , and the physical arrangement of the stationary phase must be considered in distinguishing the many types of chromatography . The physical states of the mobile and stationary phases give rise to four basic types of chromatography :-

1- gas-liquid chromatography (GLC) .
2- gas-solid chromatography (GSC) .
3- liquid liquid chromatography (LLC) .
4- liquid solid chromatography (LSC) .

The two gas systems are independent and not subjected to subdivisions . Thus the terms Gas liquid Chromatography , and Gas solid chromatography identify the techniques involved. The liquid systems are not as easily described and are not mutually exclusive , which can lead to certain confusion . Since the stationary phase could appear for the first time as a solid matter , for example the (Poropack Q) type looks granular media , but it is considered a liquid phase since the the surface of this matter contain a liquid layer. For the purposes of environmental analysis , the chromatographic classification was not structured in order to allow reclassification of these systems , because these systems are improving rapidly and now highly related to the technological improvements . In other words the present classification only describes the process in general.

When one is faced with analyzing a sample using the gas chromatography , this sample requires separation , by separation it is meant that each component of the sample must be separated over the stationary phase . If the sample is relatively simple the separation may be affected by nonchromatographic techniques , such as extraction process , precipitation , distillation . However , if the sample has many components of if the components of interest have similar chemical and physical properties , one of the chromatographic system is generally necessary to accomplish the analysis . The selection of a particular chromatographic system is determined by a variety of factors such as :-

1- nature of sample .

2- available equipment .

3- type of information required .

4- preference of analyst .

The nature of the sample is the first consideration in the choice of a chromatographic method . Frequently the sample alone determines the method . For example , inorganic gases are resolved only by gas chromatography , and solutions of inorganic ions are usually resolved by ion - exchange chromatography . In other words any sample analysis depends on the method to be applied to prepare the sample and / or the availability of different detectors , and this would affect the results of the analysis obtained .

3.2.1 Sensetivity Of Gas Chromatography

Gas chromatography has a number of advantages over the separation techniques . Gas chromatography is fast and extremely sensitive . For example , gas chromatographic analysis of a fraction of a micro liter of a certain pollutant , provides quantitative and quantitative data for some hundred compounds in a very short period of time , even the newly computerized gas chromatographic devises are able to give an exact result with digital and graphical representation . The extreme sensitivity of (G C) is due to the variety of detectors , which are still generally unavailable to other forms of chromatography . However the gas chromatography has severe limitations which are the volatility and stability requirements . The components of interest in a sample must be sufficiently volatile to allow migration through the system at a temperature which dose not induce thermal degradation , although sometimes low volatility is overcomed by using derivative compounds having the same analysis characteristics . In addition the sample should be inert with respect to the mobile phase (gas)(16) .

3.2.2 GC Components And Accessories

The minimum requirements for a gas chromatographic system are a pressurized gas supply (the mobile phase) and a column containing the stationary phase , in order to perform the sample component separation , then a detector with the required type (depending on the sensitivity required and the sample being analyzed) , and finally a recorder to record the data given by the detector . And in the new GCs the whole process is controlled by computer systems (16) . Figure (3.2.1) describes the whole process .

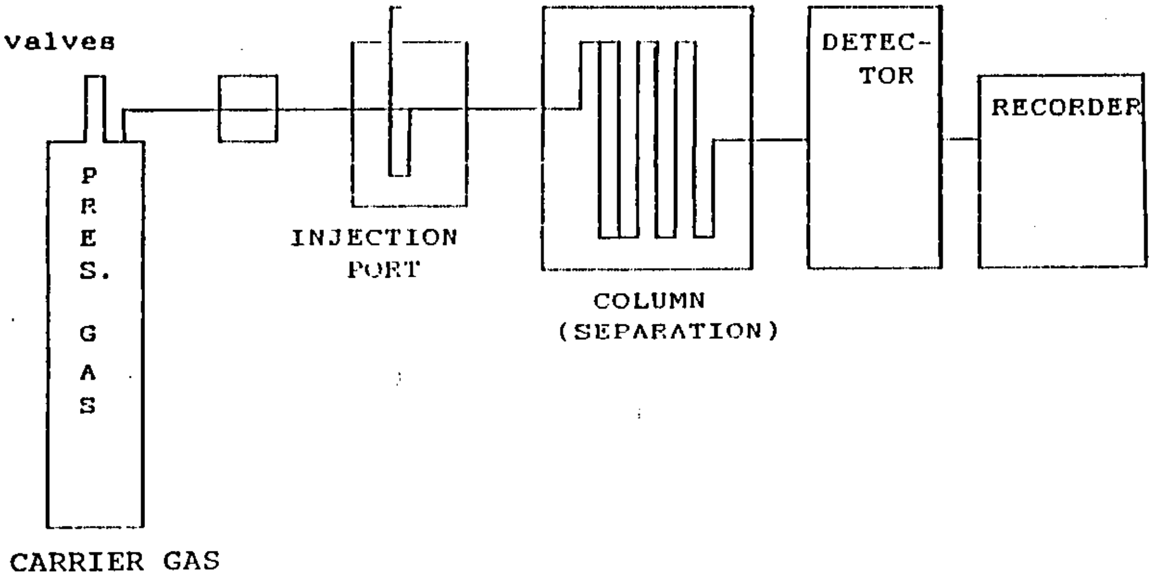


Figure (3.2.1)

Components Of A Gas Chromatography Meter (16).

3.3 Analytical methods

Several methods are available for measurements of trihalomethanes . Some of these are specific for trihalomethanes , and others can be applied for general chlorinated hydrocarbons , and total organic halogens . Most of these methods are fully described in Standard Methods , For examination of water and wastewater (17).

In this study two methods were tested and tried . First , the Liquid Liquid Extraction Gas Chromatographic Method (12) . Second , The Head Space Analysis Method (18).

This method is applicable only to the determination of four trihalomethanes (THMs) which are :-

- chloroform .
- bromodichloromethanes .
- dibromochloromethane .
- bromoform .

In finished drinking water , also in any stage in the treatment process .

3.3.1 General Principle

Sample to be tested is extracted once with solvent and the extract is injected into a gas chromatograph equipped with a linearized electron capture detector for separation and analysis . Extraction analysis type is 10 to 50 min per sample. depending on the analytical conditions and also on the solvents used . When component concentration are greater than 50 micro grams per litter , halogen specific detectors may be used . and at a level below 50 micro thier blanks showed readings greater than 10 micro gram per litter , and that would depend on the expected sample concentration . Accidental sample contamination has been attributed to diffusion of volatile organics through the septum seal on a sample bottle during shipment or storage . Use the sample blank to monitor this problem .

The liquid liquid extraction technique efficiently extracts a wide boiling range of nonpolar organic compounds and also extracts the polar organic components of the sample with varying efficiencies . To analyze rapidly for trihalomethanes with sensitivities in the low microgram per litter concentrations which is the case of this study , the usage of semi-specific electron capture detector and chromatographic columns that have relatively poor resolving power . Because of these concessions the probability of encountering chromatographic interferences is high . The absence of peaks with retention times similar to the trihalomethanes in raw source water analysis is evidence of an interferences - free finished water . If the interferences appeared in a disturbing way ,change the present column and use the alternative columns , and re-analyze (18) .

3.3.3 Detection limits

This method is useful for trihalomethane concentration from approximately 0.5 to 200 micro gram per litter . But actual detection limits are highly dependent on the characteristics of the gas chromatographic system used , and also depends a great deal on the analyst himself .

3.4 Sampling and Storage

Do not add any preservatives at the time of sample collection if maximum trihalomethanes formation is to be measured . If chemical stabilization is not used at time of sampling , add the reducing agent just before extraction the sample . The raw source water sample must be clearly identified in order to figure out the importance chemical addition , in order to eliminate certain compounds which are then , expected to be present in the sample . Then the sample is filled into a seal screw-cap bottles. These bottles or the sample could be filled directly through the tested tubes , which are also sealed screw-cap tubes with an inert septum inside . The sample should be free of entrapped air bubbles , and to achieve that , the bottles or used tubes should be filled to the over flow limit , then the septum screw-cap is placed over the sample . After placing the sample , be sure that no air bubbles still entrained by inverting the sides of the tube , if some small air bubbles are still entrained open the sample and add more drops to the bottle and re-seal it again .

3.4.1 Storage of samples

Store blanks and samples collected at site , in a protected area which is hundred percent free of contamination , as mentioned before , laboratory environment in general is considered a source for trihalomethane contamination . Then the samples should be kept at a temperature equal about (4 C) .If possible analyze the samples within 14 days from the collected date.

If the samples taken just after the chlorination process some reducing agent must be added in order to prevent the formation of (THMs) in the bottles through the storage period. These reducing agents must be selected with care to , prevent the interferences in the GC detectors . In this study collected samples after chlorination , were reduced with sodium thiosulphate , on which will react with the available free chlorine , an so , the analysis of results would be accurate and not misleading . (For more information see sec. 62332 B in Standard Method 7th edition) (18).

After collecting the samples a certain volume is taken and extracted , following the Chloroform extraction method then the sample is located in a separation funnel , on witch the water would be separated from the solvent which extracted the (T H M) from the sample , in this study Chlorofom was the indicator for the presence of trihalomethanes . Then the lower part is collected in the test tubes , and a small quantity is taken about 3 to 7 micro litters of the sample , and then injected in the GC device . At the beginning of this study this procedure was followed , but unfortunately the results obtained were confusing and could not be reliable , plus the incredible interference which appeared in the results . The results were as mentioned above because of the following reasons .

1- Some of the chemicals used in (chloroform extraction) were never found , and because of that alternatives were added instead , and also some chemicals used were not GC grade .

2- The gas chromatography used deals with pesticide analysis in general (located in the Pesticides Inspection department , in Albaqa area) , and here chloroform is used as solvent matter. And when the column was changed the readings were not clear , as if no separation is taking place over the column.

3- Lak of confidence shown by the analyst working in that station , because they are not familiar in dealing with residual concentrations in (parts per billion) ppb , because the routine work deals with the (parts per million) ppm .

Because of the problems mentioned above , it was impossible to be confident of the results obtained . Because we are talking about very low residual concentration witch is presented in parts per billion . Because of that this procedure and the results were discarded . And though a second procedure was tried.

3.5 The Head Space Sampling

The US Environmental Protection Agency 's (USEPA) recommended method for analysis of volatile priority pollutants in water and waste water (method 624) which utilize the Purge and trap technology with packed chromatographic columns . It has been shown that fused silica columns produce much better peak resolution and that the resolution of volatile compounds can be improved further with the use of capillary traping method (for exact method of traping and purge techniques see ref (18)) .

The advantages of headspace sampling over other methods of analysis include minimal sample preparation , injection of larger samples amounts into the system , and shorter analysis times because all compounds being analyzed are volatile . This method as clearly mentioned above , would be sufficiently used for volatile organic analysis . Head space sampling coupled with column gas chromatography and electron capture detector, has demonstrated excellent precession for halocarbon analysis . This technique was also recommended and used by the British engineers too (London ql Her Majesty's Stationary Office) . a full description of the process is represented below . This method Is used to determine the concentration of trace Volatile Haloginated solvents in drinking and river waters.

3.5.1 Basis Of Method

This method is based upon the equilibration of sample with its headspace vapour under controlled conditions. Then The vapour of the sample is injected into a gas Chromatograhy fitted with an electron capture detector . Using this simple technique would compensate for the injection of the extracted solvent if the extraction method was used , and here all the problems associated with extraction would be discarded . And also the results would be reliable since minimal interferences is expected.

3.6 Range Of Application & Calibration Curves

In order to be able to perform the exact analysis a certain calibration curve must be performed . This calibration curve is basically a graph showing the relation ship of standard concentration , and thier peak height response over the used GC . This curve would be used later on to figure out the concentration of a certain compound after knowing the peak height . Some GC (Column Type) some times are based the area under the peak rather than the peak height , if the peak was not sharp . It is preferable to get a linear relation ship , and that may be achieved by drawing the exact figures , or using semi log scale , or even log log scale . The range of the calibration curve can be extended by injecting a smaller sample or by using the non - linear portion of the calibration curve .

Table (3.6.1)
Limits of detection of the Head Space method (1) (18).

Compound	limit of detection micro gram per litter
dichloroethylene	0.60
trichloroethane	0.60
trichloroethane	2.0
tetrachloroethylene	1.6
tetrachloroethane	0.57
carbon tetrachloride	0.13
* trichloroethylene	1.0
* chloroform	==> 0.66 <==
* dibromochloromethane	0.45
* bromoform	0.7

* = trihalomethanes

Interferences And Contamination

Any compound which has a similar retention time to the determinand and which gives a detector response will interfere . Some of the determinands do not completely separate on a single GC column and the use of two more columns is usually necessary with certain compounds . Laboratory atmosphere contains traces of chlorinated solvents (particularly chloroform and carbon tetrachloride) which give rise to high bank values . In these circumstances the sample can be taken directly into the sample vails , or poured from the sample bottles . Syringes may also show a certain effect , to over come these problems , Perform analysis for blank samples . Or Clean all used equipment with sulfuric acid , and then with distilled water and after that use a furnace with a temperature about 400 degrees , keep all used equipment in the furnace for 24 hrs . This way of cleaning will assure the analyst that all the used tools are chloroform free ,and ready to be used.

3.7 Hazards

The used chemicals , especially chloroform are Toxic Narcotic , and Carcinogenic . Don't Even Open Pure Compound In A Closed Environment Such As The Lab. (OPEN ONLY UNDER NIOSH / MESA APPROVED TOXIC GAS RESPIRATOR OR UNDER TOXIC GAS HOODS) .

3.8 Apparatus And Reagents

- Sample vials : 30 ml glass screw capped tubes fitted with a teflon -faced silicon rubber cap .
- Syringe : 1 ml pressure - lock gas tight syringe fitted with an open / close valve .
- water bath : capable of being maintained at 25 + 0.2 degrees .

- Gas chromatography : Packed column instrument operated isothermally and fitted with an electron capture detector.

3.9 Experimental Procedure

To achieve the objectives of this study , the work was divided into two parts .

i- Part one of this study is to investigate the presence of the Trihalomethanes In treated wastewater .

ii- The second part , is to study different removal techniques . The first part of the study was carried out , by collecting treated wastewater samples from different locations within the treatment plant and from different , locations after being treated (from the main line of effluent flow) .

3.9.1 Collection Preparation , And Storage of Samples.

Samples from different locations , were collected using clean screw cap tubes . The used tubes were filled to the top and using the screw cap the tubes were sealed in order to prevent any air bubbles inside the tubes . Then these tubes are stored at a temperature of 4 C . Sodiumthiosulphate was added to the samples which were collected after the chlorination process . Because these samples are believed to have residual chlorine , Sodiumthiosulphate was added to react with the residual chlorine , in order to prevent the formation of trihalomethanes in the samples under captivity . Because many experiments showed that trihalomethanes will form in the presence of chlorine and organic matters . Then these samples were tested using the GC as mentioned in section (3.5.1).

The second part of this study was the study of selected removal techniques . The following removal techniques were studied .

1- Diffused Aeration .
2- Mechanical Surface aeration .
3- Adsorption (batch) using the following adsorbers .
   a- Antracite .
   b- Activated Carbon .
   c- Jordanian Zeolite .

3.9.2 Preparation Of Stock Solution

Stock solution of 100 ppm of chloroform (the predominant trihalomethane compound) was prepared by using (GC grade) pure chlorofom and (GC grade) pure methanol . The reason for using methanol is because chloroform is very soluble in methanol , and methanol is more stable if compared with chloroform , and also have no interferences on the tested column of the GC . Then working standards of chloroform were prepared by taking dilution from the 100 ppm solution in distilled water . The working standards were used to draw the calibration curves , between the GC peak heights and chloroform concentrations . Validity of the 100 ppm stock solution is one month if stored at temp. of 4 C .

3.10 Diffused Aeration

The following procedure was used to study the removal of chloroform by diffused aeration .

1- A volume of 5 litters of distilled water was used to prepare a stock solution of 80 ppb of chloroform . This is done by using 4 ml of the stock solution of 100 ppm of .

2- The pH of the water is calibrated on the required pH .

3- A controllable air flow diffusers was placed in the middle of the 5 litters jar .

4- The jar with the diffusers is placed under the hood .

5- The air flow is fixed on the desired air flow rate .

6- Blank sample is taken before starting (at time zero).

7- Then 10 ml samples were collected from the diffused jar at different periods of times , and sealed immediately with no air bubbles inside the tubes .

8- Then the 10 ml samples are stored at a tem. of 4 C , and then the samples were tested using the GC .

9- The whole procedure was repeated for three different pH in order to figure out weather , the process is affected by the value of pH or not .

3.11 Mechanical Surface Aeration

The mechanical surface aeration procedure is the same procedure followed in the diffused aeration , but instead of using the diffusers an electrical , surface aerator was used with a certain air flow . After placing the electrical aerator and the 5 litter jar , under the hood , a blank sample was taken at time zero (before starting aeration). And then , 10 ml samples were taken from the jar, and sealed with no air bubbles inside , after different time periods . Then the 10 ml samples were tested using the GC .

3.12 Chloroform removal by adsorption

Removing chloroform by adsorption was tried in this study , the following factors were studied .

1- The following adsorbers were studied .

A- Antracite .

B- Activated carbon .

C- Jordanian zeolite .

2- Two different sizes , of each adsorber was tried, both granular ,(passing sieve 1.7 mm retained over sieve 200), and powdered size ,(passing sieve 200 (.075 mm).

