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Treatment of Some Organic Pollutants (THMs) using Activated Carbon Derived from Local agro-residues

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ABSTRACT

Trihalomethanes (THMs) are carcinogenic by-products of disinfection that are present in drinking water. In the present research, adsorption and photodegradation, either individually or in tandem, was employed for the removal of the principal THMs found in water supply systems. The effects of pH, contact time, adsorbents and adsorbate concentration on the adsorption system were investigated .The Langmuir and Freundlich adsorption isotherm models were used to analyze the resulting adsorption data. 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. The integration of adsorption and photodegradation systems as a hybrid treatment process resulted in a synergetic enhancement of the THM removal efficiency. The kinetics of THM removal were found to follow the pseudo-second-order model rather than the Langmuir–Hinshelwood pseudo-first-order model.

Keywords adsorption, photodegradation, THMs removal, TiO_2, olive stones.

INTRODUCTION

Trihalomethanes (THMs) are considered to be the major by-products found in water after the chlorination process [1] . They mainly consist of chloroform ($CHCl_3$), bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$) and bromoform ($CHBr_3$) [2]. Their content in drinking water is regulated and the maximum contaminant level (MCL) of $100\,\mu g\,L^{-1}$ 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 THM 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 The concentrations of trihalomethanes in Cairo and Giza tap water have been found to be higher than the WHO guideline values [3].

by the U.S. Environmental Protection Agency as one of the foremost materials for use in pollution control [4]. Important studies reviewing the removal of THM and organic molecules by carbon spheres have been published [5,6]. Nevertheless, the efficiency of activated carbon as an adsorbent is dependent on the need for large dosages over short time periods, with its use being consequently limited by the associated cost. Due to the limitations associated with the above techniques, most researchers have focused on methods of reducing the potential for the formation of THMs, including the use of membrane processes and ultrasonic irradiation [7-12]. Nevertheless, an efficient destructive method for the removal of THMs contaminants from the aqueous environment is still required [13]. One promising method for destroying a wide spectrum of organic compounds is photodegradation, which has been studied extensively for the destructive oxidation of various organic pollutants. This has proved to be very effective, since many organic compounds can be degraded successfully to safer end-products such as CO_2, H_2O and mineral acids [14,15]. However, the literature is still limited concerning the photodegradation of THMs, although the degradation of chlorinated hydrocarbons with UV light has been investigated [16,17]. One of the limitations of the photodegradation process is the presence of natural organic matter in water. A high loading of suspended matter can cause light scattering effects that diminish the activity of the process [18]. For this reason, integration of the photodegradation process with a physicochemical treatment procedure, i.e. adsorption, appears to be a promising method for overcoming the above-mentioned problems and essential for developing a successful treatment process. The integration of photodegradation and adsorption treatment processes can bring several advantages to wastewater treatment plants. Such a hybrid process would be able to remedy the disadvantages of each technique when operated individually, and hence improve the overall removal efficiency. The objective of the work described in this paper was to study the applicability of two environmentally friendly processes, i.e. adsorption and photodegradation, employed either separately or in combination, as a potential water-treatment technology for the removal of THMs on a laboratory scale. The combination of adsorption and UV light methods was hypothesized as resulting in more rapid kinetics than either treatment alone.

MATERIALS AND METHODS

2.1. Materials

Olive oil waste, obtained from an oil mill located In the north Sinai governorate, was washed several times with hot water, filtered and dried at 80^{o}C. Olive stones were chosen as raw material, since they are extensively generated in Arab countries and Europe (the residues generated by the EU olive oil milling industry have been estimated to be 6.8 million tones/year). Compared to other carbonaceous materials, olive stones contains a low level of ash, the quality of final activated carbon depend on the ash content of the precursor[19].

In the present work, the preparation of activated carbon was done either by physical or chemical activation. The total samples prepared from activated carbons were 4 samples and the schematic diagram of the system used for the preparation of activated carbons from olive stone. The activated carbon used in this study was prepared by the physical activation of olive stones employing a steam/nitrogen mixture as the activating agent. The crushed olive stones were washed with distilled water and dried in air. Carbonization was carried out using a nitrogen flow of 80 ml/ min and a heating rate of 5 ºC/min up to a final temperature of 850 ºC. Then, activation was done at hold time for 1 h at 850 ºC.

