1-INTRODUCTION

1.1. GENERAL REMARKS

Water treatment began in the United States in the early 20th century. At this time, treatment typically consisted of chlorination and sand filtration. Disinfection with chlorine helped to reduce waterborne diseases significantly by inactivating harmful microorganisms and was one of the biggest advancements in disease control in the United States. Free chlorine is the most commonly used disinfectant for drinking water treatment systems. Although water disinfection is very important to the health of the public, the disinfectant itself reacts with humic substances in the water to create harmful disinfection by–products (DBPs). The production of DBPs was not discovered until the 1970's when samples were tested for the presence of certain halogenated compounds. The results of these tests found that nearly all of the United States drinking waters contained DBPs. Different disinfectants produce varying types of and amounts of DBPs. For instance, ozone can produce bromate, formaldehyde, halopropanones, and chloral hydrates. The concentration of DBPs formed by ozonation depends on the raw water characteristics. DBPs resulting from ozone disinfection are often not a problem with regard to regulations because the United States Environmental Protection Agency the U.S. EPA has not set limits on many of these types of DBPs.

Free chlorine, on the other hand, produces DBPs such as trihalomethanes (THMs) and haloacetic acids (HAAs). The concentration of DBPs formed with free chlorine depends on the raw water content but generally free chlorine produces the largest quantities of DBPs when compared to other disinfectants. Numerous studies have been conducted in the past three decades on the harmful effects of DBPs in drinking water supplies. Results have shown that DBPs are carcinogenic and can cause adverse pregnancy outcomes. Therefore, the U.S. EPA has regulated the allowable concentrations of certain DBPs in finished drinking water. The first regulations were promulgated in 1979 and set a maximum contaminant limit (MCL) of 100 μg/L for total trihalomethanes in a drinking water.

1.2. Literature Review

Water treatment is an evolving technology. Before the 1900s, drinking water in the United States was not regularly disinfected. It was not widely understood that water could transport diseases, and diseases like typhoid and cholera were once very common. In the early 20th century, disinfection of water supplies began in several U.S. cities. A recent report confirms that disinfection of water has made a significant improvement in human health during the last century (1).

When the United States government regulated water treatment in 1979 with the National Primary Drinking Water Regulations (2), drinking water was only required to be disinfected once. This process was called primary disinfection. As water treatment technology improved, it became evident that secondary disinfection was required to provide safe drinking water for the general public. Secondary disinfection was intended to keep the water microbiologically safe as it traveled through the distribution pipes by providing a disinfectant residual to the water supply.

It was not until the 1970s that scientists discovered that by-products were created while disinfecting water. Also at this time period, the negative effects of disinfection byproducts (DBPs) were first discovered. The U.S. EPA responded to these findings by setting limits for the allowable concentrations of DBPs in drinking water. Water treatment plants today have to balance providing adequate disinfection with meeting allowable concentration limits of DBPs.

1.3. Types of Disinfectants

The following sections provide historical background and chemical information for several disinfectants used. Chlorine, chloramines, chlorine dioxide, ozone and ultraviolet disinfection are discussed.

1.3.1. Chlorine Disinfection

In 1881, a German named Koch demonstrated that minute quantities of chlorine could inactivate harmful waterborne pathogens. The introduction of chlorination resulted in significant decreases in worldwide waterborne diseases, such as typhoid(3). The use of chlorination for the disinfection of drinking water first occurred in the United States in Louisville, Kentucky in 1896. By World War II, disinfection with chlorine had become a treatment that was standard worldwide (4). When chlorine reacts with water it forms hypochlorous acid (reaction 1). The hypochlorous acid can then undergo acid-base reactions to form hypochlorite ion (reaction 2). The distribution of chlorine into HOCl and OCl^- is pH dependent. HOCl is a stronger disinfectant than OCl^-, and therefore a lower pH is preferred for disinfection with chlorine. The chlorine (HOCl or OCl^-) attacks bacterial cells and the protein coat of viruses, effectively killing both bacteria and viruses. Chlorination, while highly effective at inactivating pathogens, produces several potentially harmful by-products.

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^- \qquad \text{Reaction 1}$$

$$HOCl \leftrightarrow OCl^- + H^+ \qquad \text{Reaction 2}$$

1.3.2. Chloramine Disinfection

Chloramines are an alternative disinfectant to chlorine. The main disadvantage to chloramination is that it requires a very large CT (concentration* time) value to provide effective disinfection. By the mid 1930s, chloramines were discovered to be more stable that free chlorine in the distribution system.. As a result of this discovery, chloramines were often used to limit bacterial regrowth. Chloramines have grown in popularity since the 1980s because chloramines do not produce as high concentrations of DBPs as free chlorine. Chloramination involves the addition of chlorine and ammonia to the water source. When chlorine reacts with ammonia, monochloramine (NH_2Cl), dichloramine ($NHCl_2$) or trichloramine (NCl_3) are formed (Reactions 3, 4 and 5)

$NH_4^+ + HOCl \leftrightarrow NH_2Cl + H_2O + H^+$ Reaction 3

$NH_2Cl + HOCl \leftrightarrow NHCl_2 + H_2O$ Reaction 4

$NHCl_2 + HOCl \leftrightarrow NCl_3 + H_2O$ Reaction 5

Monochloramine is the best chemical for disinfecting water because unpleasant taste and odors can arise when dichloramines or trichloramines are formed. A chlorine to ammonia ratio of 3:1 to 5:1 is commonly used to limit the amount of dichloramines and trichloramines formed and promote the formation of monochloramines. In addition, these ratios limit nitrification and biofilm growth, which can occur when higher levels of ammonia are used (5).