3- For each adsorber , three different pH were studied , the acidic pH (pH 3) , Neutral pH (pH 8) , and the alkaline pH (pH 11). In order to find out the pH effect over the removal efficiency .

3.12.1 Adsorption process .

Only batch system was carried out in this study , because the best technique for chloroform removal , is by air stripping. And if column adsorption was used , the results would be misleading . Since it is impossible to tell , whether the removal was due to adsorption , or was in due to air stripping while falling over the adsorber . The process is presented in chapter five.

CHAPTER FOUR

EXPERIMENTAL WORK AND RESULTS

CHAPTER FOUR
EXPERIMENTAL WORK AND RESULTS

4.1 Experimental Procedure

To achieve the objectives of this study , the work was divided into two parts .

i- Part one of this study is to investigate the presence of the Trihalomethanes In treated wastewater .

ii- The second part , is to study different removal techniques .

The first part of the study was carried out , by collecting treated wastewater samples from different locations within the treatment plant and from different , locations after being treated (from the main line of effluent flow) .

4.2 Collection Preparation , And Storage of Samples.

Samples from different locations , were collected using clean screw cap tubes . The used tubes were filled to the top and using the screw cap the tubes were sealed in order to prevent any air bubbles inside the tubes . Then these tubes are stored at a temperature of 4 C . Sodiumthiosulphate was added to the samples which were collected after the chlorination process . Because these samples ' are believed to have residual chlorine , Sodiumthiosulphate was added to react with the residual chlorine , in order to prevent the formation of trihalomethanes in the samples under captivity . Because many experiments showed that trihalomethanes will form in the presence of chlorine and organic matters . Then these samples were tested using the GC as mentioned in section (3.5.1). The second part of this study was the study of selected removal techniques . The following removal techniques were studied .

1- Diffused Aeration .
2- Mechanical Surface aeration .
3- Adsorption (batch) using the following adsorbers .
    a- Antracite .
    b- Activated Carbon .
    c- Jordanian Zeolite .

4.3 Preparation Of Stock Solution

Stock solution of 100 ppm of chloroform (the predominant trihalomethane compound) was prepared by using (GC grade) pure chlorofom and (GC grade) pure methanol . The reason for using methanol is because chloroform is very soluble in methanol , and methanol is more stable if compared with chloroform , and also have no interferences on the tested column of the GC . Then working standards of chloroform were prepared by taking dilution from the 100 ppm solution in distilled water . The working standards were used to draw the calibration curves , between the GC peak heights and chloroform concentrations . Validity of the 100 ppm stock solution is one month if stored at temp. of 4 C .

4.4 Diffused Aeration

The following procedure was used to study the removal of chloroform by diffused aeration .

1- A volume of 5 litters of distilled water was used to prepare a stock solution of 80 ppb of chloroform . This is done by using 4 ml of the stock solution of 100 ppm of .

2- The pH of the water is calibrated on the required pH . Because three different pH was tested :-

a- pH 3 (acidic).
b- pH 8 (Neutral).
c- pH 11 (alkaline).

3- A controllable air flow diffusers was placed in the middle of the 5 litters jar .
4- The jar with the diffusers is placed under the hood .
5- The air flow is fixed on the desired air flow rate .
6- Blank sample is taken before starting (at time zero).
7- Then 10 ml samples were collected from the diffused jar at different periods of times , and sealed immediately with no air bubbles inside the tubes .
8- Then the 10 ml samples are stored at a tem. of 4 C , and then the samples were tested using the GC .

9- The whole procedure was repeated for three different pH in order to figure out weather , the process is affected by the value of pH or not .

4.5 Mechanical Surface Aeration

For The mechanical surface aeration procedure , the same procedure followed in the diffused aeration was adopted , but instead of using the diffusers an electrical , surface aerator was used with a certain air flow . After placing the electrical aerator and the 5 litter jar , under the hood , a blank sample was taken at time zero (before starting aeration) . And then , 10 ml samples were taken from the jar, and sealed with no air bubbles inside , after different time periods . Then the 10 ml samples were tested using the GC .

4.6 Chloroform removal by adsorption

Removing chloroform by adsorption was tried in this study , the following Cases were studied .

1- Different adsorbers were studied .

  A- Antracite .

  B- Activated carbon .

  C- Jordanian zeolite .

2- Different sizes : , two sizes of each adsorber was tried , both granular ,(passing sieve 1.7 mm retained over sieve 200), and powdered size ,(passing sieve 200 (.075 mm).

3- Different pH : For each adsorber , three different pH were studied , the acidic pH (pH 3) , Neutral pH (pH 8) , and the alkaline pH (pH 11). In order to find out the pH effect over the adsorption efficiency .

4.6.1 Adsorption process .

Only batch system was carried out in this study , because of the volatility of chloroform , so if column adsorption was used , the results would be misleading . Since it is impossible to tell , then whether the removal was due to adsorption , or was in due to air stripping while falling over the adsorber .

4.7 EXPERIMENTAL RESULTS

4.7.1 Experimental Results For Chloroform Removal By Diffused Aeration

As mentioned before , diffused aeration process was carried out and the results are summarized in table (4.8.1) the results results in table (4.8.1) are represented in figure (4.8.2) from this figure , it is clear that chloroform can be easily removed by this method . Kla was computed for diffused aeration and it was found to be around (0.064). The best removal percentages started to take place after 10 minutes from aeration . This process was very efficient in removing chloroform . The achieved removal efficiency was about 98 % . As can be noticed from the figures , pH value here did not affect the removal

Table (4.8.1) a
Removal of chloroform by
diffused areation

flow = 4 litters per minuts

Batch system initial volume = 5 litters

aeration time (min)	GC Peak Hieght milimeters pH 3	 pH 8	 pH 11
0.00	278.00	278.00	278.00
1.00	269.00	246.00	250.00
2.00	262.00	273.00	237.00
3.00	260.00	189.00	229.00
4.00	250.00	205.00	218.00
5:00	243.00	189.00	203.00
10.00	163.00	118.00	159.00
20.00	70.00	51.00	87.00
30.00	34.00	24.00	46.00
40.00	13.00	9.60	23.00
50.00	35.00	6.40	18.00
60.00	6.80	3.60	12.00
70.00	4.80	2.80	7.20
80.00	17.00	1.60	6.00
90.00	6.00	1.60	7.00
100.00	6.00	1.60	7.00
110.00	4.40	1.60	7.00
120.00	4.00	1.60	7.00

Table (4.8.1) b
Removal of chloroform by
diffused areation

flow = 4 litters per minuts

Batch system initial volume = 5 litters

aeration time (min)	Concentration in PPb pH 3	pH 8	pH 11
0.00	80.00	80.00	80.00
1.00	73.00	79.00	64.00
2.00	68.00	46.00	61.00
3.00	68.00	56.00	56.00
4.00	65.00	49.00	49.00
5.00	63.00	44.00	49.00
10.00	35.00	30.00	30.00
20.00	17.00	13.00	30.00
30.00	9.00	6.00	9.50
40.00	8.00	3.00	6.00
50.00	2.80	2.00	4.00
60.00	2.80	2.00	3.00
70.00	2.80	1.50	2.10
80.00	2.80	1.00	2.00
90.00	2.80	1.00	2.00
100.00	2.80	1.00	2.00
110.00	2.80	1.00	2.00
120.00	2.80	1.00	2.00

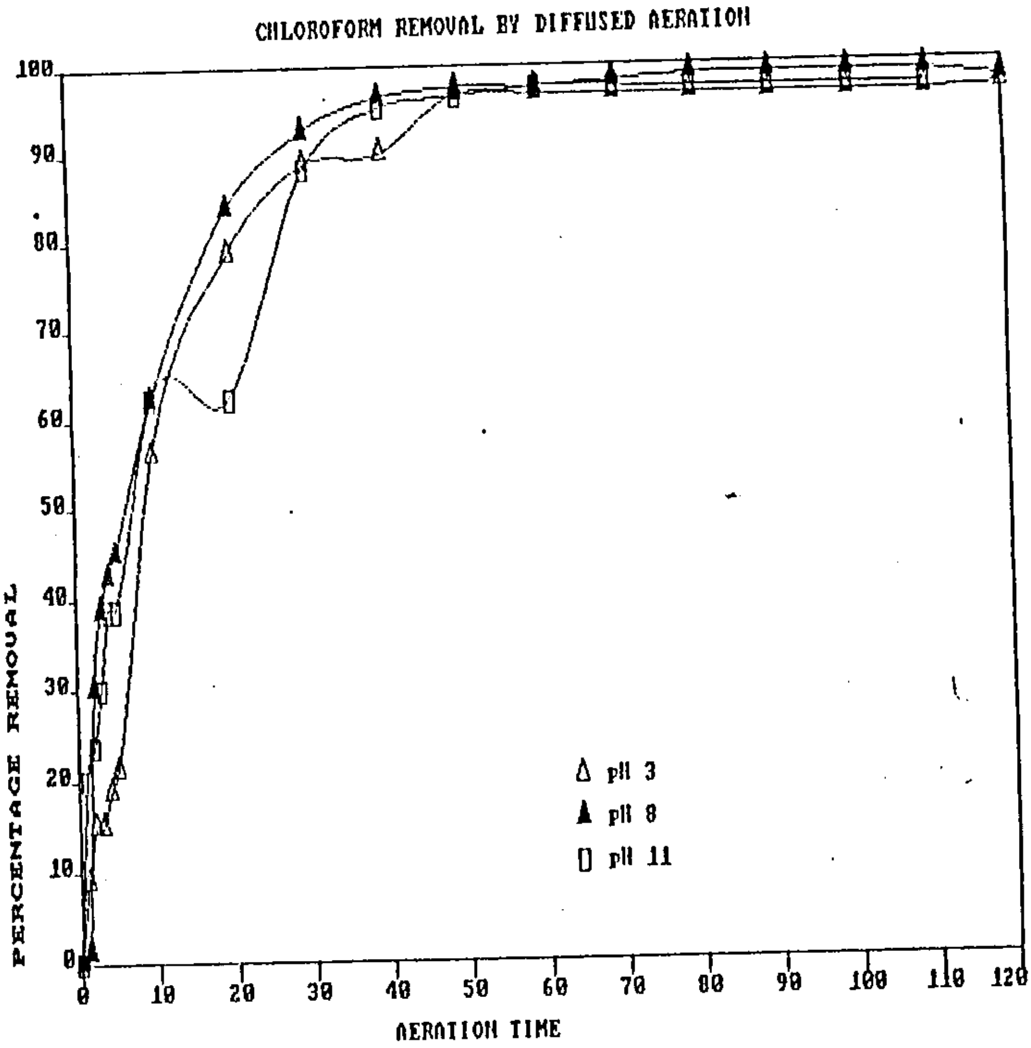

CHLOROFORM REMOVAL BY DIFFUSED AERATION
PERCENTAGE REMOVAL
AERATION TIME
0
10
20
30
40
50
60
70
80
90
100
110
120
Δ pH 3
▲ pH 8
▯ pH 11

FIGURE (4.8.2)

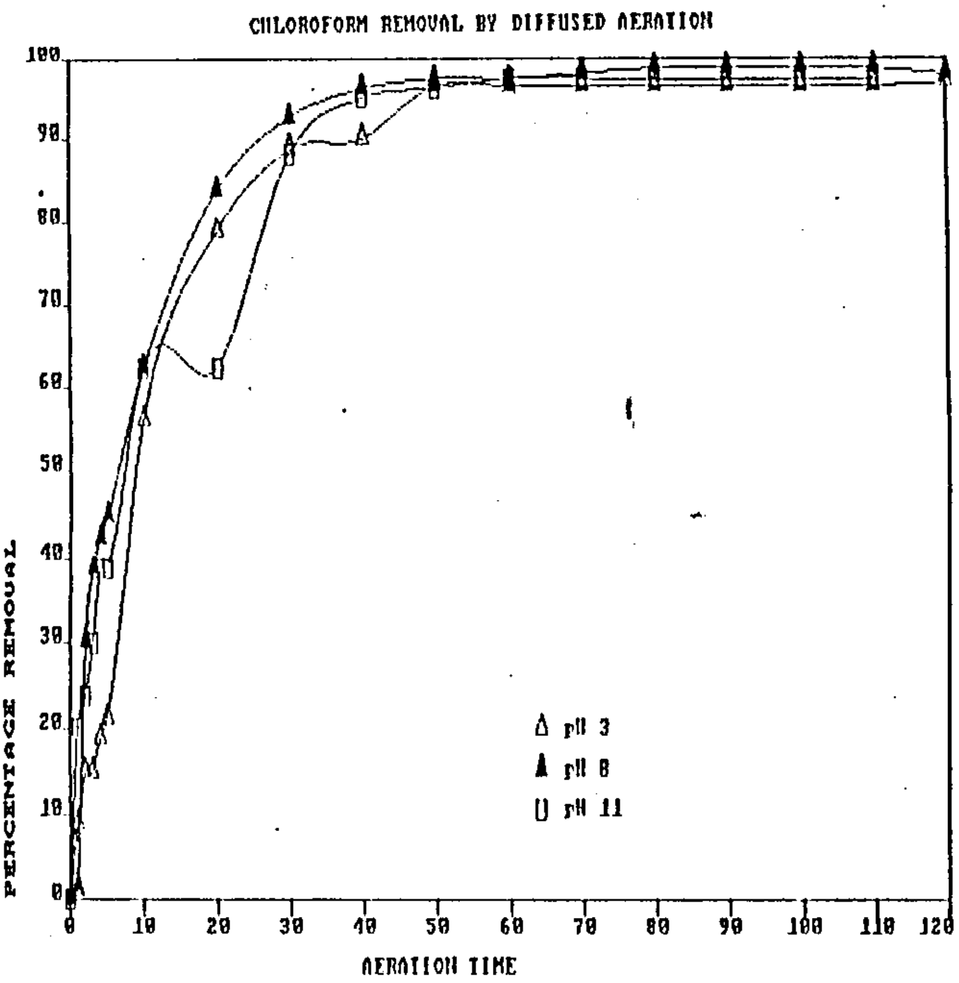

CHLOROFORM REMOVAL BY DIFFUSED AERATION
PERCENTAGE REMOVAL
AERATION TIME
0
10
20
30
40
50
60
70
80
90
100
110
120
△ pH 3
▲ pH 8
▯ pH 11

FIGURE (4.8.2)