A known quantity (50g) of the dried waste was soaked in 100 ml or 200 ml of a solution of H_3PO_4 prediluted to various concentrations 60%, 70% and 80%. The thoroughly mixed slurry was left overnight at room temperature then transferred to astainless steel reactor which was introduced into an electrically heated tube furnace. The temperature of the furnace was raised slowly (at rate of ca 200 $^oC/h$) up to the prescribed heat-treatment temperature (HTT= 500 ^oC) and held at this temperature for 2h. The resulting product was cooled to room temperature and then subjected to thorough washing with hot water. Then, dried at 100 ^oC for 24 hours and finally stored in tightly closed containers

THMs, including $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$, as purchased from Aldrich (purity >98%), were chosen as the primary adsorbates

2.2. Analytical methods

The concentrations of the THMs were determined using a gas chromatograph (model 5890 II, Hewlett-Packard, Palo Alto, CA, U.S.A.) equipped with a electron capture detector (ECD). A 30 multra1 fused silica capillary column (0.25 mm i.d., 1.5 µm film thickness) was used for the analysis of THMs. Nitrogen was used as the carrier gas at a flow rate of 2 ml/min. The GC–ECD was operated at an injection temperature of 177 ºC, a detector temperature of 272 ºC and an oven temperature of 110 ºC with sample volume of 10 ml . Duplicate analyses were performed on each sample in accordance with QA/QC requirements.

2.3. Adsorption experiment

To select a particular adsorbent to be used for all the experimental work. A single dosage experiments were carried out by contacting 5ml solution (C_o = 300 ppm for each compound) with 0.01 gm of adsorbent material (OS N –1850, OS P_{60} –2500, OS P_{70} – 2500 & OS P_{80} –2500) in a glass bottle provided with a screw cap. The bottles were then shaken for 24h at 25±1 ^oC to achieve equilibrium concentration. Each mixture was filtered and the residual concentration was measured by splitless gas chromatography with a electron capture detector (ECD).

2.4. Photodegradation experiment

The UV irradiation of solutions containing THM pollutants was carried out in cylindrical quartz tubes (12 ml) subjected to UV photolysis in a digester equipped with a 500 W high-pressure mercury lamp (model 705, Metrohm, Herisau, Switzerland). The temperature of the sample was maintained at 25 ºC via a combined water-cooling system. The UV lamp employed emitted light of 300 nm wavelength at an intensity of 3.5×10^5 E / (ℓ.min). Single –bottle experiments were carried out by contacting 5 ml of each solute (initial concentration, 100 ug/l). The Photodegradation of THMs solution was carried out : (i) in the absence of activated carbon (ii) the presence of 0.02 gm activated carbon (iii) the presence of 0.02 gm activated carbon supported with 0.01 gm TiO_2 . The bottles were then transferred to the UV digester and the concentration of THMs determined using GC–ECD according to the method described above. The titanium dioxide used in this study is Degussa P25, mainly anatase, with a BET surface area of 50 m^2/g and an average particle size of 30 nm.

RESULTS AND DISCUSSION

3.1 Preparation of active carbons

The preparation of activated carbon was done either by physical or chemical activation. The total samples prepared from activated carbons were four samples.

Table (3.1) preparation conditions of active carbons

No	Sample notation	Preparation conditions
1	OS N – 1850	Activation using steam / N_2 gas at 850 C˚for 1 h
2	OS P_{60} – 2500	Activation using 60% H_3Po_4 at 500 C˚for 2 h
3	OS P_{70} – 2500	Activation using 70% H_3Po_4 at 500 C˚for 2 h
4	OS P_{80} – 2500	Activation using 80% H_3Po_4 at 500 C˚for 2 h

3.2.Identification of Surface Functional Groups by The FT- IR specta

The FT- IR spectra of the prepared activated carbons derived from olive stone were carried out in the range 500-4000 cm $^{-1}$ as shown in Fig. (3.1). The broad band centered at 3713 – 3683 cm^{-1} may be assigned to NH_2 stretching vibration of nitrile functional groups . The broad band centered at 3448 cm^{-1} can be assigned to O-H stretching vibration of hydroxyl functional groups [20]**.** The band band around 2927 cm^{-1} are due to asymmetric and symmetric C-H stretching vibrations in aliphatic –CH, $-CH_2$, $-CH_3$. Carbon-oxygen bands have been proposed to give bands around 1705 cm^{-1}, perhaps due to ketene or ketone .A doublet bands appears: at 1627 cm^{-1} due to stretching vibrations of aromatic C=C bond, which are polarized by oxygen atoms near one of the carbon atoms [21]. The band appeared at 2367- 2369 cm^{-1}may be due to stretching vibrations of triple bond C≡C bond. The band 2337 cm^{-1}may be due to weak nitrile group attached to aliphatic chain.