However, since chloramines are capable of producing a stable disinfectant residual, chloramination is a possible secondary disinfectant to control bacterial growth in distribution systems.

1.3.3. Chlorine Dioxide Disinfection

A survey of United States water treatment facilities in 1977 showed that 84 water treatment plants used chlorine dioxide. As of 1977, 495 water treatment plants in Europe used chlorine dioxide in some part of their treatment processes, most often as a disinfectant residual for the distribution system(5). The main disadvantages of using chlorine dioxide as a water disinfectant compared to chlorine are higher operating costs, health risks caused by residual oxidants and the creation of harmful by-products. Chlorine dioxide does not react with organic material in water supplies to form trihalomethanes; however, some halogenated by-products are created when chlorine dioxide is used as a disinfectant (3).

Another disadvantage of chlorine dioxide is that it is a very unstable chemical and it rapidly dissociates into chlorite and chlorate. High concentrations of chlorite and chlorate can cause an increase in methaemoglobinemia (6).

1.3.4. Ozone Disinfection

Ozone is a very strong purifier when used for primary disinfection in water and wastewater treatment plants. Because ozone gas does not have a stable chemical residual, it is not used as a secondary disinfectant (7).

Recent changes in the cost of ozone equipment have led more communities in the United States to use ozone disinfection in their drinking water treatment plants. In addition, ozone is becoming more widely used today because very few, if any, TTHMs and HAAs are formed from this disinfectant.

When ozone reacts with water, free radicals such as HO_2 and $HO^{\cdot}$ are formed (reactions 6-9). These free radicals are thought to be the active chemicals in the disinfection of the pathogens. The free radicals disintegrate the cell wall of bacteria and act as a strong virucide also.

$O_3 + H_2O \leftrightarrow HO_3^+ + {}^{\bullet}OH^-$ Reaction 6
$HO_3^+ + {}^{\bullet}OH^- \leftrightarrow 2HO_2$ Reaction 7
$O_3 + HO_2 \leftrightarrow HO^{\bullet} + 2O_2$ Reaction 8
$HO^{\bullet} + HO_2 \leftrightarrow H_2O + O_2$ Reaction 9

Ozone is more effective at inactivating organisms than chlorine. The other advantages to using ozone treatment include taste and odor control, oxidation of humic organic substances in water, and the destabilization of particles. There have been concerns about the safety of ozone with regard to DBP formation (other than TTHMs and HAAs). Bromate and formaldehyde can be formed in water after ozone disinfection, if the water has a high bromide ion concentration. Halopropanones and chloral hydrates are some other DBPs that are formed from disinfection with ozone. All of these DBPs are toxic.

1.3.5. Ultraviolet Disinfection

Ultraviolet disinfection is the transmission of electromagnetic energy from a mercury arc lamp. As UV radiation enters the cell wall of a microorganism, the UV light damages the deoxyribonucleic acid (DNA) or ribonucleic acid (RNA), thus preventing the organism from reproducing. Pathogens are successfully killed at wavelengths ranging from 245 to 285 nm. Either low-pressure (254 nm) or medium-pressure (180 – 1,370 nm) mercury arc lamps, set at low or high intensities, can be used as the source of UV radiation(8). UV disinfection is very effective at inactivating pathogens at low dosages(9). Very small concentrations of DBPs are formed when UV disinfection is used. However, high concentrations of turbidity and certain minerals can decrease the effectiveness of UV(10). In addition, this type of disinfection does not produce a disinfectant residual; therefore it can only be used as a primary disinfectant. A secondary disinfectant, such as chlorine gas, in combination with UV radiation has to be used when treating drinking water with UV disinfection.

1.4. Disinfection By-products

Disinfection by-products (DBPs) are defined as the class of chemicals that are formed when disinfectants react with the organic compounds in water. Some of these compounds are carcinogens and some are suspected of causing acute health effects. DBPs are chemical compounds produced as anundesirable result of water disinfection and oxidation. The chemical compounds of most serious concern contain chlorine and bromine atoms. These compounds have been shown to be carcinogenic, mutagenic or hepatotoxic .