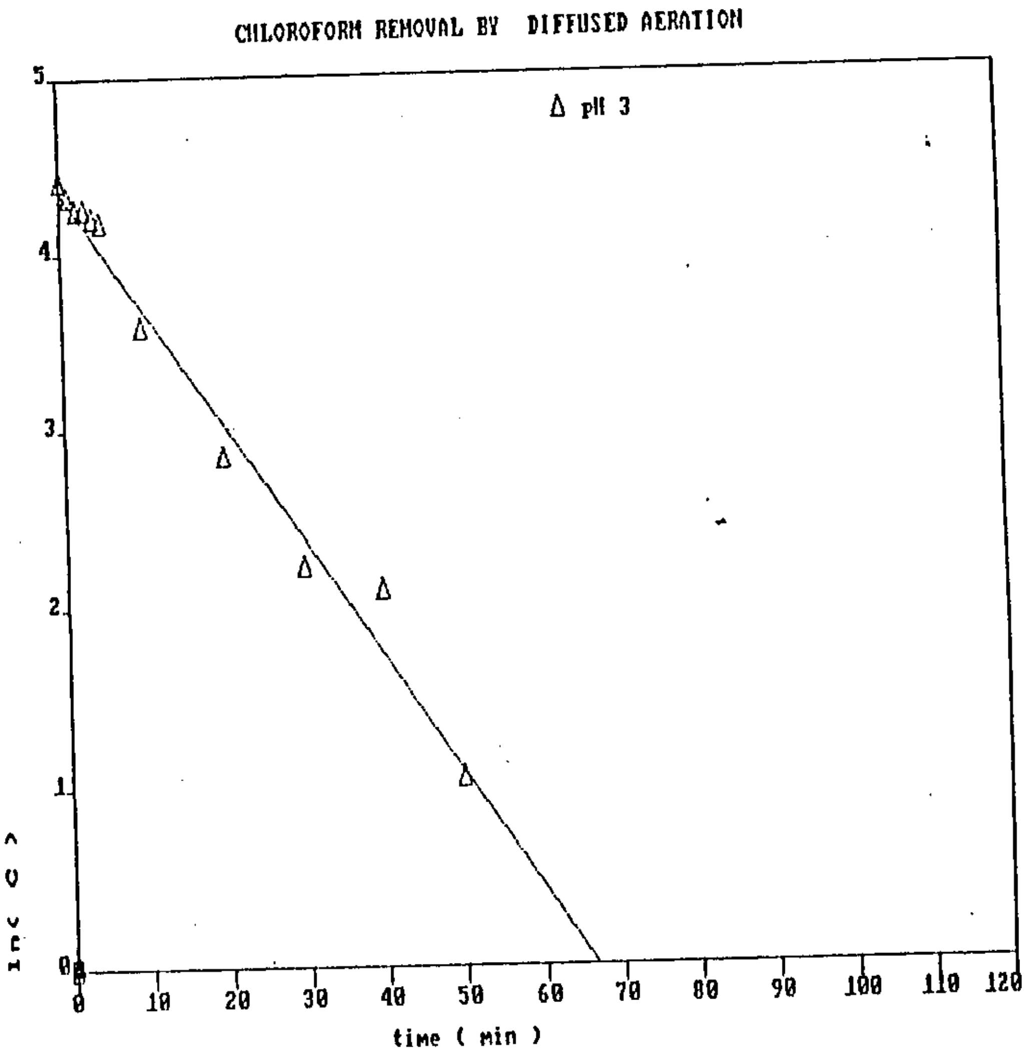


FIGURE (4.8.2)a2

CHLOROFORM REMOVAL BY DIFFUSED AERATION

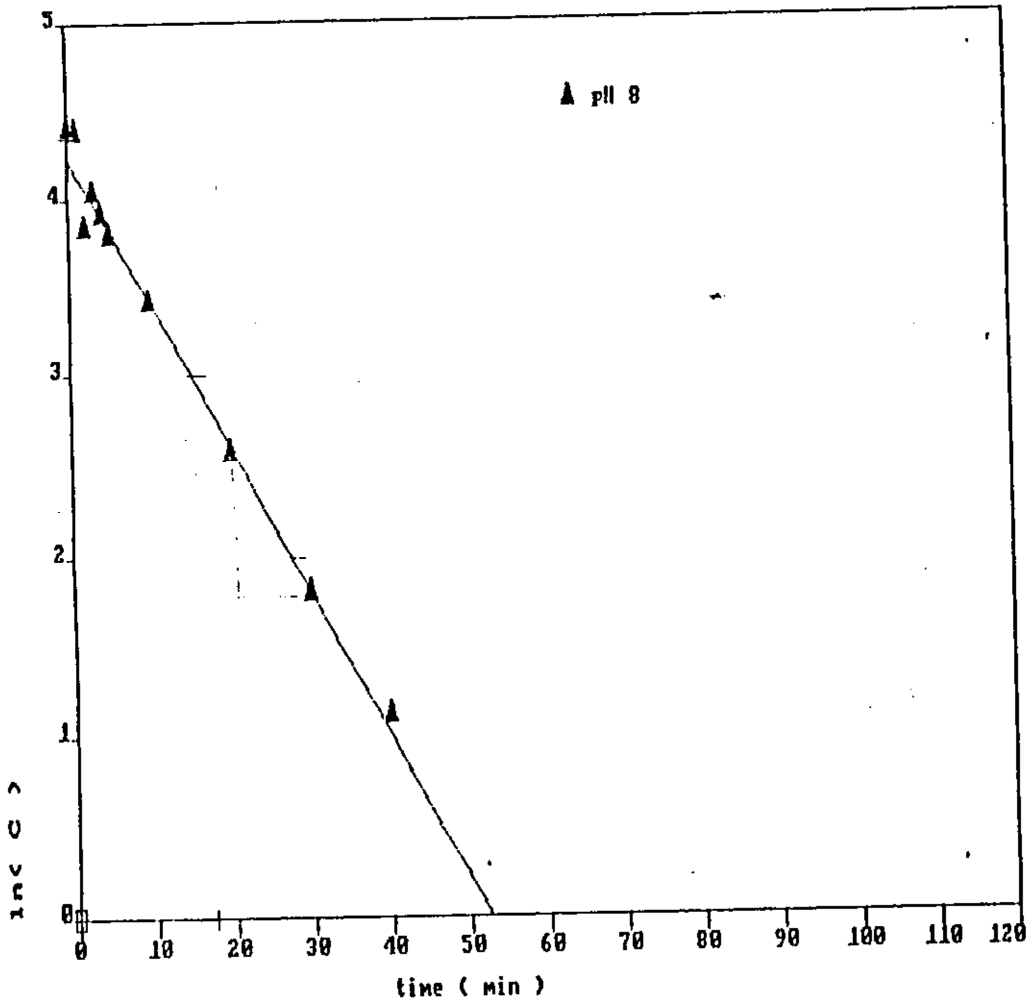


FIGURE (4.8.2)a3

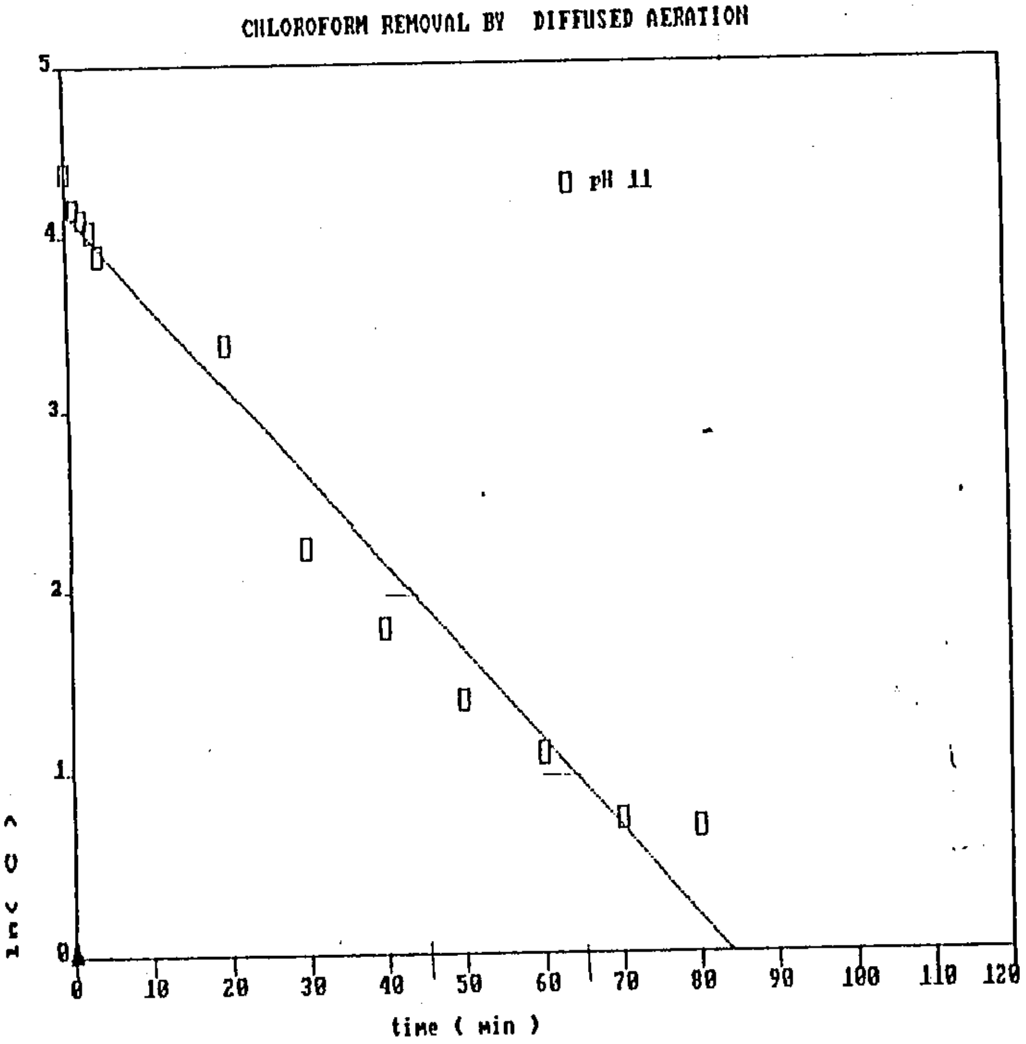


FIGURE (4.8.2)a4

efficiency in an apparent way . From some testing experiments it was proved that the rate of chloroform removal is affected mainly by the rate of air flow in the diffusers .

4.7.2 Experimental results For Chloroform Removal By Mechanical Surface Aeration

Results for the removal of chloroform by mechanical surface aeration was also carried out here .The results are presented in table (4.8.3) . And the results in the tables are represented in figure (4.8.4) . Unfortunately the used surface aerator blades , were designed for mixing and not for aeration . This is the reason explaining the results in figure (4.8.4) . The removal efficiency was excellent , it was about 96% and the removal rate started accelerating after the first 10 minutes . But sort of equilibrium took place . Since as can be seen in figure (4.8.4) the removal percentages is reduced to a level and then comes to a level on which no removal is being achieved by aeration . The reason here is not clear , since , the used aerators are originally mixers and the amount air volume used is not known too . And Secondly the motors used are not controllable , nor the house power of them is known. The only aim for using the mechanical surface aeration , in this study is to figure out weather chloroform removal in this , process is efficient or not , and as can be seen from the the accompanied figures , this

Table (4.8.3)a
chloroform remmoval by surface aeration

Initial volume = 5 litters

mechanical surface aeration time	GC PEAK HIEGHT (mm)		
	pH 3	pH 8	pH 11
0.000	255.000	280.000	280.000
1.000	181.000	277.000	224.000
2.000	125.000	246.000	184.000
3.000	85.000	200.000	143.000
4.000	61.000	162.000	118.000
5.000	56.000	126.000	45.000
10.000	8.000	80.000	30.000
20.000	4.000	53.000	15.000
30.000	3.500	38.000	10.000
40.000	3.200	38.000	48.000
50.000	3.200	38.000	6.400
60.000	3.200	38.000	2.000
70.000	3.200	38.000	2.000
80.000	3.200	38.000	2.000
90.000	3.200	38.000	2.000

Table (4.8.3)b
chloroform remmoval by surface aeration

Initial volume = 5 litters

mechanical surface aeration time	Final Concentration In PPb		
	pH 3	pH 8	pH 11
0.000	80.000	80.000	80.000
1.000	42.000	75.000	74.000
2.000	25.000	48.000	61.000
3.000	16.000	42.000	50.000
4.000	12.000	26.000	38.000
5.000	10.000	9.500	27.000
10.000	3.000	6.500	16.000
20.000	2.000	4.000	10.000
30.000	2.000	3.500	7.000
40.000	2.000	1.500	7.000
50.000	2.000	1.500	7.000
60.000	2.000	1.500	7.000
70.000	2.000	1.500	7.000
80.000	2.000	1.500	7.000
90.000	2.000	1.500	7.000

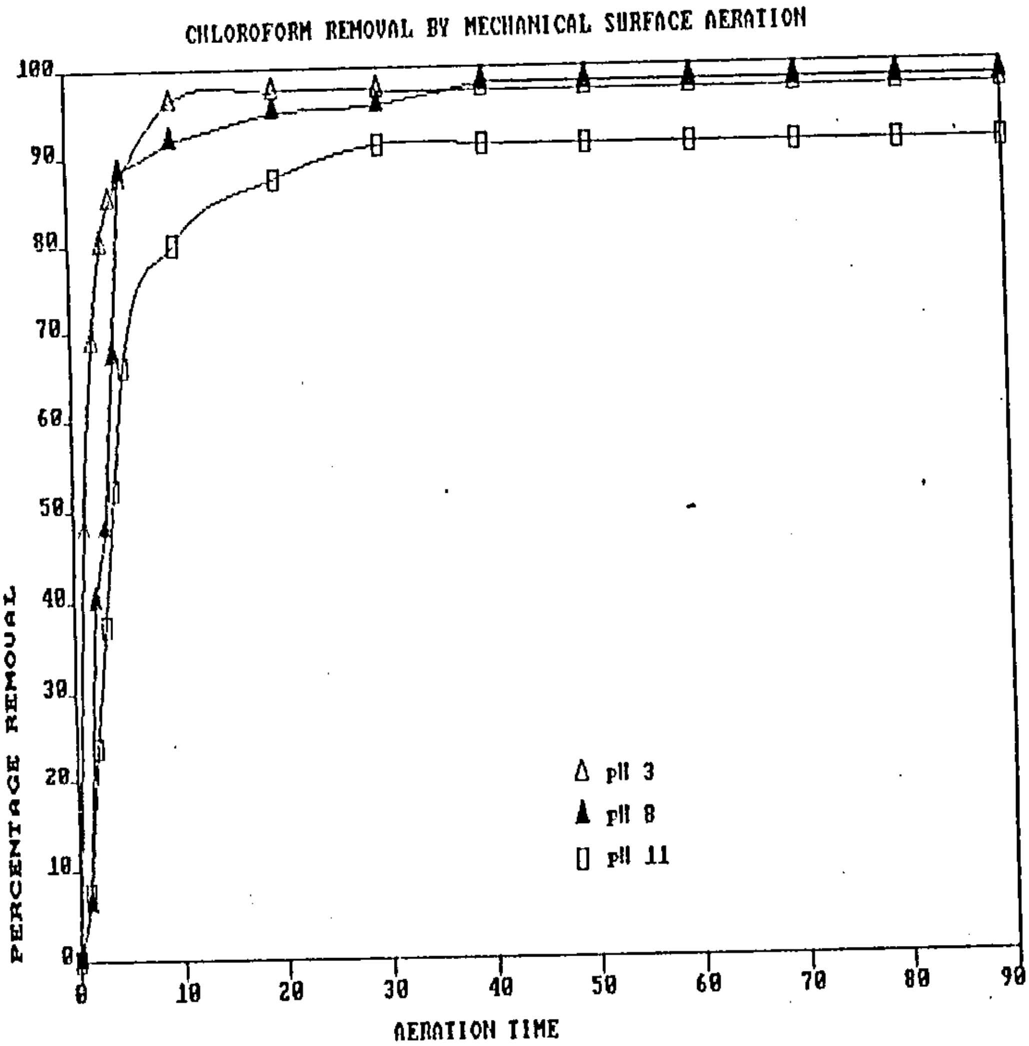

CHLOROFORM REMOVAL BY MECHANICAL SURFACE AERATION
PERCENTAGE REMOVAL
AERATION TIME
0
10
20
30
40
50
60
70
80
90
100
Δ pH 3
▲ pH 8
▯ pH 11

FIGURE (4.8.4)

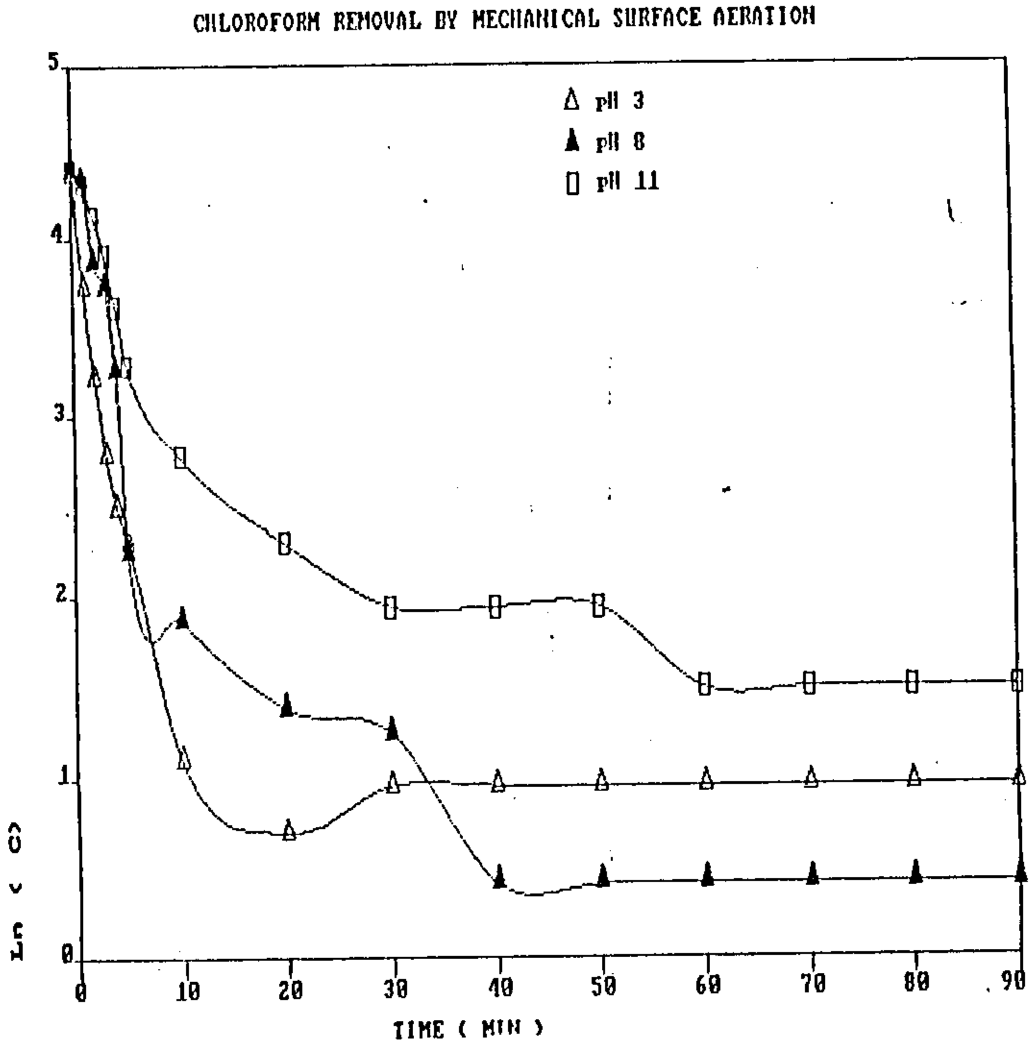

CHLOROFORM REMOVAL BY MECHANICAL SURFACE AERATION
△ pH 3
▲ pH 8
▯ pH 11
Ln (C)
0
1
2
3
4
5
0
10
20
30
40
50
60
70
80
90
TIME (MIN)

FIGURE (4.8.4)a

process was very efficient in removing chloroform .

4.8 Experimental results For ChloroForm Removal By Adsorption

4.8.1 Using Antracite As An Adsorber

In this Study Antracite was used as an adsorber for two different sizes , powdered (passing sieve 200) , and granular size , (passing sieve size 1.7mm and retaining on sieve 200) . As mentioned latter only batch reactor was used . Results Are shown in table (4.9.1) for powdered and in table (4.9.2) for granular size of antracite . From figures (4.9.3) and (4.9.4) it is clear that powdered size was able achieve a removal efficiency of about (96 %) and the value of pH showed no effect . While using the granular size here showed a removal efficiency of about 67 % , and the the value of pH showed a a clear difference , since the best removal was when the pH value was (3) and (8) while when the pH value was 11 only 33 % of removal efficiency was achieved using the same dose (0.8 grams).