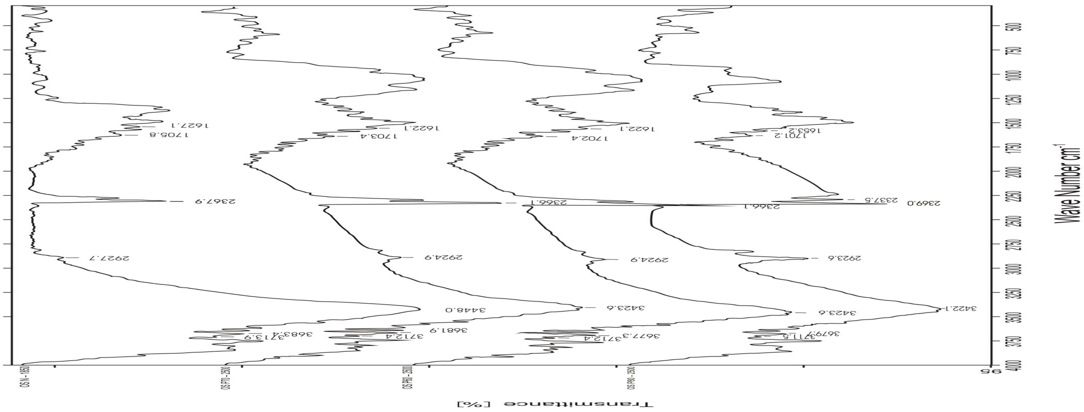


Fig (3.1) FT-IR spectra of prepared carbons

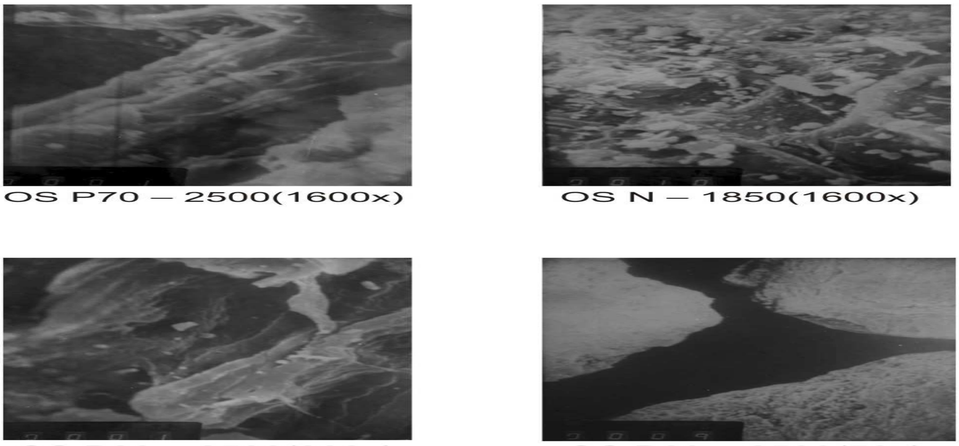
3.3.. Scanning electron Microscope

The scanning electron microscopy images gave insight into the olive stone structure with respect to its shape. The dark areas are macro pores and the pale grey areas are due to the carbon matrix.

Figs.(3.2) represent the morphology of the resulting activated carbon prepared via physical and chemical activation methods, respectively. It can be clearly seen that physical and chemical activations show some changes in the surface of the particles after activation. The different pore structures of the activated carbon prepared from either physical (using nitrogen as activating agent) or chemical (using H_3PO_4) activation are observed, which depend upon different reaction mechanisms. Fig (3.2) depicts three magnifications: 1600 x; 800x and 50x. For comparison between chemical and physical activations, same magnification 1600x may be useful. In this concern, the sample OSN-1850 activated by N_2 gas indicated that the carbon matrix are greater than the dark areas. This is referred to the nature of the micro pores resultant from the activated N_2 gas. Whereas, the dark areas are greater than the carbon matrix using H_3PO_4 as activated in chemical activation. This implies to the higher surface area of sample OSP_{70}-2500 due to meso-pores as well as to micro-pores.

Also, this shows that the olive stone activated by H_3PO_4 have irregular carbon matrix. i.e., of different shapes and sizes. This was proved by nitrogen adsorption isotherms of activated olive stone which indicated that they were mainly micro pores only in physical activation and mixture from micro- and meso pores in chemical activation.