1.4.1. History of Disinfection By-products

In 1974, public awareness in USA about DBPs was increased by several events (5,9,10,11) . On November 8, 1974, the U.S. EPA announced that it would conduct a nationwide survey, called the National Organics Reconnaissance Survey (NORS), to find the concentrations and possible effects of certain organic chemicals in drinking water. The survey(11) concluded that TTHMs were present in finished waters due to chlorination practices. All the samples tested in the NORS contained detectable levels of chloroform. Ground water sources had a lower average TTHM concentration than surface waters. The survey noted higher average TTHM concentrations in locations where raw-water chlorination was practiced. Higher levels of TTHMs were also found when surface water was the source water and more than 400 μg/L free chlorine residual was present. When powdered activated carbon (PAC) was used, the average TTHM concentration was lower than when PAC was not used. The survey also showed that higher TTHMs were found at higher pH levels. The results of NORS showed that TTHMs were the most prevalent organic compounds in drinking water and that chloroform was one of the more common THMs. Other compounds that were found were 1,2-dichloroethane, carbon tetrachloride and nonvolatile total organic carbon. As a result of this survey, the U.S. EPA set regulations for controlling THMs in drinking water systems (12).

1.4.2. Trihalomethanes

Trihalomethanes are organohalogen compounds; they are named as derivatives of the compound methane. Trihalomethanes are formed when three of the four hydrogen atoms attached to the carbon atom in the methane compound are replaced with atoms of chlorine, bromine and/or iodine. Trihalomethanes are formed when chlorine has a chemical reaction with the organic material that is already present in the water supply.

Trihalomethanes (THMs) include chloroform ($CHCl_3$), dibromochloromethane ($CHBr_2Cl$), bromodichloromethane ($CHBrCl_2$), and bromoform ($CHBr_3$). Chloroform is the THM most commonly found in drinking water and is usually present in the highest concentration(13). The existence of disinfection by-products, such as chloroform and other trihalomethane compounds, in chlorinated drinking water supplies was first discovered in 1974 (14).

1.4.3. Other Disinfection By-products

The first regulations to limit DBPs were only concerned with TTHMs. More recent regulations rule set limits for both TTHMs and HAAs . New DBPs are constantly being discovered , e.g bromate , chlorate , chlorite .

1.5. Factors Affecting the Formation of DBPs

There are several factors affecting the formation potential of DBPs. Research studies have shown that the major variables that affect DBP formation are: residence time, temperature, pH, disinfectant type and concentration, total organic carbon concentration and chlorine to nitrogen levels (for chloramination).

Each different type of disinfectant has both advantages and disadvantages in drinking water treatment. Free chlorine is very effective at inactivating pathogens but it produces some of the highest concentrations of DBPs. Chloramination is a weaker disinfectant compared to free chlorine but very few DBPs are formed when water treatment plants use chloramination. Ozone is an effective disinfectant and doesn’t produce many DBPs of concern but ozone is not capable of providing a residual through the distribution system. Ultraviolet light has been shown to be effective at inactivating pathogens and it doesn’t produce any DBPs that are yet regulated by the U.S. EPA but like ozone it does not produce a residual. Regarding chloramination, the best Cl_2:N ratio for minimizing DBP formation depends on raw water quality. The type and concentration of humic substances present in the raw water source are the most important parameters that dictate which Cl_2:N ratio is the best. In a study examining chloramine disinfection,(15) it's found higher TTHM levels when disinfecting with chloramines at a Cl_2: N ratio of 7:1. They also found that as the Cl_2: N ratio decreased the HAAs decreased. The experiment showed that a Cl_2: N ratio of 3:1 was ideal for controlling DBP formation, but this ratio might not be suitable for controlling bacterial regrowth.

1.5.1. Disinfectant Concentration

The studies have shown that as the disinfectant concentration increases, DBP formation also increases (16).

1.5.2. Residence Time

The studies have shown that as residence time increases, TTHMs increase (up to day one) and HAAs decrease (17). also The results showed that TTHM levels increased and HAAs levels decreased as the distance from the treatment plant increased.

1.5.3. Temperature

Many studies have been conducted to evaluate how temperature affects the rate of DBP formation and the concentration of DBPs that are formed. Some studies have shown that as the temperature increases, the concentration of TTHMs also increases.

However, the results are not conclusive because conflicting results have been found from different research studies.(18) it's examined TTHM and HAAs concentrations (during all four seasons) in 14 conventional water treatment plants which disinfect with chlorine. In this study, the mean TTHM levels for summer, fall, winter, and spring were 32.1 µg/L, 28.7 µg/L, 17.6 µg/L, and 16.5 µg/L, respectively. This study showed that the highest TTHM concentrations were found in the summer and fall seasons, and the lowest TTHM concentrations were present in the winter and spring(18). Chen and Weisel’s research showed that TTHM levels increased significantly in the summer and the HAA levels remained the same throughout the year. An addition study was conduct (13), on water disinfected with chlorine and treated by conventional treatment. The smallest concentrations of HAAs were formed in January, February, and March (total HAAs concentration of less than 13 μg/L). The highest concentrations of HAAs occurred in May and June, when the levels reached 120 μg/L. The results are in contradiction with the results of the Chen and Weisel study. Therefore, the impact of temperature on HAAs levels is unclear.