Table (4.9.1)a
Antracite Dose [granular]

Antracite wieght [grams]	G C Peak Hieght milimeters		
	pH 11	pH 8	pH 3
0.00	278.00	278.00	278.00
0.10	273.00	273.00	252.00
0.20	270.00	256.00	250.00
0.30	269.00	240.00	240.00
0.40	265.00	240.00	234.00
0.50	262.00	208.00	208.00
0.60	250.00	221.00	202.00
0.70	245.00	221.00	202.00
0.80	235.00	125.00	125.00
0.90	230.00	125.00	120.00
1.00	224.00	125.00	119.00

Table (4.9.1)b
Antracite Dose [granular]

Antracite wieght [grams]	Final concentration in ppb		
	pH 11	pH 8	pH 3
0.00	80.00	80.00	80.00
0.10	80.00	79.00	65.00
0.20	73.00	60.00	64.00
0.30	73.00	62.00	62.00
0.40	70.00	62.00	61.00
0.50	68.00	56.00	56.00
0.60	65.00	55.00	49.00
0.70	63.00	55.00	49.00
0.80	57.00	27.00	30.00
0.90	56.00	27.00	26.00
1.00	55.00	27.00	26.00

Table (4.9.1)c
Antracite Dose [granular]

Antracite wieght [grams]	G C Peak Hieght milimeters		
	pH 11	pH 8	pH 3
0.00	0.00	0.00	0.00
0.10	0.00	1.25	18.75
0.20	8.75	25.00	20.00
0.30	8.75	22.50	22.50
0.40	12.50	22.50	23.75
0.50	15.00	30.00	30.00
0.60	18.75	31.25	38.75
0.70	21.25	31.25	38.75
0.80	28.75	66.25	62.50
0.90	30.00	66.25	67.50
1.00	31.25	66.25	67.50

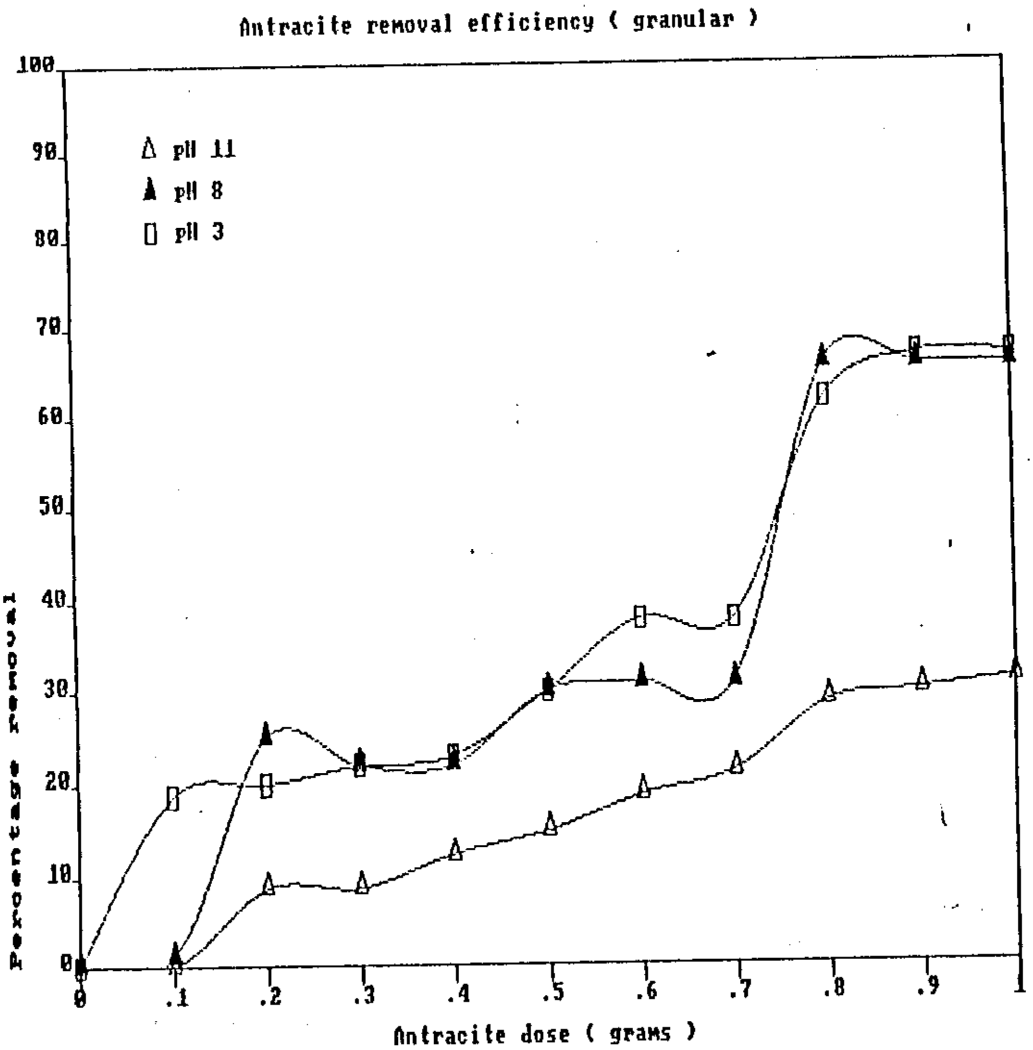

Antracite removal efficiency (granular)
Δ pH 11
▲ pH 8
▯ pH 3
Percentage removal
100
90
80
70
60
50
40
30
20
10
0
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
Antracite dose (grams)

FIGURE (4.9.4)

Table (4.9.2) a
Antracite Dose [powdered]

Antracite wieght [grams]	G C Peak Hieght milimeters		
	pH 11	pH 8	pH 3
0.00	256.00	273.00	273.00
0.10	126.00	133.00	126.00
0.20	58.00	38.00	58.00
0.30	30.00	25.00	30.00
0.40	28.00	22,00	28.00
0.50	46.00	14.00	46.00
0.60	14.00	10.00	14.00
0.70	9.60	8.00	9.60
0.80	10.00	7.50	9.60
0.90	8.80	7.00	8.80
1.00	8.80	7.00	8.80

Table (4.9.2) b
Antracite Dose [powdered]

Antracite wieght [grams]	Final concentration in ppb		
	pH 11	pH 8	pH 3
0.00	80.00	80.00	80.00
0.10	27.00	29.00	27.00
0.20	14.00	8,00	14.00
0.30	7.00	6.00	7.00
0.40	7.00	6.00	8.00
0.50	******	3.00	*****
0.60	3.00	2.00	3.00
0.70	2.00	2.00	2.00
0.80	2.00	2.00	2.00
0.90	2.00	2.00	2.00
1.00	2.00	2.00	2.00

Table (4.9.2) c
Antracite Dose [powdered]

Antracite wieght [grams]	Final concentration in ppb		
	pH 11	pH 8	pH 3
0.00	0.00	0.00	0.00
0.10	66.25	63.75	66.25
0.20	82.50	90.00	82.50
0.30	91.25	92.50	91.25
0.40	91.25	92.50	90.00
0.50	93.20	96.25	95.20
0.60	96.25	97.50	96.25
0.70	97.50	97.50	97.50
0.80	97.50	97.50	97.50
0.90	97.50	97.50	97.50
1.00	97.50	97.50	97.50

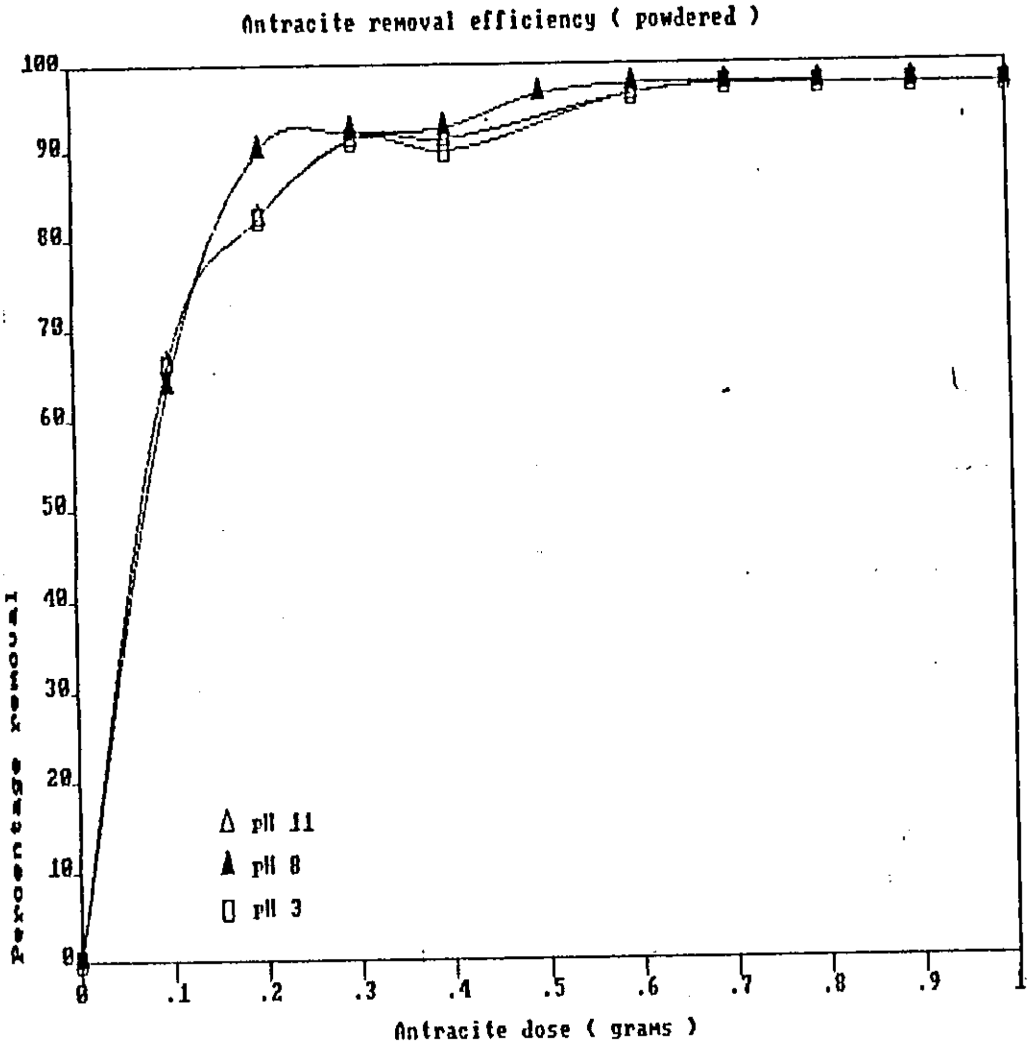

Antracite removal efficiency (powdered)
100
90
80
70
60
50
40
30
20
10
0
Percentage removal
0
.1
.2
.3
.4
.5
.6
.7
.8
.9
1
Antracite dose (grams)
Δ pH 11
▲ pH 8
□ pH 3

FIGURE (4.93)

4.8.2 Using Activated Carbon As An Adsorber

Activated carbon was used in this study for chloroform removal , as an adsorber , and also here two different sizes of activated carbon were used . Results are represented in tables (4.9.5) and (4.9.6) . From the tables , it is very clear that both sizes (granular and powdered) were excellent in removing chloroform . The removal efficiency was about (97 %) in both sizes , and the effect of pH was not significant in both powdered and granular .

4.8.2.1 Adsorption Isotherm

The adsorption Isotherm for Antracite and the Activated Carbon was following the Freundlich Isotherm. The Freundlich and Langmuir Isotherm figures are represented in figures (F.Iso) and (L.Iso). The values of K and 1/n for Freundlich Isotherm are presented in table (4.8.2.1).

Table (4.10.3)

Adsorber	k	1/n
Antracite Coal (pow)	1.82	0.57
Antracite Coal (gra)	1.35	0.37
Activated Carbon(pow)	2.69	2.0
Activated Carbon(gra)	2.7	1.5

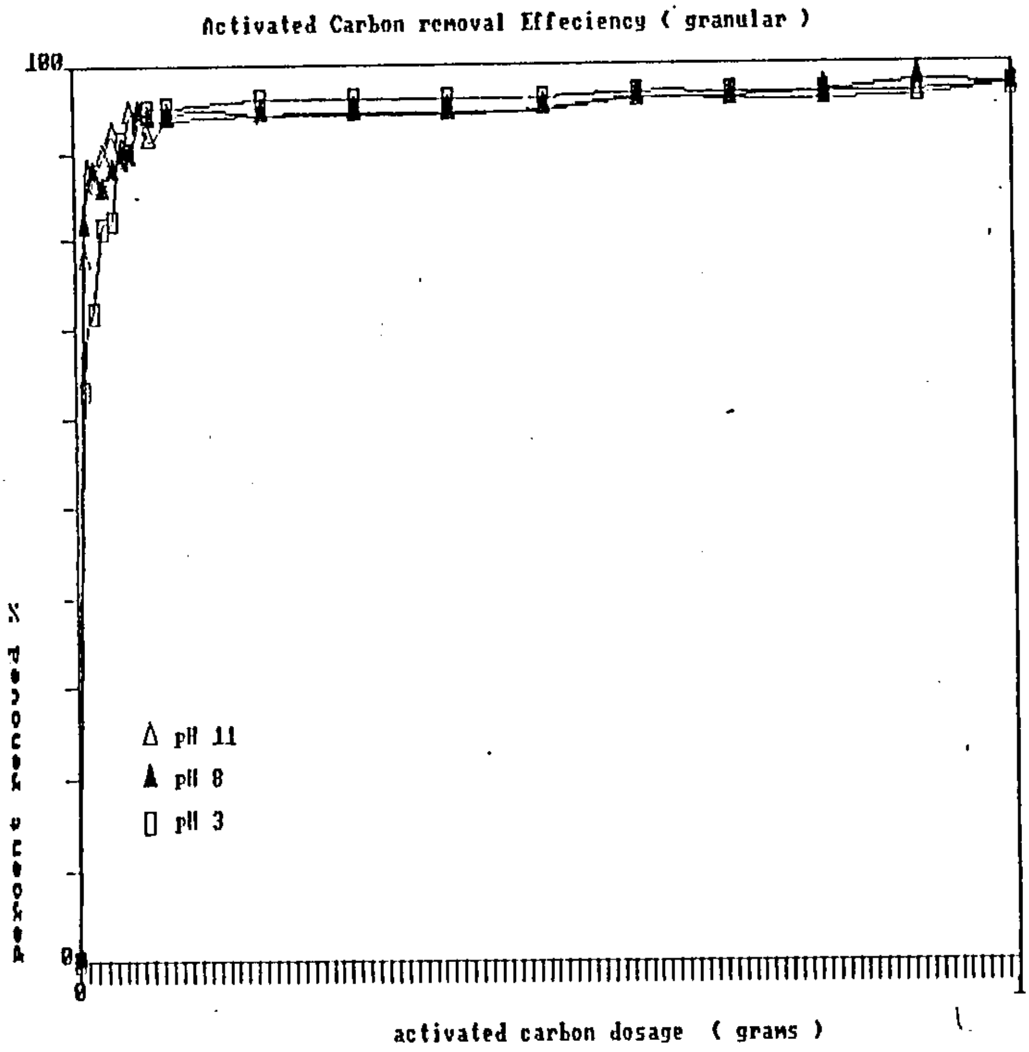

Activated Carbon removal Effeciency (granular)
100
0
0
1
% Percent removal
Δ pH 11
▲ pH 8
▯ pH 3
activated carbon dosage (grams)

FIGURE (4.9.5)

Table (4.9.5) a
Chloroform Concentration After AC. addition -granular-

Activated Carbon Dosage [grams]	Chloroform concentration ppb		
	pH 11	pH 8	pH 3
0.000	80.000	80.000	80.000
0.010	10.000	15.000	29.500
0.020	11.000	10.000	22.500
0.030	8.500	12.000	15.000
0.040	6.300	10.000	14.300
0.050	8.500	9.000	6.800
0.060	4.500	8.500	7.900
0.070	4.500	4.900	5.200
0.080	6.800	4.900	4.000
0.100	4.800	4.900	3.800
0.200	4.400	4.500	3.100
0.300	4.300	4.500	3.100
0.400	4.300	4.500	3.100
0.500	4.100	4.000	3.000
0.600	3.200	3.000	2.500
0.700	3.200	3.000	2.500
0.800	3.200	2.500	2.500
0.900	3.000	2.500	2.500
1.000	2.000	2.000	2.000

Table (4.9.5) b

Activated Carbon Removal Effeciency (Granular)

Activated Carbon Dosage [grams]	Chloroform removal %		
	pH 11	pH 8	pH 3
0.000	0.000	0.000	0.000
0.010	77.500	81.250	63.125
0.020	86.250	87.500	71.875
0.030	89.375	85.000	81.250
0.040	92.125	87.500	82.125
0.050	89.375	88.750	91.500
0.060	94.375	89.375	90.125
0.070	94.375	93.875	93,500
0.080	91.500	93.875	95.000
0.100	94.000	93.875	95.250
0.200	94.500	94.375	96.125
0.300	94.625	94.375	96.125
0.400	94.625	94.375	96.125
0.500	94.875	95.000	96.250
0.600	96.000	96.250	96.875
0.700	96.000	96.250	96.875
0.800	96.000	96.875	96.875
0.900	96.250	96.875	96.875
1.000	97.500	97.500	97.500