This may be explained by progressive changes in the surface of the cellular structure of the parent material with H_3PO_4 solution used as shown in Fig (3.2). The cellulose units are hydrolyzed by the acid and thus the main components of the inter cellular wall are broken down to smaller structure. Thus it is apparent that the external surface of olive stone is quite rough, consisting of cavities, cracks, and irregular protrusions.



OS P70 — 2500(1600x)

OS N — 1850(1600x)

OS P80 — 2500(800x)

OS P60 — 2500(50x)

Fig (3.2) Scanning electron microscope (SEM) of prepared carbons

Table (3.2) Adsorbability of THMs using the prepared activated carbons

Compound	**Adsorbability**							
	OSN – 1850		**OS P_{60} – 2500**		**OS P_{70} –2500**		**OS P_{80} – 2500**	
	R%	Uptake (ug/g)	R%	Uuptake (ug/g)	R%	Uptake (ug/g)	R%	Uptake (ug/g)
Chloroform	9	5.9	18.3	27.5	37.8	56.7	46.6	69.9
Dichloroboromomethane	10	14.8	38.3	57.5	58	87.5	40.3	60
Boromoform	8.5	13.4	58	78	45	25	16.9	75.1
Diboromochloromethane	33.7	50.6	50.2	81.2	37	56.2	59.2	89.4

3.4. Adsorption Experiments:

3.4.1. Selection of active carbons

Table (3.2) shows the results of the initial laboratory tests for removal of THMs. The results of adsorption experiments are presented either by uptake (ug/g) or percent removal (%R) and indicated that activated carbon prepared by H_3PO_4 is better than N_2 gas in removal of trihalomethanes (THMs). In this concern, sample OS P_{60}-2500 is suitable to remove boromoform ($CHBr_3$) whereas sample OS P_{80} -2500 is suitable to remove either chloroform ($CHCl_3$) or dibromochloromethane ($CHBr_2Cl$) and sample OS P_{70}-2500 is suitable to remove dichlorobromomethane ($CHBrCl_2$). Consequently, four adsorption systems were chosen for further investigations. These are: OS P_{60}-2500 : $CHBr_3$; OS P_{80} -2500 : $CHCl_3$; OS P_{80} -2500 : $CHBr_2Cl$ and OS P_{70}-2500: $CHBrCl_2$

3.5.1. factors affecting adsorption process

3.5.1.1. Effect of agitation time

The kinetic investigations on the adsorption of THMs using (OS P_{80} -2500 , OS P_{60} -2500 and OS P_{70} -2500) carbons are given in Fig.(3.3). As agitation time increased, the THMs removal also increases initially, but then gradually approaches a constant value, denoting attainment of an equilibrium. Obviously, the equilibrium was attained after shaking for about 1750 min in case of boromoform and shaking for about 1200 min in case of chloroform , shaking for about 600 min in case of diboromochloromethane , shaking for about 1200 min in case of dichloroboromomethane., beyond which there is no further increase in the adsorption.

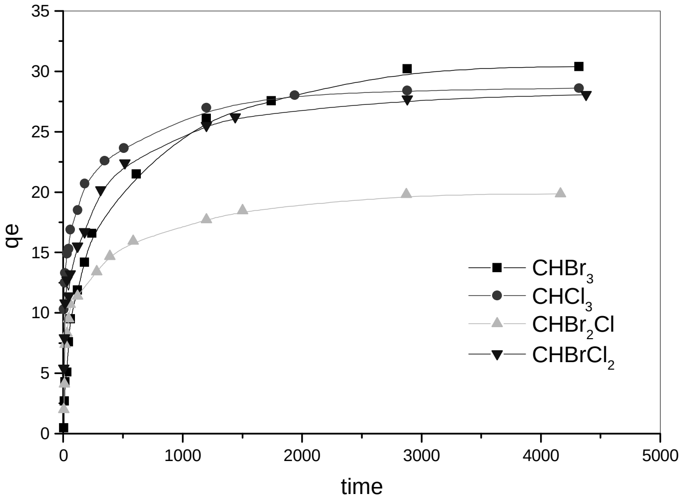


Fig (3.3) Effect of agitation time on the adsorption of THMs. Experimental conditions employed: (V) = 5 ml ; (m) = 0.01 gm ; (C_o) = 100 ug/ℓ