1.5.4. pH

Several studies have been done to analyze concentrations of DBPs and how they relate to pH levels of the water supply. The findings support the conclusion that higher pH conditions cause HAA concentrations to decrease and TTHM concentrations to increase (14,17,19)

1.5.5. Total Organic Carbon Concentrations

Several researchers have studied the impact of total organic carbon concentration on DBP formation. These experiments showed that as TOC concentrations increased so did TTHM and HAAs levels(14,20) . also it was found HAAs formation was dependent on the organic matter present in the sample: higher concentrations of HAAs were formed at higher TOC concentrations.

1.5.6. Bromide Concentrations

Recent studies have been completed which examined the relationship between bromide concentration in a drinking water supply and DBP formation. These studies have shown that as the concentration of bromide is increased, the concentration of TTHMs and HAAs also increases. When there are high bromide concentrations in a raw water source and chlorine is added to the water supply(20,21) , Also , it was found the highest HAA values were observed when the largest amount of bromide was added to the water (22).

1.6. Health Risks

Many DBPs are known carcinogens, and some could possibly have adverse affects on pregnancy.

1.6.1. Animal Studies

Animal studies have shown the effect of DBPs on pregnancy outcomes. Table (1.1) is a summary of some of the results found by researchers examining the effect of TTHMs on animals. When the highest doses of chloroform were administered to the animals, either orally or by inhalation, all of the studies showed some type of embryotoxic or fetotoxic effect. Such effects included reduced fetal size and weight, and retarded skeletal Ossifications (23,24,25).

Table 1.1: Chloroform developmental studies

Species	Dose (s)	Gestational Days administered	Route of Administration	Results	Reference
Rat	30, 100, 300 mg/L	6-15 (7 hr/day)	Inhalation	Embryotoxic, Fetotoxic, Teratogenic	26
Rat	20, 50, 126 mg/kg/day	6-15	Oral	Fetotoxic	27
Rat	100, 200, 400 mg/kg	6-15	Oral	Fetotoxic	28
Mouse	100 mg/L	1-7, 6-15, 8-15 (7 hr/day)	Inhalation	Embryotoxic, Fetotoxic, Teratogenic	21
Rabbit	20, 35, 50 mg/kg/day	6-18	Oral	Fetotoxic	27

1.6.2. Human Studies

Several studies have shown the association between chlorination by-products and the cancer in humans, especially bladder cancer(29). and rectal cancer(30). Further studies on the relation between TTHM concentrations and adverse birth outcomes have been conducted (1,2,18 , 30-34) .

The findings showed an association between stillbirths and TTHM concentrations. Another study found an association between pregnant women, in their third trimester, being exposed to high trihalomethane levels and a risk of term low-birth weight deliveries (22,35) . The study further concluded that an increase in risk of growth retardation with respect to higher trihalomethane levels could be expected.

1.7. Water pollutants

Effluents are classified by their origin as domestic or public sewage, industrial effluents, and atmospheric runoff. Depending on the degree of pollution and sanitary requirements, all effluents can be either discharged straight into a watercourse or only after an appropriate mechanical, physicochemical, chemical, or biological treatment. The degree of water pollution is determined by sanitary and chemical analysis.

1.8. Regulations

In the early 1970s, DBPs were first discovered to have harmful health effects to, animals and humans. On November 29, 1979, the first legislation to limit the concentration of TTHMs in drinking waters was passed (2). This rule set a TTHM limit of 100 µg/L.

1.9. Removal of DBPs After Formation

Removal of THMs has the advantage of allowing treatment plants to continue with their current disinfection practices. Chlorination could continue to be used as a disinfection process, and the trihalomethanes could be removed by adding an additional treatment process. One disadvantage of this type of treatment is that the objective is to remove trihalomethanes after they have formed. Other DBPs may not be removed by the treatment process, only the specific one that the process is designed for. Another disadvantage is the fact that chlorine is an oxidant; therefore the possibility of producing oxidation by-products during chlorination still exists. The biggest disadvantage to trihalomethane removal after they have been formed is the problem that it is not cost effective.

Several methods are available to remove trihalomethanes from waters after formation. These methods include: 1) oxidation; 2) aeration; and 3) adsorption.

1.9. 1. Oxidation

The possibility of removing trihalomethanes by oxidation, using either ozone or chlorine dioxide as the oxidant, has been investigated (34) . Ozone alone had little or no influence on the two trihalomethanes (chloroform and bromodichloromethane) tested while ultraviolet radiation alone (photolysis) destroyed both slowly. Combined treatment by ozone and UV was much more effective, lowering the concentration of these trihalomethanes to one–half of their initial values in 3.3 to 6.3 minutes for the laboratory prepared water .