Table (4.9.6) a
Chloroform Concentration after AC. addition (powdered)

Activated Carbon Dosage [grams]	Chloroform concentration ppb		
	pH 11	pH 8	pH 3
0.000	80.000	80.000	80.000
0.010	6.000	4.500	3.100
0.020	5.000	4.800	3.100
0.030	4.500	3.500	3.100
0.040	4.400	3.500	3.000
0.050	4.100	2.800	2.500
0.060	3.100	2.800	2.500
0.070	3.100	2.800	2.500
0.080	3.100	2.800	2.000
0.090	3.100	2.800	2.000
0.100	3.000	2.000	2.000

Table (4.9.6) b
Activated Carbon Removal Effeciency (powdered)

Activated Carbon Dosage [grams]	Chloroform removal %		
	pH 11	pH 8	pH 3
0.000	0.000	0.000	0.000
0.010	92.500	94.375	96.125
0.020	93.750	94.000	96.125
0.030	94.375	95.625	96.125
0.040	94.500	95.625	96.250
0.050	94.875	96.500	96.875
0.060	96.125	96.500	96.875
0.070	96.125	96.500	96.875
0.080	96.125	96.500	97.500
0.090	96.125	96.500	97.500
0.100	96.250	97.500	97.500

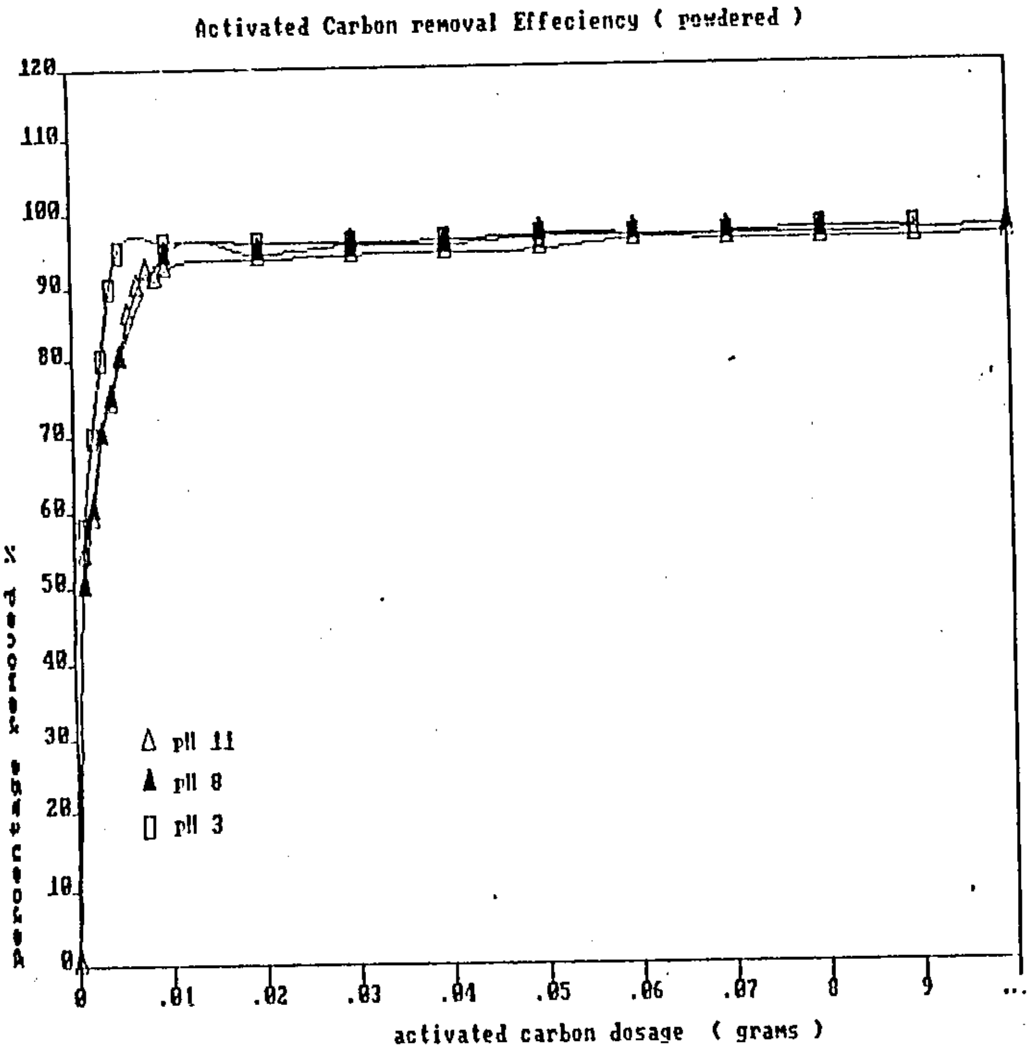

Activated Carbon removal Effeciency (powdered)
%
120
110
100
90
80
70
60
50
40
30
20
10
0
Δ pH 11
▲ pH 8
▯ pH 3
0
.01
.02
.03
.04
.05
.06
.07
8
9
...
activated carbon dosage (grams)

FIGURE (4.9.6)

4.8.3 Using Jordanian Zeolite As An Adsorber

Jordanian zeolite was studied for the removal of chloroform , Zeolite in this study was treated as a normal adsorber , and two different sizes were studied too (powdered and granular) . Although Zeolite is being used as an ion exchanger , this study tried to figure out weather Zeolite is capable is removing chloroform as an adsorber (chemisorption). Unfortunately no removal what so ever was achieved using Zeolite at any size nor at any pH values , which means that zeolite is not sufficient in removing any portion of chloroform ,even at high Zeolite dosage . This is very clear in table (4.9.7) which shows no removal what so ever was achieved .

Table (4.9.7)

loroform Concentration after Zeolite addition

Two Sizes (Granular & Powdered)

osage [grams]	Chloroform concentration ppb		
	pH 11	pH 8	pH 3
0.000	80.000	80.000	80.000
0.100	80.000	80.000	80.000
0.200	80.000	80.000	80.000
0.300	80.000	80.000	80.000
0.400	80.000	80.000	80.000
0.500	80.000	80.000	80.000
0.600	80.000	80.000	80.000
0.700	80.000	80.000	80.000
0.800	80.000	80.000	80.000
0.900	80.000	80.000	80.000
1.000	80.000	80.000	80.000

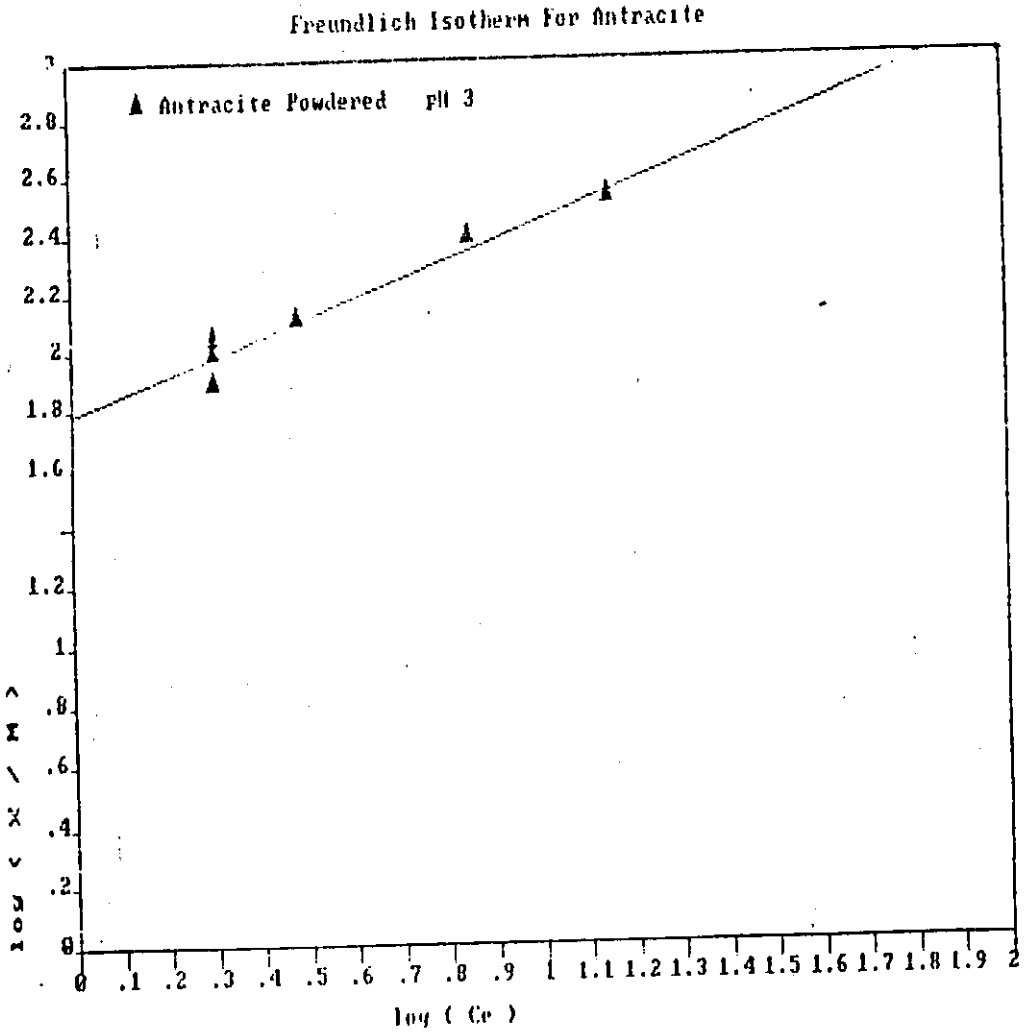


Figure (F. ISO 1)

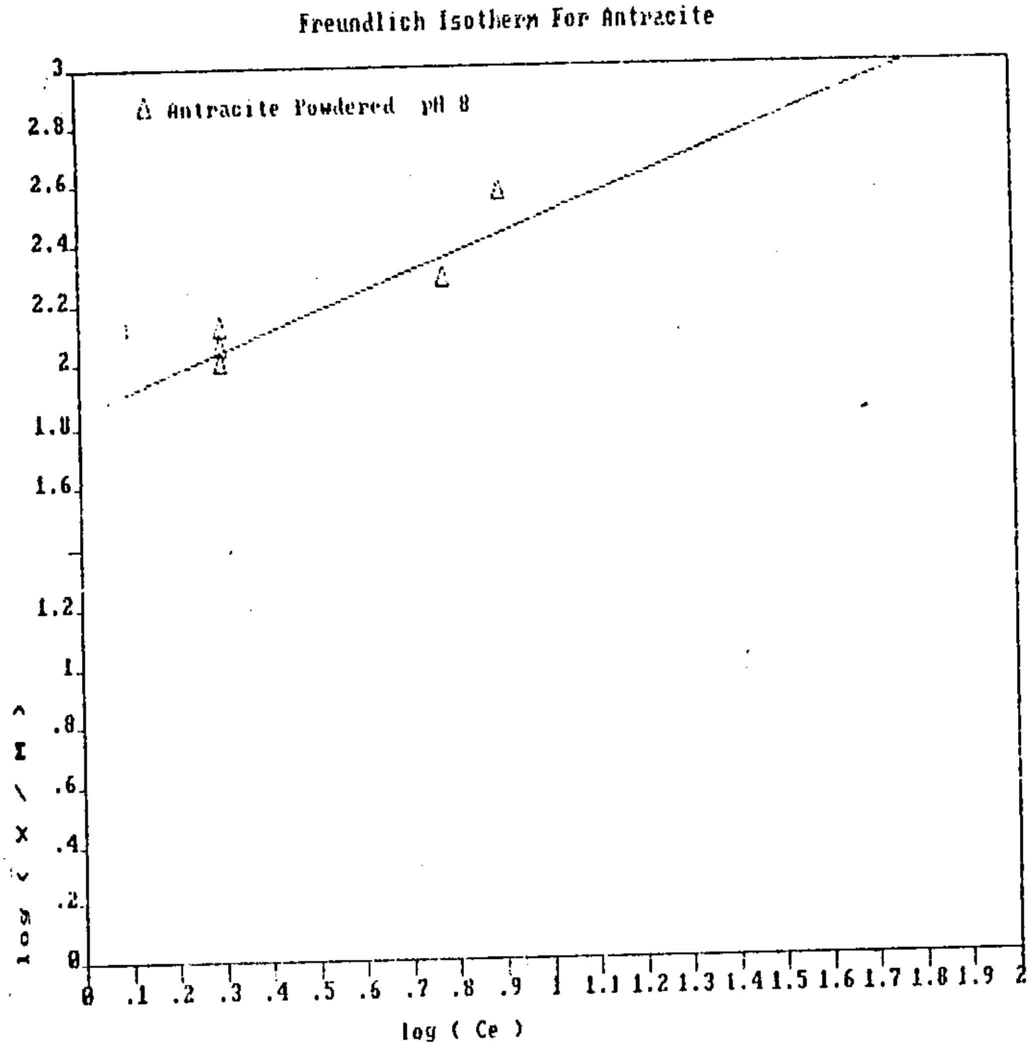


Figure (F. ISO 2)

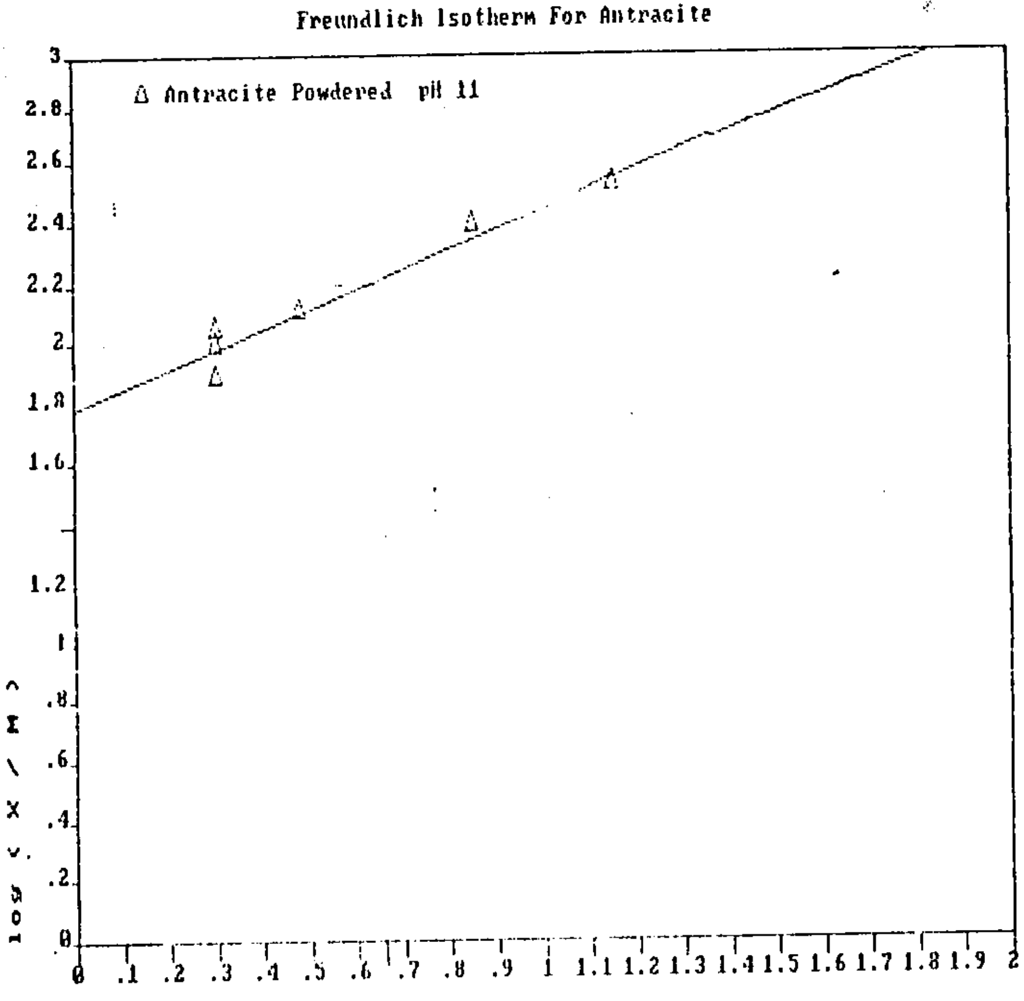


Figure (F. ISO 3)