3.5.1.2. Effect of initial Concentration of THMs.

The effect of the initial adsorbate concentration on the removal of THMs by activated carbons was studied over an initial THM concentration range of 10-300 ug/l. Fig (3.4) shows that, as adsorbate concentration increases, the adsorbed amount increases too. Increasing the initial concentration provides an important driving force to overcome all mass transfer resistance of each THM between the aqueous and solid phase and accelerates the diffusion of THMs from solution onto adsorbents [22]. And this would result in higher adsorption. However, the increase in each initial THM adsorbate concentration beyond about 100 ug/l causes little increase in the amount adsorbed for each indicating that the adsorption sites are saturated. At different initial concentrations of THMs for a fixed adsorbent mass, the surface sites are fully exposed. With increased concentration there is an increase in adsorption capacity up to a certain values, which may be due to a high intramolecular competitiveness to occupy the lower energetic surface sites left behind. After saturation point the process becomes purely reversible and there will be no adsorption [23].These results may be explained considering that, at low adsorbate concentration, the ratio of surface active sites to TTHMs concentration is high, hence the THMs could interact with the sorbent to occupy the active sites on the carbon surface sufficiently and be removed from the solution [22] .

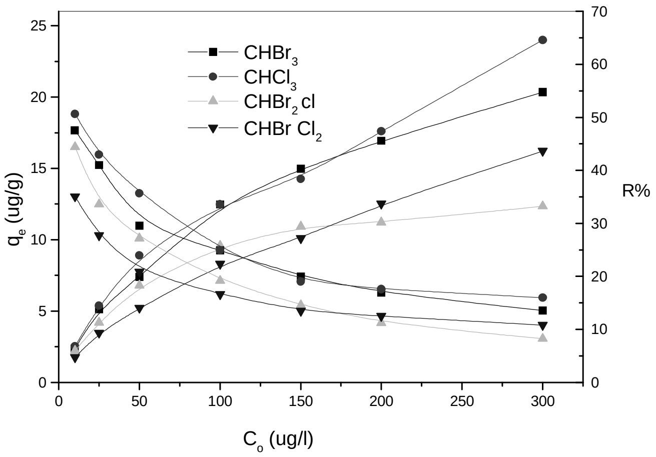


Fig (3.4) Effect of initial concentration of THMs on adsorption. Experimental conditions employed: (V) = 5 ml; (m) = 0.02 gm and ; initial THMs conc. (C_o) = 10-300 ug/ℓ

3.5.1. 3. Effect of pH value

Fig. (3.5) shows the effect of pH range (1.3-8) on adsorption of chloroform or Bromoform or diboromochloromethane or dichloroboromomethane onto olive stone activated carbons with initial concentration of 100 ug/l. It is obvious that the adsorption of THMs removal followed the same pattern for all the compounds.

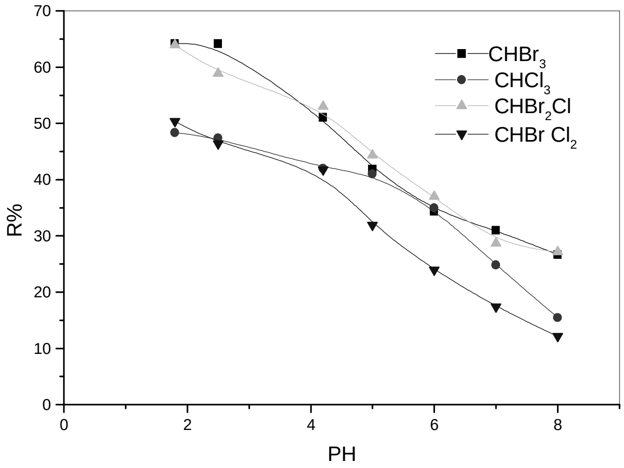


Fig (3.5). Effect of pH on the adsorption of THMs . Experimental conditions employed: (V) = 5 ml; (m) = 0.01 gm; (C_o) = 100 ug/ℓ.

This may be due to the fact that the employed olive stone activated carbon have been purified by acid solution to improve their properties which may enhance the resistance of olive stone activated carbon to acid environment. However, 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 [24]. The formation of water clusters on these groups would block the access of THM molecules to the adsorption sites and lead to a smaller adsorption of THMs.

Second, there are many oxygen-containing groups attached on the surface of purified olive stone activated carbon, which made olive stone activated carbon become more hydrophilic and suitable for adsorption of relatively polar molecules [25].