1.9. 2. Aeration

Chloroform was very effectively removed. Aeration is a feasible approach for trihalomethane removal, with the difficulty of removal increasing with molecular weight from chloroform to bromoform (36,37)

1.9.3. Adsorption

Much attention is being paid to the development and introduction of adsorptive methods of treating drinking water. Many investigators have studied the feasibility of using cheap, commercial available materials as potential adsorbents e.g. activated carbons, bone char, alumina, silica, bauxite, betonies, fuller's earth, molecular sieves, peat, lignite, chitin, chitosan, and ion exchange resins. (38,39,40)

Sorption on granular activated carbon is one of the most effective methods for the removal of dissolved organic substances from waste. Powdered activated carbon is also used. It is added in small quantities directly to a biological system with the aim to remove toxic substances and/or to enhance the capacity of the system.

The effectiveness of adsorption by activated carbon depends on the type of activated carbon used and the composition of the wastewater. Most organic and elementary organic compounds are adsorbed by it, which makes it possible to remove many toxic substances from the wastewater in the purification process.

The wide utilization of activated carbon is due to its hydrophobic properties, its availability (many brands of carbon have been developed and put on sale), its immense adsorptive capacity and the non-selective nature of adsorption on it. Most non-biodegradable organic compounds can be adsorbed on carbon. This method has found greatest application in removing coloured compounds, pesticides and halogenated organic compounds from wastewater.

Many factors influence the rate at which adsorption reactions occur and the extent to which a particular material can be adsorbed. Some of the more important factors are : particle size and surface area are important properties of an activated carbon (41,42) ; solubility and size of adsorbate molecules (42) **;** and The temperature at which an adsorption process is conducted(42,43).

Granular activated carbon (GAC) adsorption systems used in drinking water treatment typically use stationary beds with the liquid flowing through the absorbent (GAC) . The U.S. EPA's Drinking Water Research Division prove that THMs containing bromine were more effectively adsorbed by the GAC(44).

1.10. Activated Carbon.

The term active carbon (AC) actually implies a rather broad family of substances, with highly developed internal surface area, porosity and individual species being characterized by sorptive and catalytic properties rather than by definite structure or specific chemical composition. Porous carbon materials or activated carbons have been used for thousands of years and have become extremely versatile adsorbents. Active carbon is a broad-spectrum agent that effectively removes toxic and bio-refractive substances such as insecticides, herbicides, chlorinated hydrocarbons, heavy metal ions, and phenols, typically present in many water supplies (45-54) The major applications of activated carbon are in solution purification and for the removal of taste, color, odors and other objectionable impurities from liquids, water supplies and vegetable and animal oils. In the recent years, it has been increasingly used for the preventation of environmental pollution and antipollution laws have increased the sales of active carbons for control of air and water pollution.

Activated carbon can be manufactured from any material that has reasonable elemental carbon content. Any lignocellulosic material can be converted to an activated carbon. The literature mentions many precursors for activated carbon such as bagasse (55) scrap tires and saw dust (56) almond, pecan, English walnut ,black walnut and macadamia nut (57) pistachio (58) hazelnut shells (59) rice husk (60) rice bran (61) Particular properties may be imparted to an active carbon either by starting with different raw material or by utilizing different preparative procedures.

1.10.1. Preparation of active carbon

According to (62), the preparation of activated carbons involve two main steps; carbonization of the carbonaceous raw material at temperature below 700 ^{o}C in the absence of oxygen, and activation of the carbonized product. During carbonization most of the non- carbon elements such as oxygen and hydrogen are first removed in gaseous form by the pyrolytic decomposition of the starting material. The free atoms of elementary carbon are grouped into sheets of condensed aromatic ring systems with a degree of planar structure. The arrangement of these aromatic sheets is irregular and leaves interstices between them, which may, filled with tarry matter or products of decomposition or at least blocked partially by disorganized carbon. The important parameters that determine the quality and the yield of the carbonized product are:(i) rate of heating, (ii)final temperature and (iii) soaking time(63).

Simple cooking or carbonization does not give rise to products that have adsorption capacity because of their less developed pore structure and low surface area. This pore structure is enhanced during the activation process, which convert the carbonized raw material into a form that contain the greatest possible number of randomly distributed pores of various shapes and size giving rise to an extended and extremely high surface area of the product (64). The objective of the activation process is to enhance pore volume and to enlarge diameter of the pore, which were created during carbonization process, and to create new porosity. Activation process removes the disorganized carbon, exposing the aromatic sheets to the activation agent in the first phase and leads to the development of microporous structure. In the later phases of the reaction the significant effect is widening the existing pores or the formation of large-sized pores by complete burn- off of the walls between the adjacent pores .

1.10.2. Methodes of activation

Typically, the activation of carbon can be divided into two processes. First, the *physical method* consists of the pyrolysis of the precursor material and gasification of the resulting char in steam, nitrogen gas, air or carbon dioxide. The formation of the porous structure is achieved by elimination of a large amount of internal carbon mass. High porosity carbons can be obtained only at a high degree of char burn off. For the chemical method, pyrolysis char would be impregnated with some chemical reagents, such as $ZnCl_2$, H_3PO_4, NaOH, and KOH. Because of the dehydrogenation process, the chemical reagents promote the formation of cross-links, leading to the development of a rigid matrix, less prone to volatile loss and volume contraction upon usage. According to (65-68) major advantages of the chemical activation compared to the physical activation are lower treatment temperatures and shorter treatment times. In addition, activated carbon obtained by chemical activation exhibits a larger surface area and better developed mesoporosity than physical activation.