Freundlich isotherm for Antracite

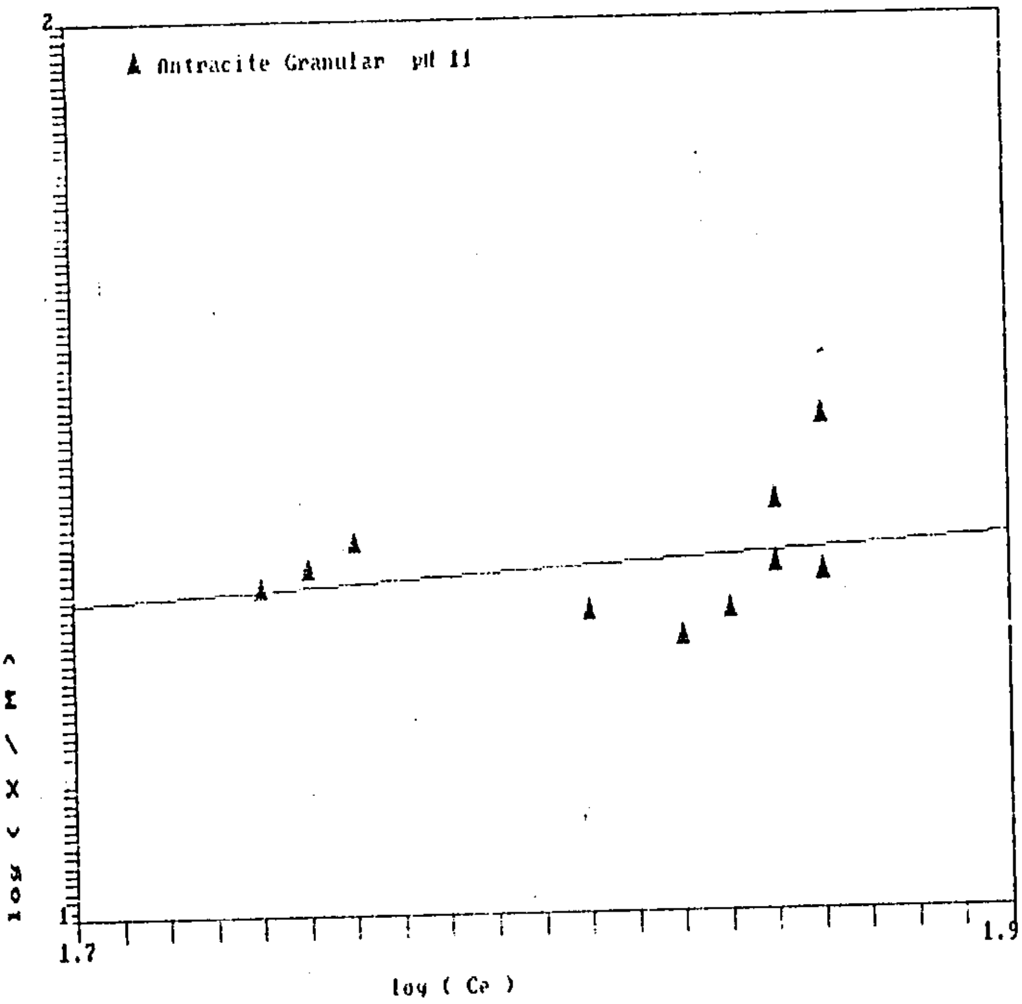


Figure (F. ISO 4)

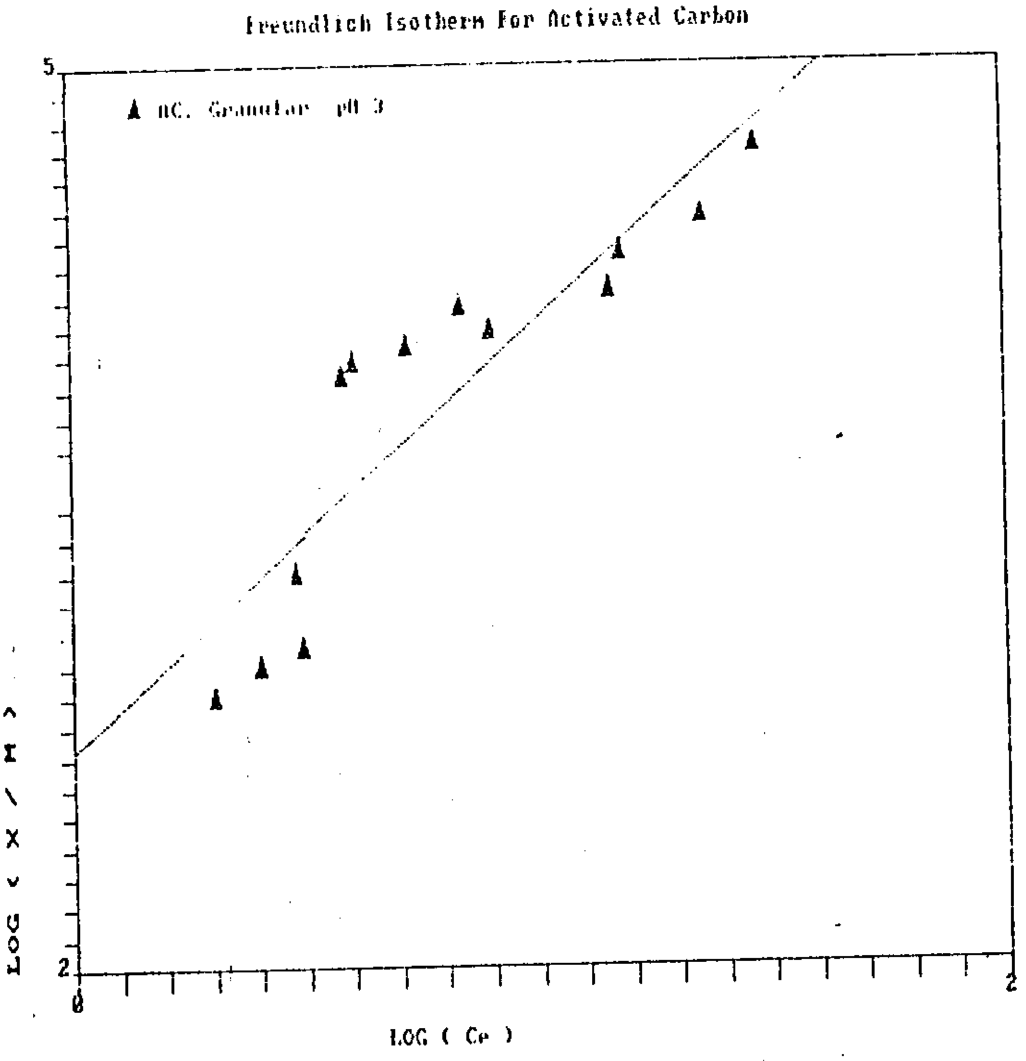
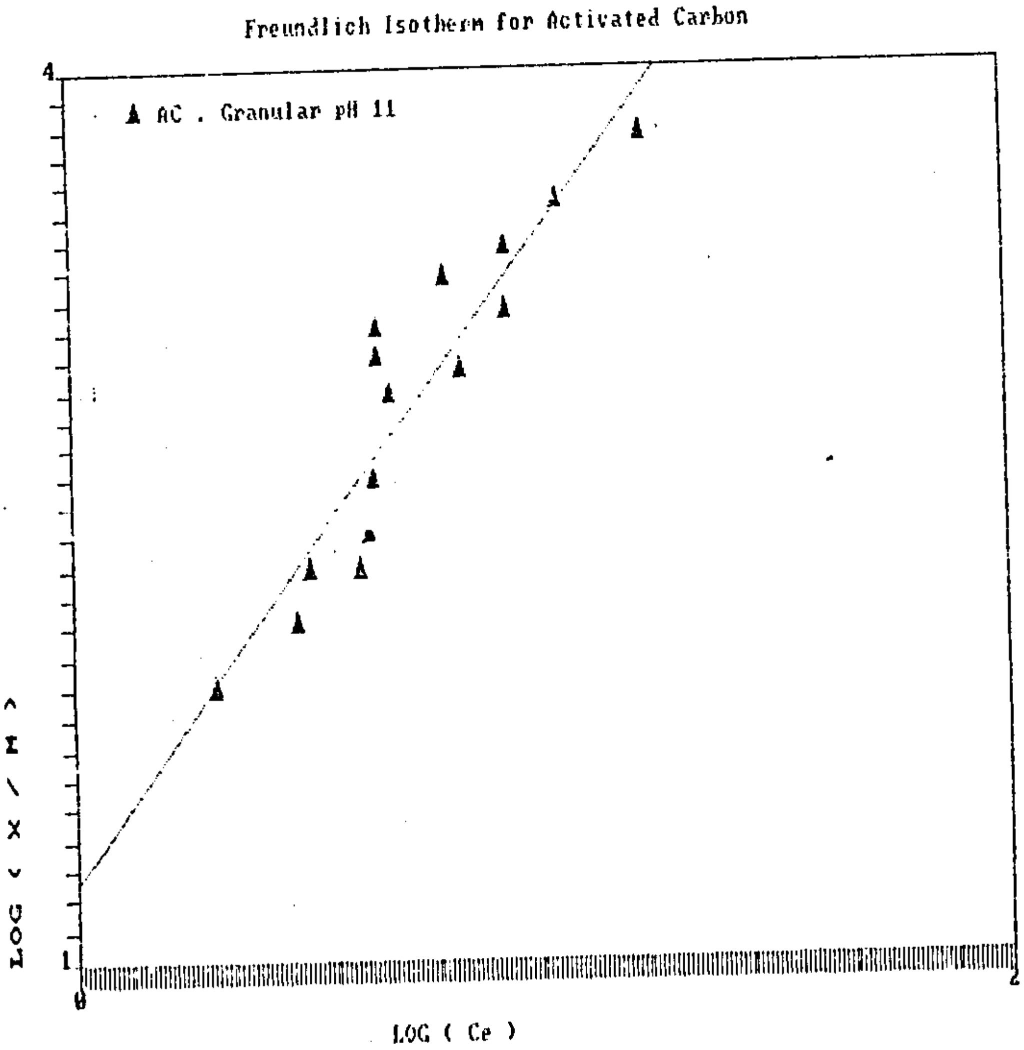


Figure (F. ISO 5)



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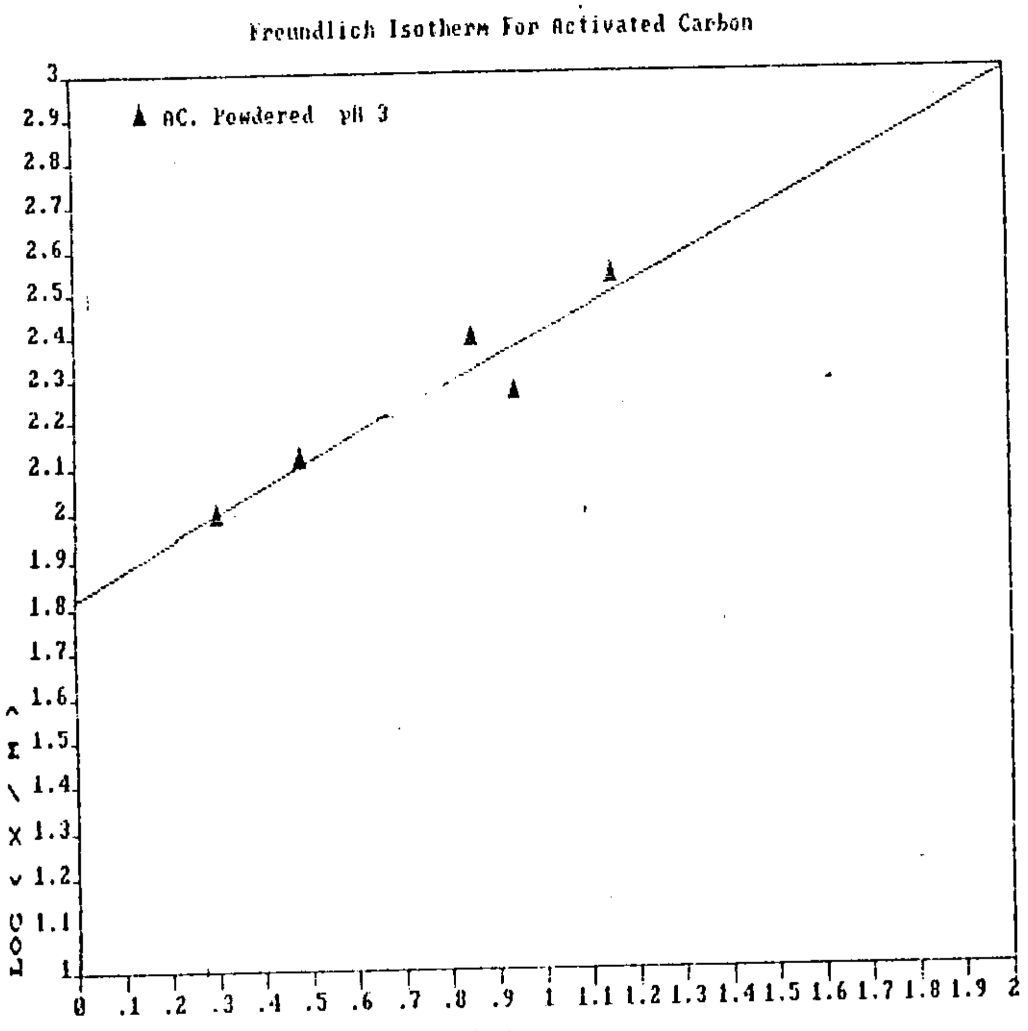
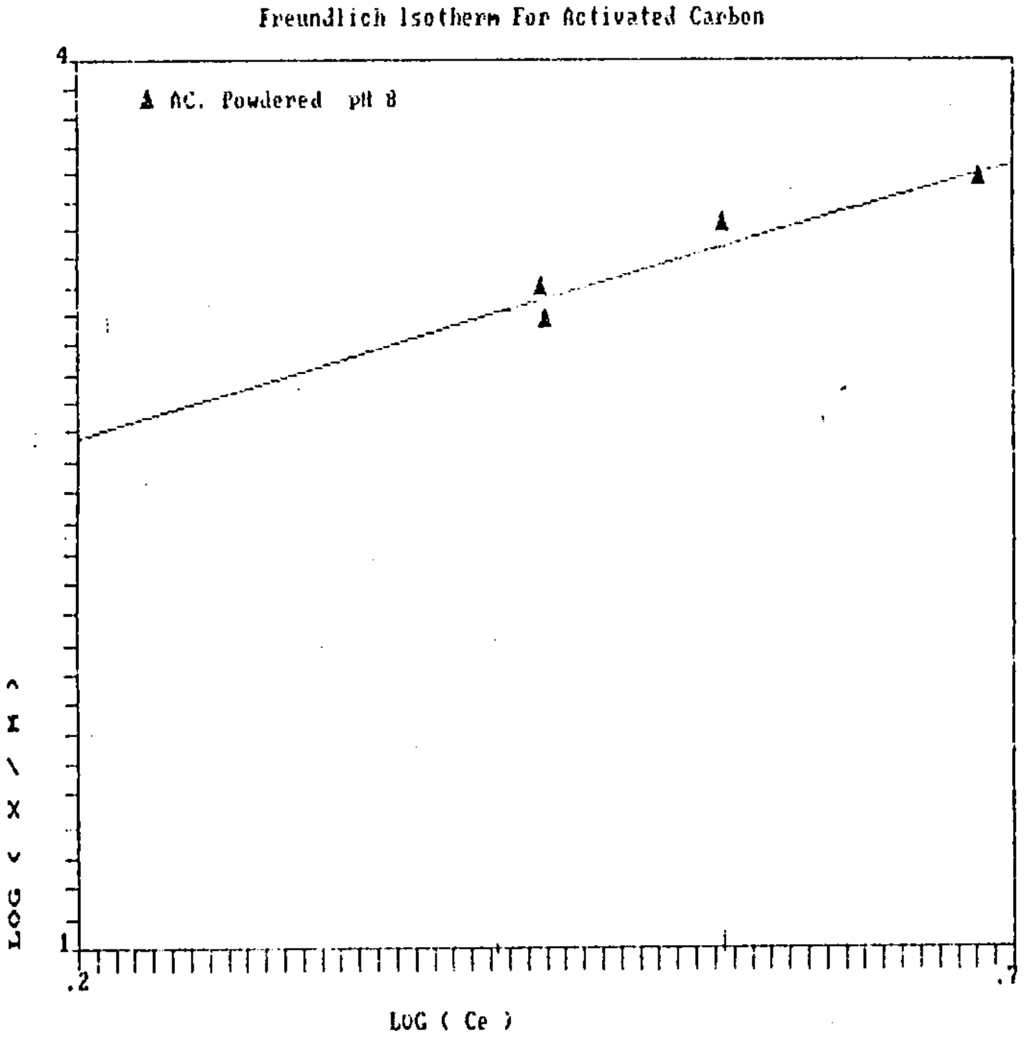


Figure (F. ISO 8)