3.5.1.4. Temperature Effect

Variations in temperature cause adsorbent rearrangements and also Changes in the adsorption/ desorption equilibrium. The uptake of bromoform onto OSP_{60}- 2500 and chloroform onto OSP_{80}- 2500 at 25°C, 35°C and 45°C are presented in Fig (3.6) and (3.7) respectively. It is clear that both adsorption systems indicate a normal trend associated with physical adsorption. In this concern, an increase in the temperature, will result in a reduction of the equilibrium adsorptive capacity, whereas lower temperature will favor an increased capacity [26].

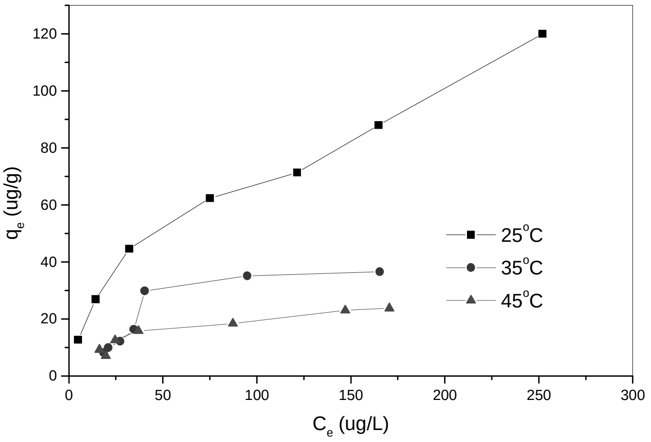


Fig (3.6) Effect of Temperature on adsorption of chloroform. Experimental conditions employed: V = 5 ml; (m) = 0.01 gm and initial conc. (C_o) = 100 (ug/ℓ).

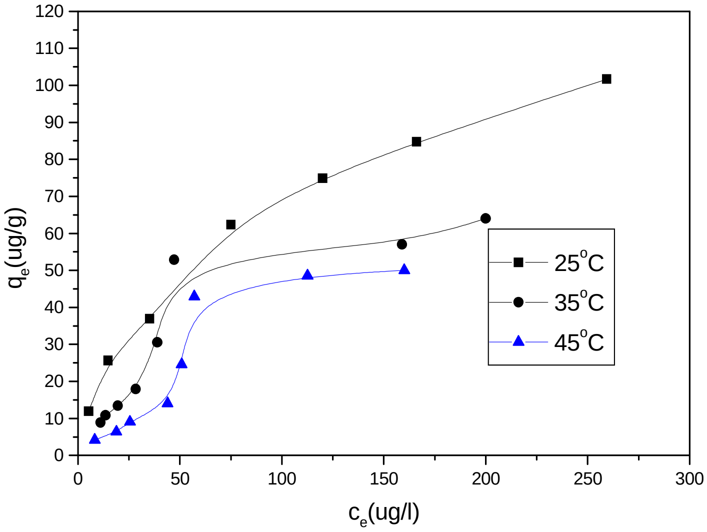


Fig (3.7)Effect of Temp on adsorption of boromoform. Experimental conditions employed: solution THMs: (V) = 5 ml; (m) = 0.01 gm and (C_o) = 100(ug/ℓ).

3.6. Photodegradation studies

In the present work, the photodegradation of the THMs solutions was undertaken by exposing them 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 (see data depicted in Figs. (3.8), (3.9) (3.10) and (3.11). It was observed that, when olive stone activated carbon was added under UV light illumination, the percentage removal of THMs was greater than in the absence of olive stone activated carbon. The results proved that the percent removal (%) for all THMs were more better when TiO_2 impregnated on olive stone activated carbon in presence of UV illumination.

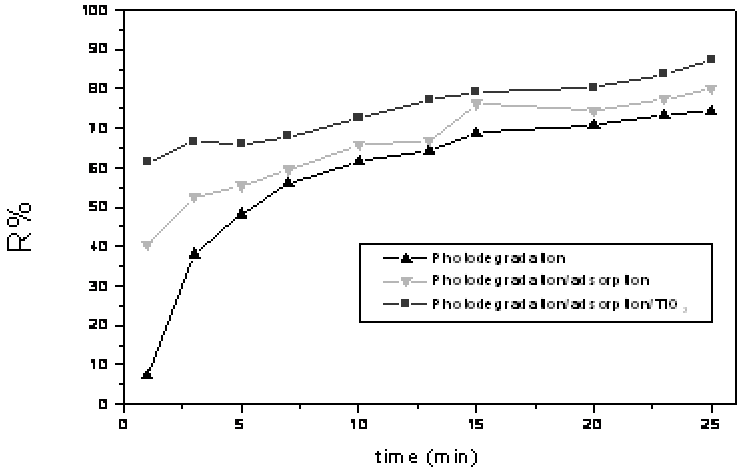


Fig. (3.8) Removal of boromoform from aqueous solution through photodegradation only & hotodegradation in the presence of OS P_{60} -2500 and photodegradation in the presence of OS P_{60} -2500 and TiO_2. Data points relate to the following $CHBr_3$. Experimental conditions employed: (V) = 10 ml; (m) = 0.02 gm; initial THMs conc. (C_0) = 100 ug /ℓ