1.10.3. Structure of activated carbon

Activated carbons are highly porous materials with surface areas of up to 3000 $m^2.g^{-1}$. The surface area of a typical activated carbon is about 1000 $m^2.g^{-1}$. These high surface areas are the result of development of mainly micro- and mesopores while a little contribution is also come from macropores. According to the

IUPAC classification, pores having the radii less than 2 nm are called micropores whereas pores having the size of radii in between 2 to 50 nm are identified as mesopores. Macropores are defined as pores having the radii size above 50 nm. Cokes, chars and activated carbons are often termed as amorphous carbon. X-ray diffraction and electron microscopy have shown that these materials have crystalline characteristics, even though they may not show certain features, such as crystal angles and faces, usually associated with the crystalline state. The existence of submicroscopic dimensions in so called amorphous carbons makes the microcrystal structure known as crystallites. The basic structural character of amorphous carbons is closely approximated by the structure of pure graphite. The graphite crystal is composed of layers of fused hexagons held approximately 0.335 nm apart by van der Waals forces (69).

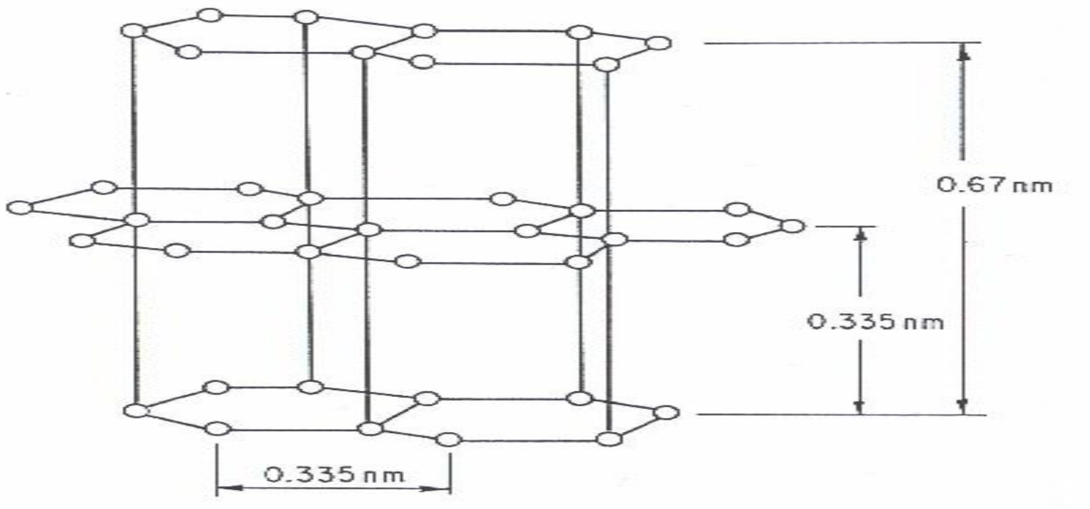


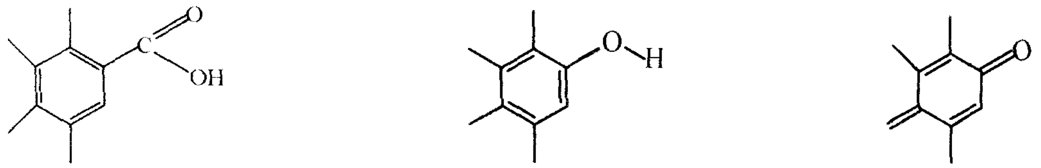
Figure 1.1 Carbon Atom Arrangements in Graphite Crystal

However, the structure of activated carbon differs some what from that of graphite. During carbonization process, several aromatic nuclei, having a structure similar to that of graphite are formed. Planar separation distance in carbon is approximately 0.36 nm. From X-ray spectrograph, these structures have been interpreted as microcrystallite consisting of fused hexagonal rings of carbon atoms structurally, carbon can therefore be considered to consist of rigid interlinked cluster of microcrytallites. Each microcrystallite comprises a stack of graphite planes. Microcrystallites are interconnected by interaction of functional groups terminating the graphitic planes. The diameter of the planes forming the microcrystallites, as well as the stacking height, has been estimated at 2 -5 nm indicating that each microcrystallite consists of about 5-15 layers of graphite planes(70).

It can be summarized that AC is black, amorphous solid containing major portion of fixed carbon content and other materials such as ash, water vapor and volatile matters in smaller percentage. Beside that, AC also contain physical characteristic such as internal surface area and pore volume. The large surface area results in a high capacity for absorbing chemicals from gases or liquids. The adsorptive property stems from the extensive internal pore structure that develops during the activation process.

