Summary

Trihalomethanes (THMs) are considered to be the major by-products found in water after the chlorination process. They mainly consist of chloroform ($CHCl_3$), dichlorobromomethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$). Their content in drinking water is regulated and the maximum contaminant level (MCL) of 100 µg/L established in 1979 by the United States Environmental Protection Agency (USEPA) for total THMs, based on a running annual average, still prevails and has been adopted in many other countries. Prolonged consumption of drinking water containing high levels of THMs has been linked with diseases of the liver, kidneys, bladder, or central nervous system, and may result in an increased likelihood of cancer. A small risk exists for THMs exposure via inhalation while showering, bathing or washing clothes and dishes. In this article, we describe The work recorded in this thesis affords possibilities of THMs removal from potable water utilizing activated carbons derived from olive stone as well as an opportunity to study the adsorption process. This thesis consists of three chapters:

Chapter "1" provides historical background and chemical information for several disinfectants used. Chlorine, chloramines, chlorine dioxide, ozone and ultraviolet disinfection are discussed. Also, it includes history of disinfection by-products (DBPs) and factors affecting the formation of DBPs and their health risk. The methods available to remove THMs from waters after described. These methods are: oxidation; aeration; and adsorption. Sorption on granular activated carbon is one of the most effective methods and in this concern, preparation of active carbon;

methods of activation; its structure and surface functional groups as well as a review on olive stone as precursor for activated carbons.

Chapter "2" It contains the experimental part. In this concern, Olive stone was used as a precursor for preparation of 4-activated carbon samples either by: (i) by physical route (using N_2 gas); or (ii) by chemical route (using H_3Po_4). The 4-samples were taken the notations: OSN-1850; OSP_{60}-2500; OSP_{70}- 2500 and OSP_{80}- 2500.

The physicochemical characterizations of the 4-samples were investigated using various techniques. In this concern, bulk density, pH, FT-IR, SEM, BET- surface area and pore structure were determined. The factors affecting adsorption were studied (e.g. time, initial adsorbate concentration; adsorbent mass, pH and temperature) on four adsorption systems. The kinetic and diffusion studies were tested. The experimental data of equilibrium isotherms for the 4-adsorption systems were modeled using Langmuir and Freundlich models.

The photodegradation of the THMs solutions was undertaken by exposing each component for 25 min. to (i) UV light alone or (ii) UV light in presence of activated carbon derived from olive stone or (iii) UV light in presence of activated carbon loaded by TiO_2.

Chapter "3" includes the results and discussion of this study. The physicochemical characterizations of the 4-samples were investigated using various techniques. In this concern, sample OSN-1850 prepared via physical route has less bulk density (0.671 g/ml) and shows basic surfaces (pH= 10.4) whereas samples prepared from olive stone through chemical activation are OSP $_{60}$-2500; OSP $_{70}$ – 2500 and OSP_{80}- 2500 have high density, in the range of 0.776-0.833 g /ml. and give pH < 4. The FT- IR spectra showed stretching vibrations due to the functional groups NH_2,

OH, C-H, C-O, C=C and C≡C bonds. In general, Textural characteristics of the prepared activated carbons have the following order :
S_{BET} were: OSP_{80}- 2500 > OSP_{70}- 2500 > OSP_{60}- 2500> OSN-1850.

V_{mic} were: OSN-1850 > OSP_{70}- 2500 > OSP_{80}- 2500 > OSP_{60}- 2500.

Vmeso were: OSP_{60}- 2500> OSP_{80}- 2500> OSP_{70}- 2500> OSN-1850.

From the economic or commercial application point of view, the sample OSP_{80}- 2500 has the advantages: micro- and meso-porosity; high surface area 2050 m^2/g, high bulk density 0.833 g/ml and total pore volume, Vp, 1.0836 ml/g which is comparable for activated carbons in markets. Therefore, it is useful in wide applications in wastewater treatment plans, not only for purification of drinking water.

The SEM morphology of the resulting activated carbons proved the presence of micro pores only in physical activation and mixture from micro- and meso pores in chemical activation.

The initial laboratory tests of adsorbability (uptake and Re%) indicated that the prepared activated carbons using H_3PO_4 were better than that prepared via N_2 gas in removal of THMs. Consequently, 4-adsorption systems were chosen for further investigations. These are:
1- OS P_{60}-2500 : $CHBr_3$ 2- OS P_{80} -2500 : $CHCl_3$
3- OS P_{80} -2500 : $CHBr_2Cl$ 4- OS P_{70}-2500: $CHBrCl_2$.