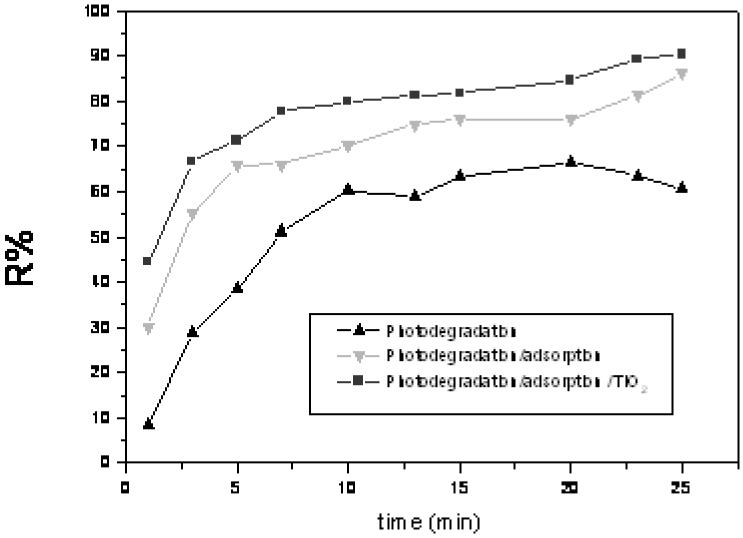


Fig. (3.9) Removal of chloroform from aqueous solution through photodegradation only & photodegradation in the presence of OS P_{80} -2500 and photodegradation in the presence of OS P_{80} -2500 and Tio_2. Data points relate to the following $CHCl_3$. Experimental conditions employed: solution volume (V) = 10 ml; adsorbent mass (m) = 0.02 gm; initial THMs conc. (C_0) = 100 ug /ℓ.

TiO_2 was impregnated on various adsorbent supports to increase the surface area of the supported catalysts. Loading TiO_2 on the adsorbent surface increases the probability of photocatalytic oxidation due to: (i) increased adsorption, (ii) support may enhance catalytic activity by introducing acidity to the surface, (iii) increased catalytic efficiency due to TiO_2 polar surface and (iv) reactive intermediate stabilization. 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. Thus, olive stone activated carbons used in the present studies would appear to play 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[28].

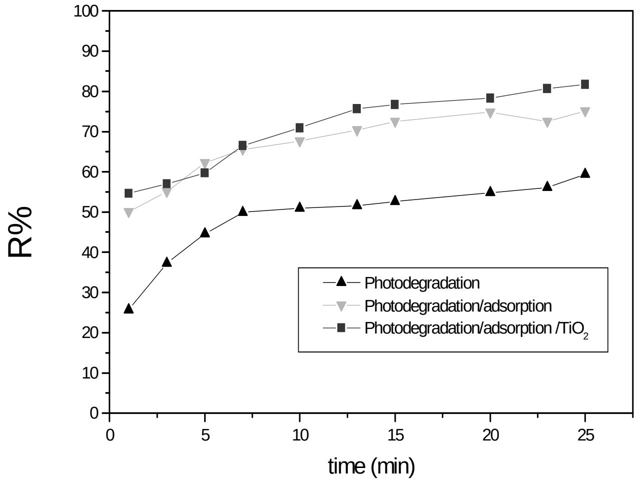


Fig (3.10). Removal of dibormochloromethane from aqueous solution through photodegradation only & photodegradation in the presence of OS P_{70} -2500 and photodegradation in the presence of OS P_{70} -2500 and Tio_2. Data points relate to the following $CHBr_2Cl$. Experimental conditions employed: solutionvolume (V) = 10 ml ; adsorbent mass (m) = 0.02 gm; initial THMs conc. (C_0) = 100 ug /ℓ.