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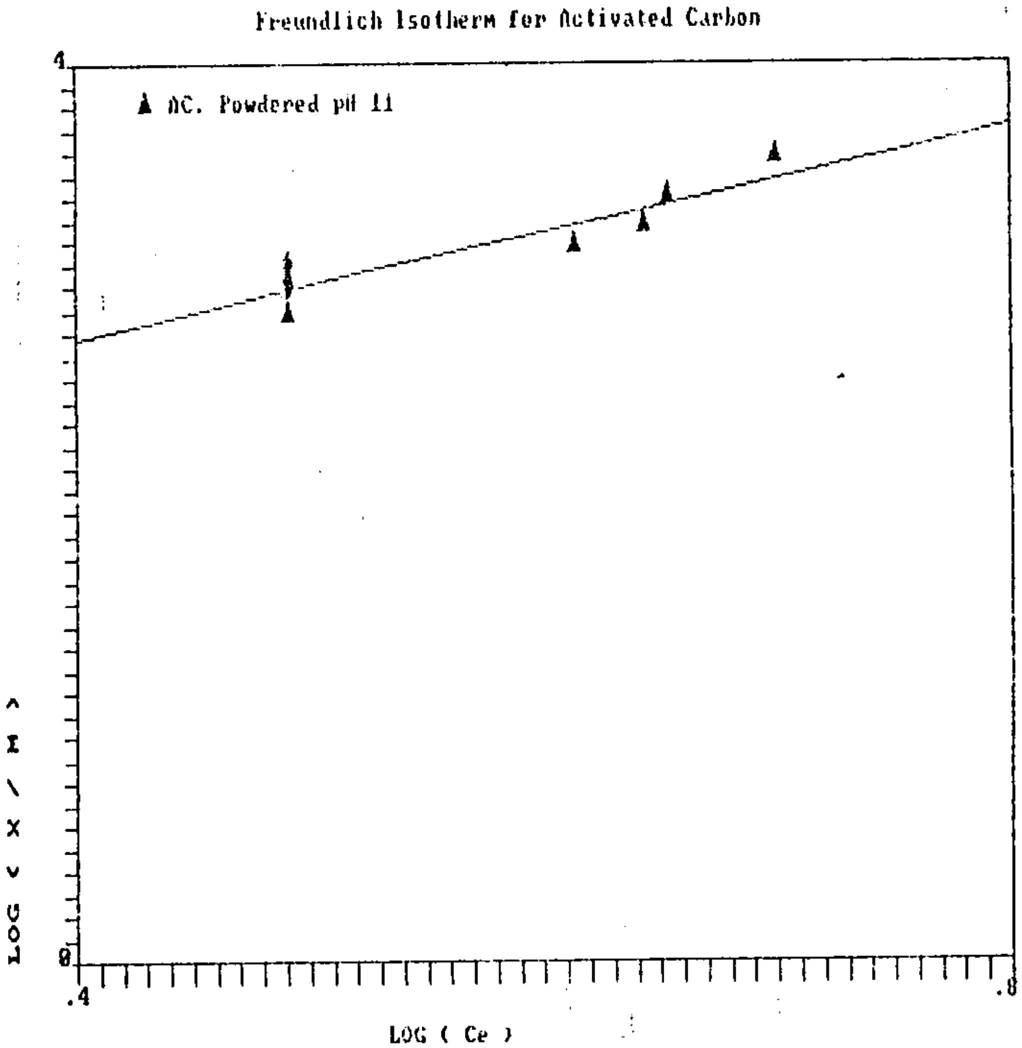

Figure (L. ISO 10)

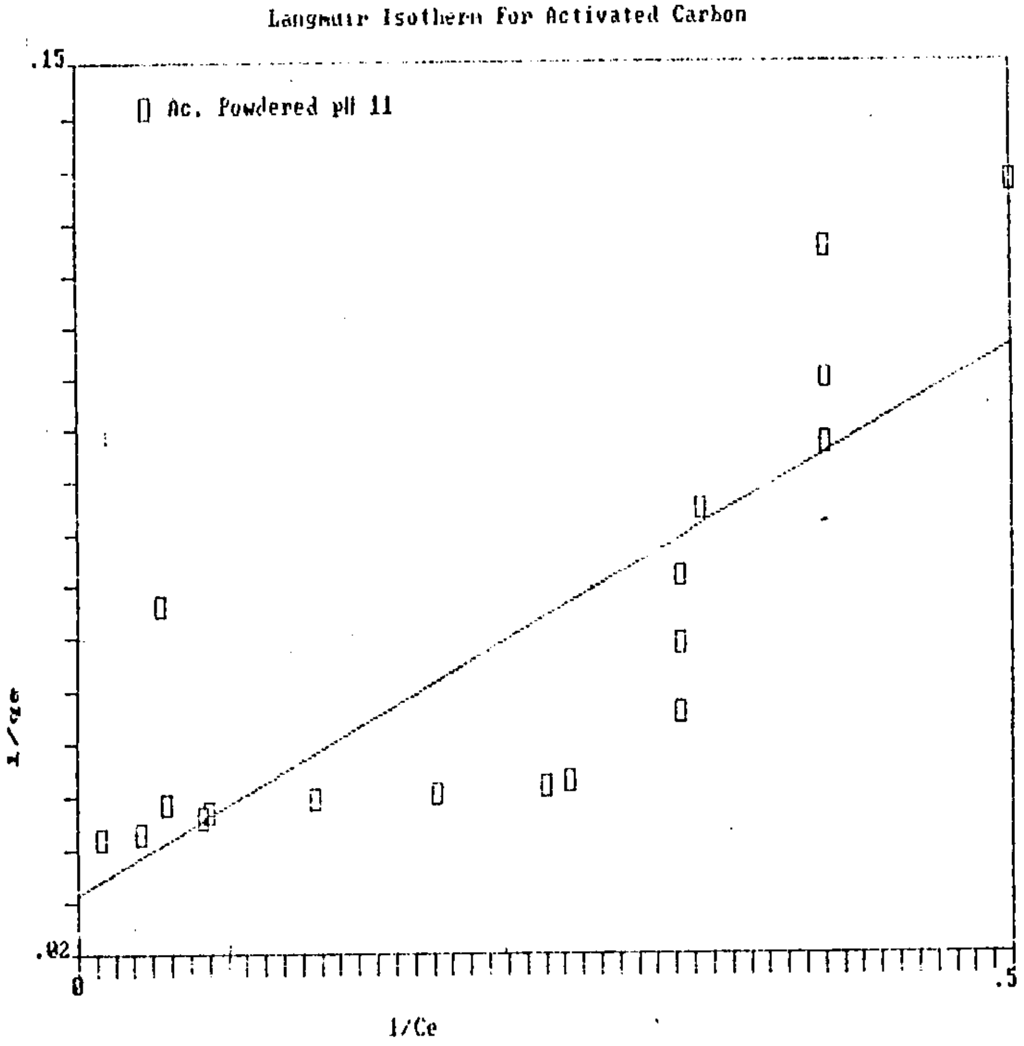

Figure (L. ISO 1)

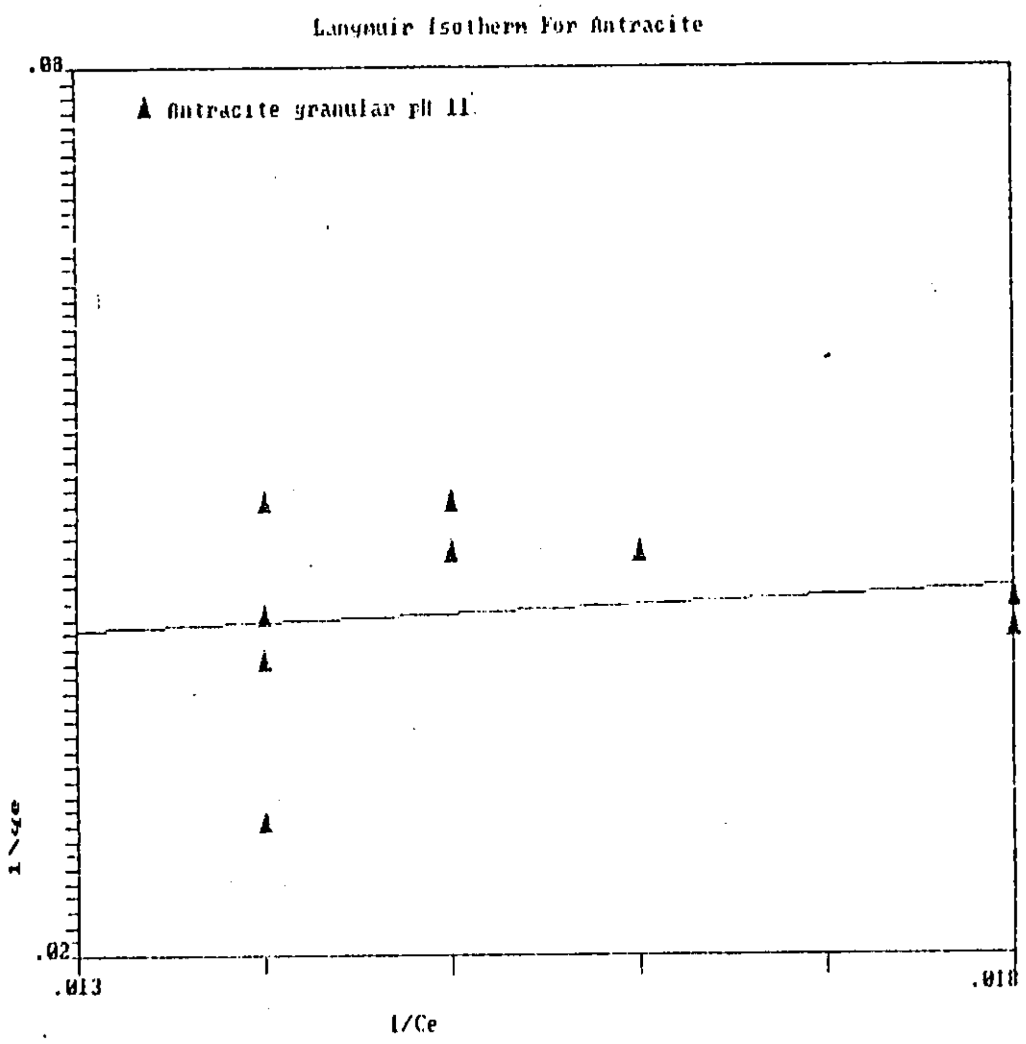

Figure (L. ISO 2)

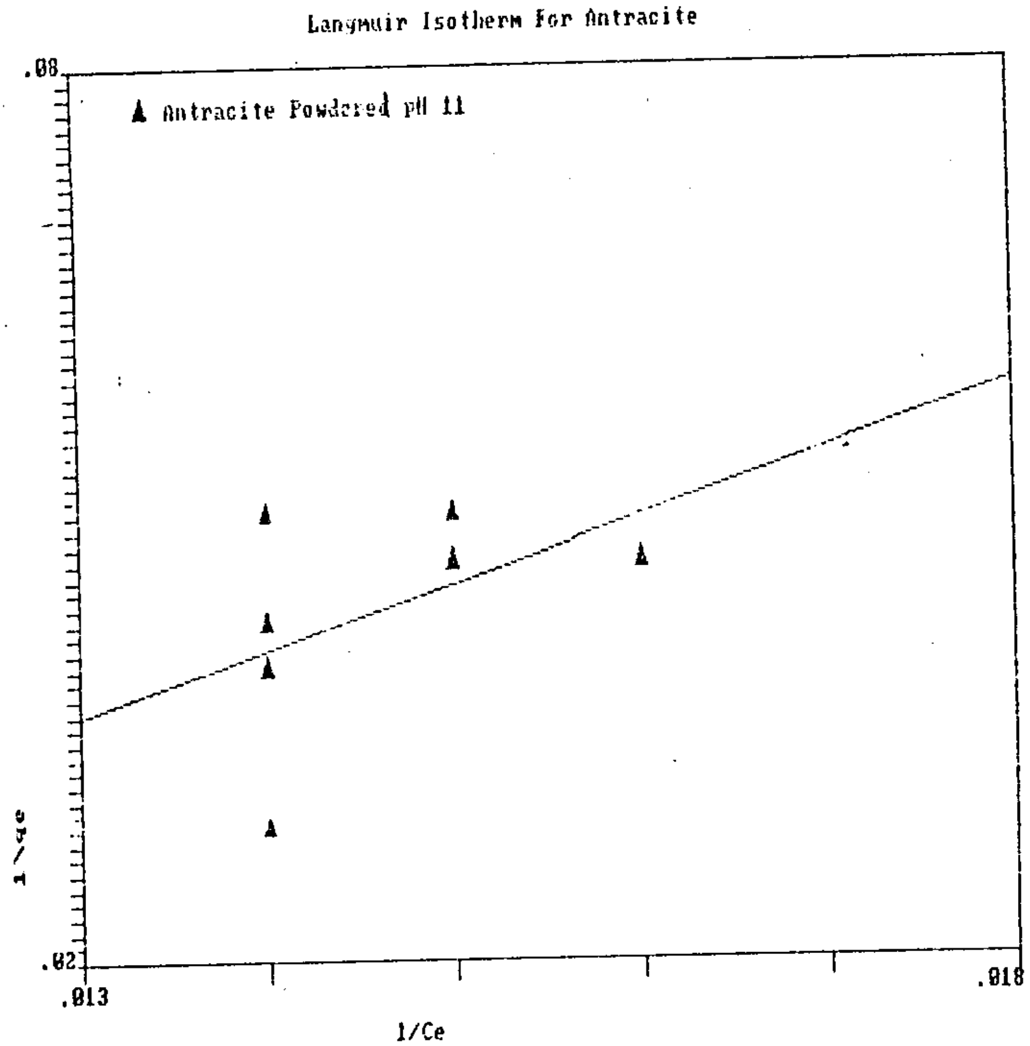

Figure (L. ISO 3)

4.9 Experimental Results for the Investigation Of Trihalomethanes In Treated Wastewater

4.9.1 Results Obtained From Abu Nusier Treatment Plant

In this study chloroform was considered to be the trihalomethane indicator . This consideration was based on the data available in the (water laboratory dept.) and also based on the analytical data of this study . Chloroform is considered the predominant compound in treated wastewater . Besides this , Chloroform is considered to have the severest adverse effect over the human health . This is not the general case since some research done by the water authority showed that Bromoform would be the predominant compound in waters containing Bromide. This is presented in figues (4.9)

Samples from the following location within the treatment plant were taken for THM investigation .

1- The final settling tanks .(after the oxidation ditch).
2- The chlorination basin (different location) .
3- The final effluent (just leaving the treatment plant).

Sodiumthiosulphate was added to the samples expected to have residual chlorine (sample taken after the chlorination process) , in order to eliminate the presence of residual chlorine . Some samples were collected from the effluent stream to figure out the presence of THM . The results are presented in figures (4.9.1).

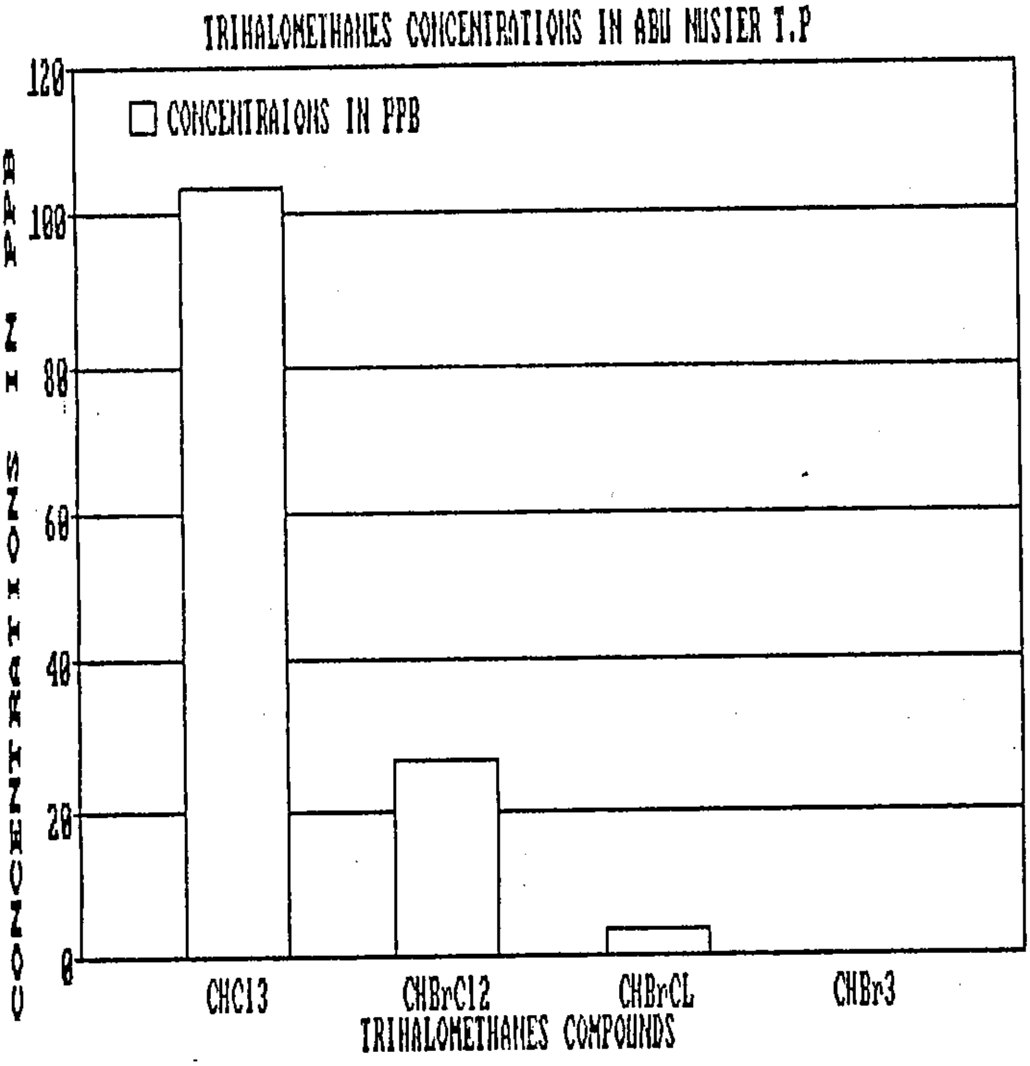
TRIHALOMETHANES CONCENTRATIONS IN ABU NUSIER T.P
□ CONCENTRAIONS IN PPB
CONCENTRATIONS IN PPB
120
100
80
60
40
20
0
CHCl3
CHBrCl2
CHBrCL
CHBr3
TRIHALOMETHANES COMPOUNDS