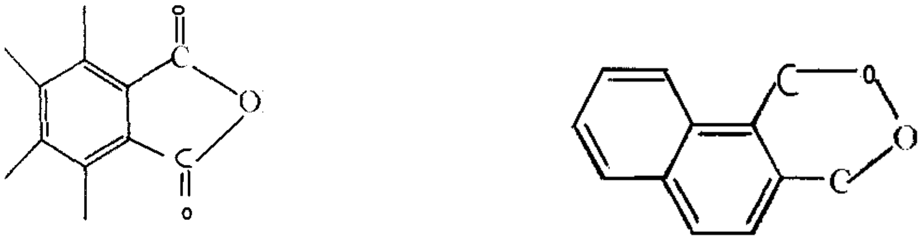
1.10.4. Surface functional groups on active carbon

Wheeler (71) reported that when oxygen contacts carbon surfaces some sort of oxygen-carbon complex is formed. It is known that surface functional groups are formed during the carbon activation process. In general, acidic oxides are predominantly formed in carbon when it is prepared under moist air at 300 to 500°C, and basic oxides in those carbons prepared at 800 to 900°C in air, steam, or carbon dioxide. Amphoteric properties are found in carbons prepared between 500 to 800°C. The activated carbons prepared at low activation temperature, below 500-600°C, adsorb OH^- ions primarily are called L-carbons. Those activated carbons are prepared at above 500-600°C and adsorb H^+ ions are called H-carbons. Almost every type of functional group in organic chemistry has been suggested to be present on activated carbons surface. The ones suggested most often acidic functional groups are: carboxyl, phenolic-hydroxyl, and quinone-type carbonyl groups (Figure 1.2) while other suggested groups are ether, peroxide and ester groups in the forms of normal lactones and fluorescein-like lactones, carboxylic acid, anhydrides and the cyclic peroxide (Figure 1.3). On the other hand, proposed basic surface groups include chromene and pyrone.



Carboxyl groups Phenolic hydroxyl groups Quinones

Fig.(1.2) Structures of carboxyl, phenolic hydroxyl and quinines carbonyl groups



carboxylic acid anhydrides Cyclic peroxide

Fig.(1.3) Structures of carboxylic acid anhydrides and cyclic peroxide

1.11. Olive stone as precursor for activated carbon

Interest in chemical activation with phosphoric acid has grown during the past decade, particularly as a method of activation for lignocellulosic materials e.g. coconut shells, wood sawdust, peach stones, rice husks, apricot stones, corn cobs and cotton stalks (72) . This process offers better conditions of preparation as it may be carried out as a one-step heating process (thus saving time and energy), is effective at lower temperatures and leads to a higher carbon yield with the most of the acid capable of being recovered economically. Important consideration to be made in selecting a source include cost, availability consistency of quality and mineral matter content (including sulphur content). Mechanical hardness adds to the quality actived carbon to be used for purification processes.

Olive stones or (olive oil wastes) were investigated for many decades by the Spanish group of workers(73- 78). They generally employed activation of high temperature chars (produced at 850 -1000^{o}C) in a steam of CO_2 gas or a steam /N_2 steam at (750 - 1000^{o}C). Some modifications were tried, such as using a gasification catalyst, changing the heating furnace position or subsequent gasification with are at (350 - 500^{o}C).

In this concern, literature on previous studies of activated carbon derived from olive stones depicted that the result of the adsorption of two basic dyes (Methylene Blue and Rhodamine B) in aqueous solution by activated carbon prepared from olive stones were found to be respectively 303 mg/g and 217 mg/g (79).

Activated carbon prepared from carbonized olive stones in presence of nitrogen at 700 - 800°C and activated by $ZnCl_2$ and KOH, can be used for Pb^{2+} ions removal from potable water in the presence of other metal ions and found that NaCl will interfere in adsorption. The sample activated by KOH has the highest adsorption capacity followed by $ZnCl_2$ (80) .

The characterization of activated carbon(olive stones) obtained by chemical activation by KOH and $ZnCl_2$ of a lignocellulosic material, by the techniques of adsorption of nitrogen at 77 K and immersion calorimetry in cyclohexane and water. The obtained results show that the enthalpy of immersion in these two liquids is in perfect correlation with the specific surface area(81). Different activated carbons were prepared by KOH-activation of carbonized olive stones by varying the KOH/carbon weight ratio and the particle size of the precursor. The activated carbon with the best surface characteristics was furthermore steam-activated. Other activated carbon was obtained by using directly olive stones as raw material. In this case the precursor particles were broken by the KOH solution, obtaining an activated carbon with an extremely fine particle size. Different monoliths were prepared from this powder activated carbon by using a binder and pressure. Carbon monoliths were used to remove toluene from a toluene/air flow under dynamic conditions. Amounts adsorbed at saturation were much higher than others reported in the literature and that were obtained by using different activated carbons(82).

The activated carbon produced from olive stones was chemically activated using sulfuric acid, (OS-S), and utilized as an adsorbent for the removal of Cr(VI) from aqueous solution in the concentration range 4-50 mg/L (83) .