There are many factors affecting adsorption of THMs were investigated. In this concern, The equilibrium time was attained after shaking time for about 1750; 1200; 600 and 1200 min. in case of $CHBr_3$; $CHCl_3$; $CHBr_2Cl$ and $CHBrCl_2$, respectively. The kinetic data of THMs may be described well by second-order rate equation due to the high values of correlation coefficient R^2 for second-order adsorption model compared to that of pseudo-first-order model. The values of adsorption rate constant for $CHCl_3$, $CHBr_3$, $CHBr_2Cl$, $CHBrCl_2$ were 0.15 , 0.13 , 0.092 and 0.0712, respectively. These results suggest that the rate-limiting step may be chemical sorption involving valency forces through sharing or exchange of electrons between THMs and adsorbent. Also, the results confirmed the data obtained by maximum adsorption capacity from equilibrium time curves.

The intra-particle diffusion rates, k_{int} , were determined and their values were: 0. 58, 0.51, 0.2 and 0.6 $mg.g^{-1}min^{-0.5}$ for bromoform; chloroform; dibromochloromethane and dichlorobromomethane, respectively. It may be concluded that the intra-particle diffusion was not the only rate-controlling step. The sorption mechanism of THMs from aqueous solution is rather complex process, probably a combination of external mass transfer, and intra-particle diffusion. The results clearly indicate that the removal of THMs from the aqueous solution was dependent on the concentration of THMs present in the system. At low concentration (below 100 µg/L for THM) sorption was 85-95%. This suggests that olive stone activated by H_3Po_4 is suitable to remove most of THMs exist as DBPs in drinking water. Thus, concentration of THMs reaches the permissible levels according to the standard regulations. Consequently, the drinking water will be safe without any health risk. It was clear that as the adsorbent dosage increases the percent removal (Re%) of each THMs increases too. This is occurred from 5 ml solution containing 100 µg/L of chloroform or boromoform or diboromochloromethane or dichloroboromomethane and then attained constant removal after a particular carbon concentration (optimum dosage) beyond which there is no significant increase in removal for THMs studied. The adsorption of each THMs decreases as the pH increased. This is due to the fact that more oxygen-containing groups on the olive stone activated carbon surface are ionized at higher pH values and thus they adsorbed more water. The formation of water clusters on these groups would block the access of THMs molecules to the adsorption sites and lead to a smaller adsorption of THMs.

The experimental data of equilibrium isotherms for the 4-adsorption systems were modeled using Langmuir and Freundlich adsorption models. According to the Langmuir equation, the adsorption capacity or the monolayer coverage determined follows the order : $CHCl_3 > CHBr_3 > CHBrCl_2 > CHBr_2Cl$

and adsorption affinity follows: $CHBr_2Cl > CHBr_3 > CHCl_3 > CHBrCl_2$.

According to Freundlich equation, the values of the Freundlich exponent “ n ” are greater than one, indicating that the adsorption of THMs by carbon samples are favorable, indicating that surface structures of sorbents are heterogenous. However, the adsorption of chloroform and diboromchloromethane is more favorable than the boromoform then dichlorobormomethane as indicated by their higher capacity at the same equilibrium concentration and their higher intensity. The effect of temperature on two adsorption systems were studied. In this concern, The uptake of bromoform onto OSP_{60}- 2500 and chloroform onto OSP_{80}- 2500 at 25°C, 35°C and 45°C indicate a normal trend associated with physical adsorption. i.e., an increase in the temperature, will result in a reduction of the equilibrium adsorptive capacity, whereas lower temperature will favor an increased capacity. This may be referred to the fact as the temperature increases, the solubility increases which lead to decreasing of affinity of THM to olive stone activated carbons.

The photodegradation studies of THMs solutions was undertaken in three processes by exposing each THMs compound for 25 min. to (i) UV light alone or (ii) UV light in presence of activated carbon derived from olive stone or (iii) UV light in presence of activated carbon loaded by TiO_2. The results proved that the percent removal (Re%) for all THMs were more better when TiO_2 impregnated on olive stone activated carbon. This may be explained by the fact that the adsorption rates of THMs (on olive stone activated carbon) and their photodecomposition rates (on UV irradiated olive stone activated carbon/ on UV irradiated olive stone activated carbon loaded by TiO_2) are influenced by the nature of active sites on the carbon employed and it plays a dual role in both retaining and allowing the photodegradation of THMs and the hydroxyl radicals (HO*) was the primary reactive oxygen species for the photodegradation of THMs.

On the basis of this study, it is concluded that the coupling techniques (adsorption and photodegradation) are more influence for removal of THMs from solution.