FIGURE (9.1)a

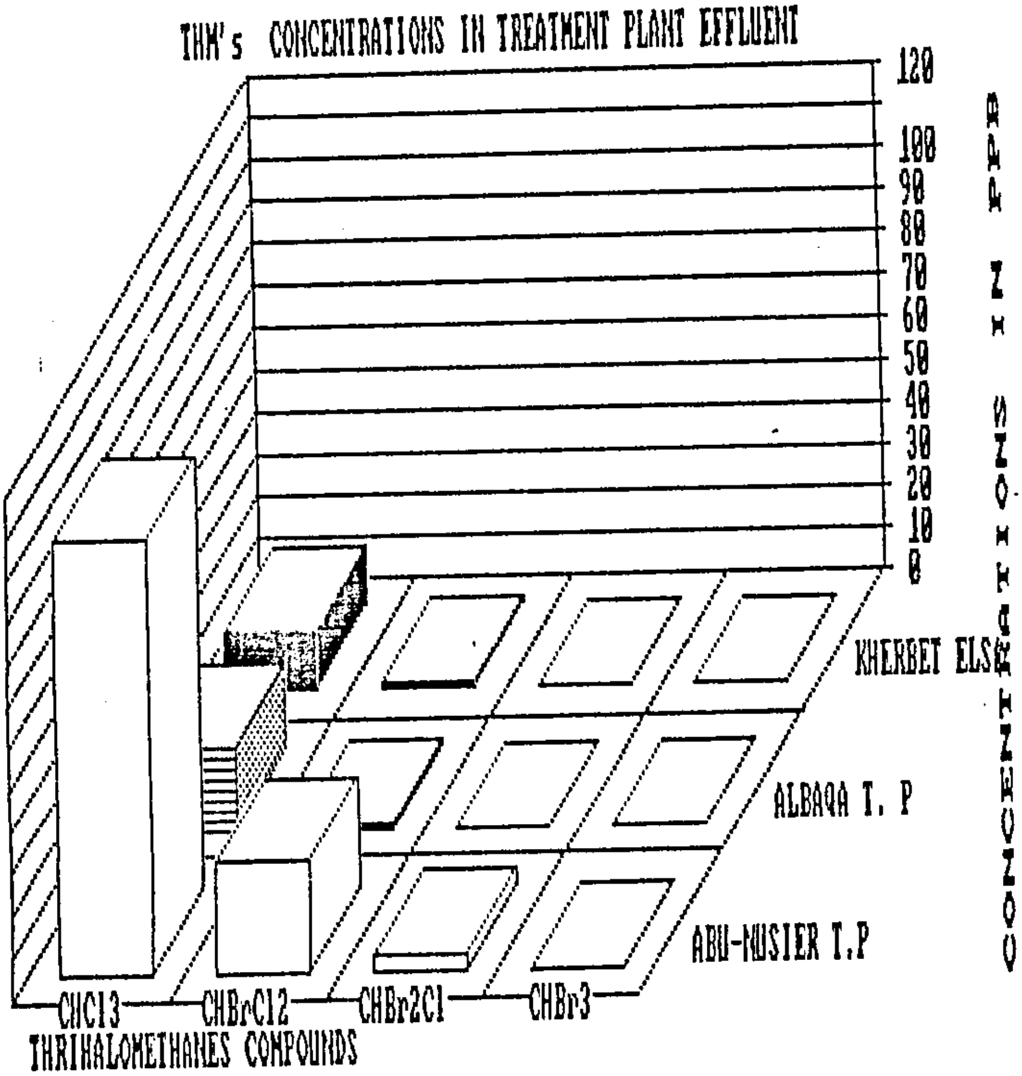
THM's CONCENTRATIONS IN TREATMENT PLANT EFFLUENT
120
100
90
80
70
60
50
40
30
20
10
0
CONCENTRATIONS IN PPB
KHERBET ELSA
ALBAQA T. P
ABU-NUSIER T.P
CHCl3
CHBrCl2
CHBr2Cl
CHBr3
THRIHALOMETHANES COMPOUNDS

FIGURE (9.1)b

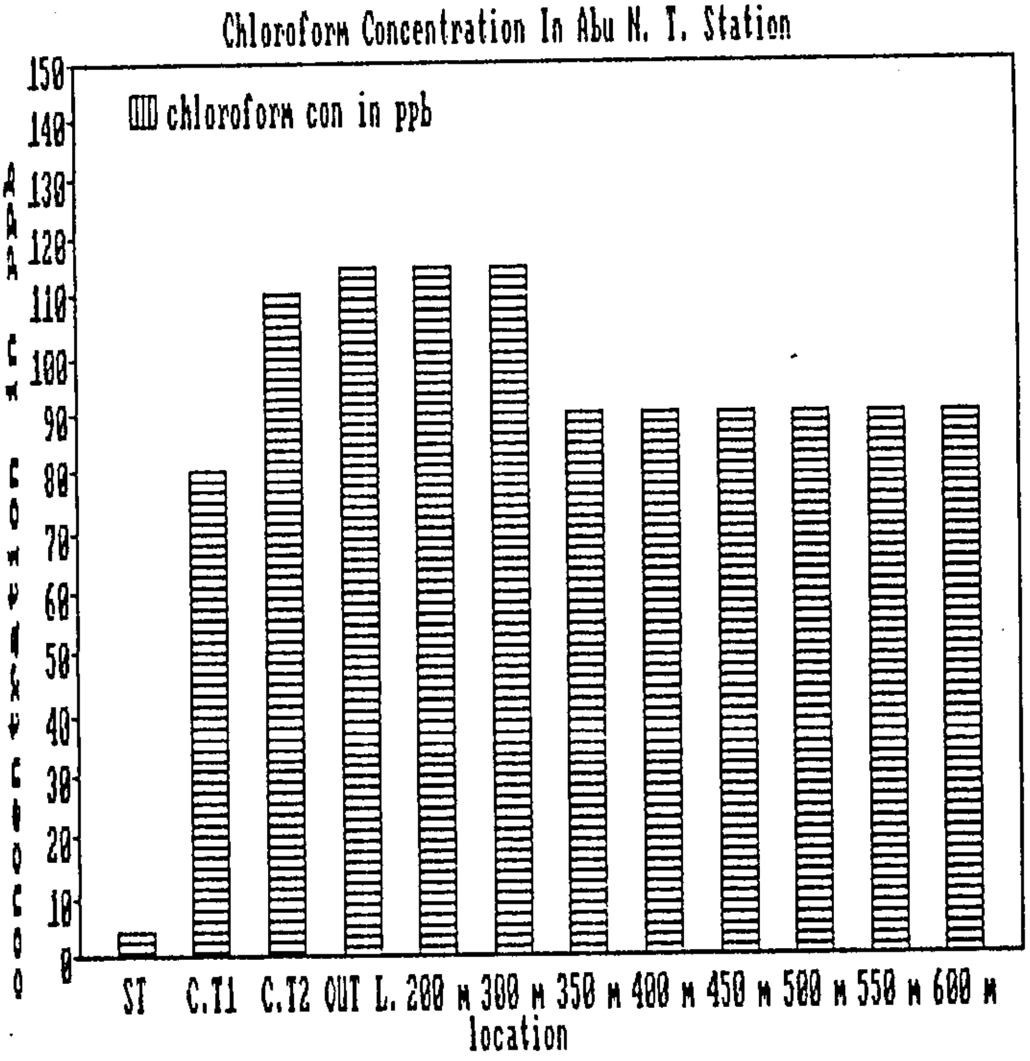
Chloroform Concentration In Abu N. T. Station
chloroform con in ppb
concentration in ppb
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
ST
C.T1
C.T2
OUT
L. 200 m
300 m
350 m
400 m
450 m
500 m
550 m
600 m
location

FIGURE (4.10.1)

4.9.2 Results Obtained From Albaqa Treatment Plant

The Same procedure followed in AbuNusier Treatment plant Was adopted in Albaqa treatment plant .
the following is the locations from which samples were collected from :-

1-Final settling tank (After coming out the trickling filters).
2- In side the chlorination tank .
3- From the final effluent .

Unfortunately it was not possible to take some samples from the stream effluent , because the effluent flow inside a closed pipe system for a distance of about 7 Km before comes out in the valley . The results are presented in figure (4.9.2). It must be noted here that a reducing agent must be added to the wastewater samples collected after the chlorination process , to eliminate the presence of residual chlorine . Because the presence of organic matter in the water with the presence of residual chlorine would cause further chloroform formation . This is very clear in table (4.9.2). This table shows the chloroform concentrations in samples after being stored for different periods of time . Samples containing sodiumthiosulphate were able to maintain the chloroform concentration . While Samples without Sodiumthiosulphate showed a great variance . That means that chloroform is being formed under captivity .

Table (4.9.2)

GC PEAK HEIGHT WITH SAMPLES WITH AND WITHOUT SODIUMTHIOSULPHATE

figures are for GC peakhieght mm	SAMPLES WITHOUT SODIUMTHIOSULPHATE	SAMPLES WITH SODIUMTHIOSULPHATE
SAMPLE 1	1958mm (Two weeks	149 mm (two weeks)
SAMPLE 2	2816mm (4 weeks)	184 mm (4 weeks)

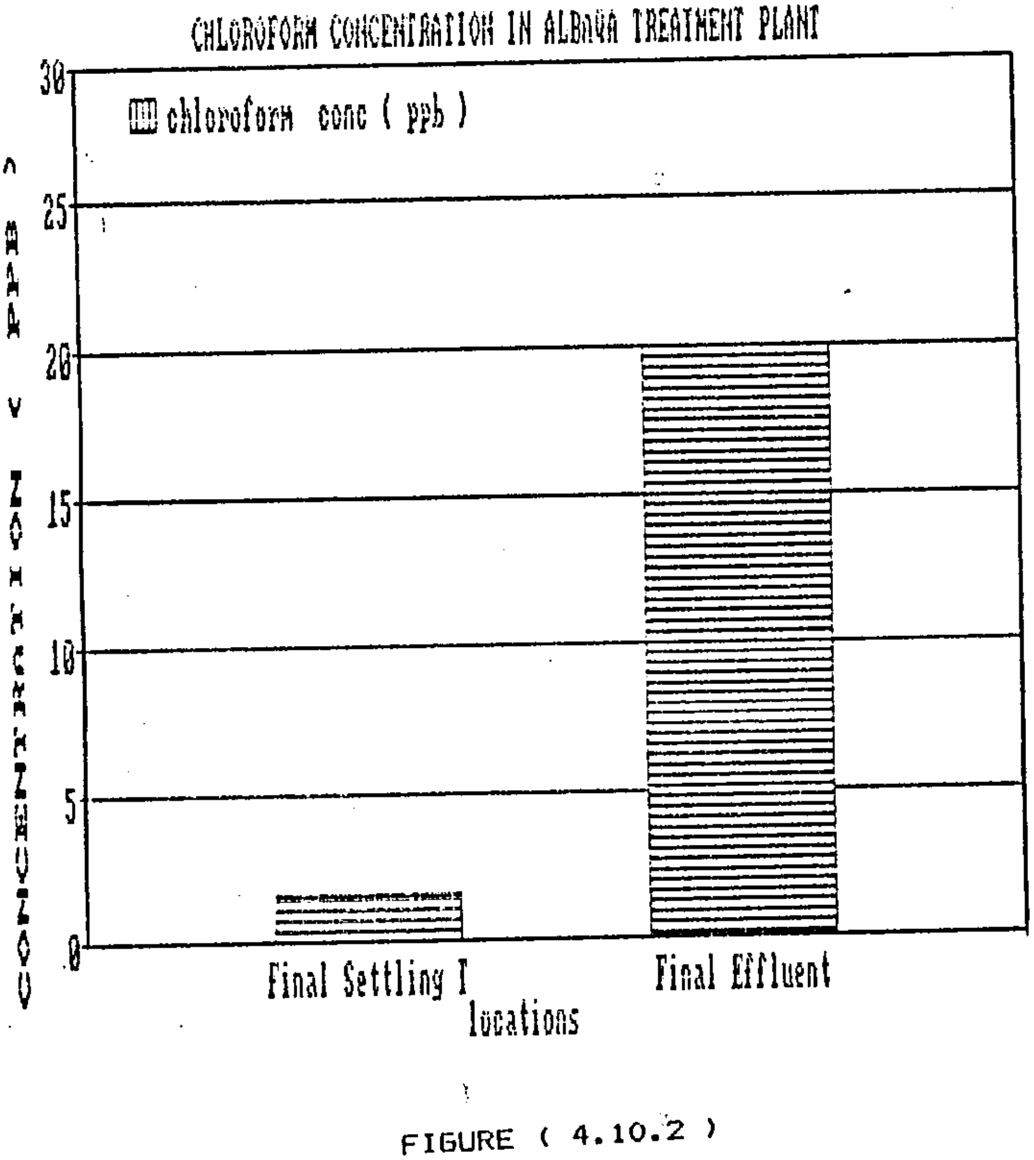
CHLOROFORM CONCENTRATION IN ALBAQA TREATMENT PLANT
chloroform conc (ppb)
CONCENTRATION (PPB)
30
25
20
15
10
5
0
Final Settling T
Final Effluent
locations

FIGURE (4.10.2)

CHAPTER FIVE

DICUSSION AND CONCLUSIONS

Chapter Five

Discussion And Conclusions

The conclusions of this study are summarized in the following points :- .

1- Chloroform removal efficiencies was found to be perfect in , in air stripping , both mechanical and diffused aeration principles showed an excellent removal efficiencies .a removal effeciency in both cases (diffused and surface aeration) a perrcentage removal efficiency was about (98 %) .The large removal starts to occur after 10 minutes from aeration time . This result is considered to be the best . But a deeper look would lead to the fact that using air stripping would lead to what is called pollution diversion . Since the water pollution is being converted from water pollution into air pollution . And here the air pollution regulation must be followed and check whether the permissible limit was exceeded or not . If the air pollution regulation were violated then a certain treatment to the air is to be applied .

2- Antracite showed a good removal efficiency , although it is considered to be a filter media used in different filters. This point is very important because , this type of filter is able to remove both suspended matter and chloroform at the same time .The removal efficiency for used in removing heavy metals by ionic exchange .

6- Trihalomethanes are formed in the wastewater treatment effluent .In AbuNusier treatment plant the chloroform was 104 ppb and in albaqa treatment plant it was found to be about 20 ppb and that is most probably for the poor chlorination system.

7- This study considered chloroform as the representative compound of the Trihalomethanes compounds . This consideration was established on the base that Chloroform was the predominant compound in the wastewater treatment plants effluents (achieved from the experiments of this research and from the data available in the Water Authority Laboratories). This was proved by the results obtained in this study too .

8- This research showed that the analytical procedure is very important , and the results obtained are totally dependent on the procedure followed . Do the analytical part as soon as possible from the collection time . Since the results would be misleading after being stored .

9- Chlorination is the major reason for the formation of Chloroform . This is very clear in the results obtained from Abunusier and Albaqa treatment plants. The results showed a big jump in Chloroform concentrations just after the chlorination process . While the coloroform concentration was about 1.5 to 2 ppb in the final settling tank .

10- This study showed that residual chlorine in water systems , with the presence of organic matter will cause further chloroform formation . In other words if certain samples were collected from certain sources that has residual chlorine , these samples are to be tested directly . Which is almost impossible . Or the residual chlorine must be removed. In order to prevent the formation of Chloroform under captivity of the samples . In this research Sodiumthiosulphate was added to the chlorinated samples in order to react with the available residual chlorine .

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ملخص

التحري عن مركبات هالوجيني الميثان الثلاثي المتبقيه في المياه العادمه و دراسه طرق مختاره لازالتها .

تتشكل مركبات الهالوجيني الميثان الثلاثي (THM) في المياه او المياه العادمه نتيجه لتفاعل كيميائي بين بعض المركبات العضويه الموجوده في المياه ، و الكلور المضاف لعمليات تنقيه المياه . كثيرا من الدراسات اثبتت ان هذه المركبات مركبات مسرطنه ، حتى و ان وجدت بتراكيز قليله جدا .

وجدت هذه المركبات في محطه ابو نصير لتنقيه المياه العادمه كذلك في محطه تنقيه البقعه . وجد ان ٩٥% من التركيز الكلي لمركبات هالوجيني الميثان الثلاثي عباره عن المركب المسمى ب الكلوروفورم (Chloroform) . لهاذا السبب اعتبر ان الكلوروفورم هو المركب الممثل لهذة المركبات .

جربت في هذه الدراسه بعض الطرق لازاله الكلوروفورم من المياه ، هذه الطرق هي التهويه الفقاعيه و التهويه الميكانيكيه السطحيه . والطريقه الثانيه التي درست هي الامتزاز باستخدام ثلاثه ممزات هي

١ - الانثراسايت (Antracite) .

٢ - الكربون المنشط (Activated carbon) .

٣ - الزيولايت الاردني (Jordanian Zeolite) .

استخدم في هذه التجارب الإمتزاز القطاعي فقط وذلك لأن هذه المركبات شديده التطاير . لقد تم استخدام حجمين من كل ماده وهي الحجم الحبيبي و الجم الناعم جدا (powdered and granular sizes) . اجريت جميع التجارب على ثلاث درجات حموضه وهي الحامضيه و المتعادله و القاعديه (٣، ٨، ١١) .

كانت نسبه الإزاله ممتازه في التهويه الفقاعيه و السطحيه (تقريبا ٩٨ %) ، وايضا نسبه الإزاله في الإمتزاز باستخدام ال(antracite) الحجم الناعم اعطت (٩٧٫٥ %) اما الحجم الحبيبي اعطى نسبه ازاله (٦٧ % فقط) بدرجه حموضه ٣ وكما هو متوقع الكربون المنشط اعطى نسبه ازاله ممتازه في الحجمين (٩٨ %) . اما ال(Jordanian Zeolite) فلم يحقق ايه ازاله تذكر تحت كل الظروف المدروسه .