Olive stones based activated carbons have been tested as adsorbents for pure methane storage during cyclic operation charge- desorption at 303K up to 8 bars. The results encourage grain based activated carbons use as good candidate for gas storage to vehicular applications (84).

Two series of activated carbon monoliths (discs) have been prepared by chemical activation of olive stones with phosphoric acid or zinc chloride, without the use of any binder. Also, two equivalent series of granular activated carbons were also prepared in order to analyze the effect of conforming pressure on the porosity of the final activated carbon. The results indicate the differences between the granular and monolithic forms are more noticeable when using phosphoric acid. Thus, there is mainly a reduction in the interparticle space and macroporosity during the formation of the discs prepared using zinc chloride whereas there is an additional reduction in the volume and dimension of the meso- and microporosity when using phosphoric acid (85) .

The removel of butane storage on activated carbon prepared from olive stones precursor activated by chemical process developed. Gas storage on activated carbon is carried out on fixed bed sample at isothermal conditions during cyclic operation up to 17 cycles under 3 to 4 bars at 303 K. Stored hydrocarbon gas purity ensures total adsorption efficiency. This important results show that GAC prepared from olive stone is a potential adsorbant for hydrocarbon gas storage for vehicle uses (86).

1.12. Significance of the research

Nowadays, fossil fuels, presently contributing to 80% of world primary energy, are inflicting enormous impacts on the environment. Moreover, their future exhaustion and the absence of a clear replacement entail a threat for worldwide energy and economic system. A secure and accessible supply of energy is thus very crucial for the sustainability of modern societies. There is an urgent need for a quick switch over of energy systems from conventional to renewable that are sustainable and can meet the present and projected world energy demand.

Biomass has great potential as a clean, renewable feedstock for producing modern energy carriers. Having into account that nowadays biomass represents only 3% of primary energy consumption in industrialized countries (and according to European Community, its contribution to primary energy in Europe would reach around 9% by year 2010), is evident that intense research focused on improving biomass conversion into energy has to be done.

Among all the current technologies that convert biomass into gaseous products, biomass gasification is considered as one of the most promising thermochemical technologies and much research on it is being made on both fluidized bed and downdraft gasifiers (87).

Also biomass pyrolysis processes have been proved to be very interesting in order to obtain energetic gaseous products (88-89) Focussing on the products derived from biomass pyrolysis processes, it is well known that, apart from the gas (mainly composed by H_2, CO, CO_2, CH_4, etc, which could be employed in internal combustion engines, gas turbines and other operating devices) and tars (which have a low HHV); a solid carbonaceous residue (char) is generated. This char is characterized by a high carbon content (>75%) and a narrow microporous structure, which makes it suitable to be a good precursor for activated carbon (AC) production by physical activation.

Activated carbons are porous materials that (due to their chemical and textural characteristics) are able to adsorb certain amounts of compounds in the liquid and gaseous phases; this property makes these solids very interesting to be used in many industrial applications. AC production consists, in general terms on the activation (physical or chemical) of a suitable precursor. Chemical activation consists on the impregnation (with different chemicals) of the raw material, followed by a carbonization. Physical activation consists of the carbonization of the raw material, followed by a thermal treatment of the char with an activating agent (air, steam, CO_2...). Independently of the activation process employed, the operating parameters (time, temperature, activating agent, chemical product...) will influence the final textural and chemical surface properties of the AC produced.

There is a huge amount of research on the production of AC from biomass residues but the information about the gases generated in this process is scarce.

1.13. Aim of work

It is well known that, halocarbon such chloroform, bormoform, bormodichloromethane and diboromochloromethane can potentially cause contamination of potable water, the composition of such contaminating products consists of a complex mixture of hydrocarbons and additives.

The potential usage of adsorption for removal of dissolved organic materials from polluted water and drinking water is well recognized, and considerable research interest has focused on the exploration of the best method by which this process can be utilized for drinking water treatment. The literature on adsorption reveals that activated carbons are more frequently used as an adsorbent than any other materials in drinking water renovation operations and so it has found its largest market in industrial and municipal water purification.

The objective of this study is to make better insight on the removal of THM to know more about the efficiency of adsorption in treatment of contaminated water components.

In this concern, this study was undertaken with two purposes in mind:

-Firstly, to ascertain the ability of certain low-cost, locally available materials (e.g. agro-residues) to adsorb THMs.

-Secondly, to investigate the removal of THMs from water by adsorption / photodegradation.

The proposed research program is directed to investigate the following aspects:

1- Preparation of activated carbons from olive stone using physical or chemical activation route.
2- Adsorption of THMs (chloroform, bormoform, bormodichloromethane and dibormochloromethane) by olive stone Activated carbon
3- Factors affecting on adsorption process (time, initial concentration, adsorbent mass, pH and temperature).
4- Photodegration Studies (i) uv alone; (ii) uv/ activated carbon and (iii) uv/ activated carbon / TiO_2.
5- Chose the best conditions for removal of each component of THMs from aqueous solution.