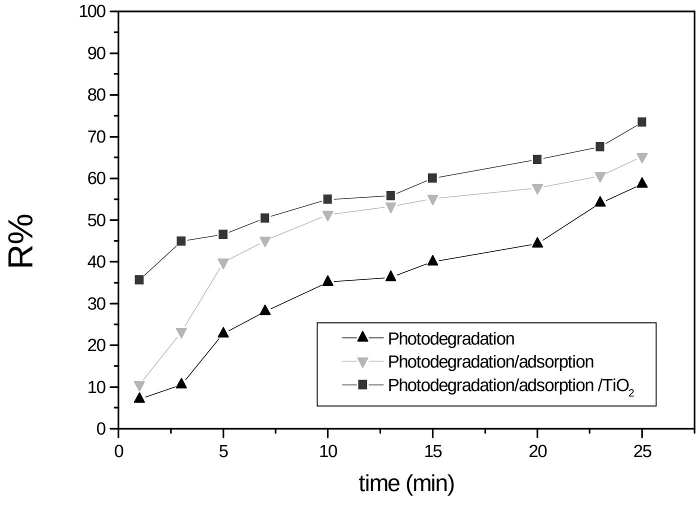


Fig (3.11) Removal of dichlorobormomethane from aqueous solution through photodegradation only & photodegradation in the presence of OS P_{60} -2500 and photodegradation in the presence of OS P_{60} -2500 and Tio_2. Data points relate to the following $CHBrCl_2$. Experimental conditions employed: (V) = 10 ml , (m) = 0.02 gm , (C_0) = 100 ug /ℓ.

All supported catalysts exhibit good photocatalytic efficiency and their performance was always better than that of bare activated carbon or UV alone. The performance improvement can be attributed to the high surface areas of the adsorbent used, crystallinity and particle size of deposited TiO_2 [29].Some general conclusions can be made: (i) All the supported catalysts possess a greater surface area compared to that of bare TiO_2 (50 m^2/g) and (ii) Photocatalytic efficiency of all the supported catalysts indicates the presence of an optimum loading of TiO_2 on the surface.

In order to investigate the photodegradation/adsorption mechanisms involved in the removal of THMs from aqueous solution, the kinetic data were evaluated and described by the Langmuir–Hinshelwood (L–H) pseudo-first-order kinetic model [30].

$$\ln (C/C_o) = -k_{app}\, t$$

where C is the concentration of the reactant at time t , C_o is the initial concentration of the reactant and kapp is the apparent rate constant. A plot of $\ln(C/C_o)$ versus the irradiation time should give a straight line whose slope corresponds to the apparent pseudo-first-order rate constant, k_{app}. Table (3.4) lists the values of the apparent pseudo-first-order rate constant and half-times, $t^{0.5}$ ($t^{0.5} = 0.693/k_{app}$), for the photodegradation, photodegradation/adsorption and photodegradation/adsorption / TiO_2 of THMs obtained in the present study.

Table (3.3) Apparent Pseudo-first-order Kinetic Rate Constants, k_{app}, Half-times, $t^{0.5}$, and Correlation Coefficient Values, R^2, for the Removal of THMs by Different Processes

Sorbate	Photodegradation			Photodegradation /adsorption			Photodegradation /adsorption / TiO_2		
	$10^4 k_{app}$ (min^{-1})	$t_{0.5}$ (min)	R^2	$10^4 k_{app}$ (min^{-1})	$t_{0.5}$ (min)	R^2	$10^4 k_{app}$ (min^{-1})	$t_{0.5}$ (min)	R^2
$CHBr_3$	752	16.90	0.945	936	20.88	0.997	1065	27.96	0.975
$CHCl_3$	639	23.41	0.839	871	31.64	0.989	940	34.01	0.928
$CHBr_2Cl$	411	35.80	0.968	693	25.03	0.879	738	29.26	0.989
$CHBrCl_2$	358	26.52	0.936	485	23.13	0.976	657	28.04	0.947

As seen from the values of the correlation coefficients, R2, the results show that the THMs removal did not follow pseudo-first-order kinetics. Hence, the pseudo-second-order kinetic model was used to explain the experimental data obtained. The pseudo-second-kinetic order rate law can be expressed by the following equation [31].

$$t/Q_t = (t / k_{app} Q_o^{\ 2}) + (t / Q_o)$$

where Q_o is the total amount of solute present in aqueous solution initially, Q_t is the amount of solute present in aqueous solution after time, t, and k_{app} is the apparent rate constant. Plotting t/Q_t versus the irradiation time, t, should give a straight line from which the apparent rate constant may be obtained from the value of the intercept with the y-axis. The correlation coefficients listed in Table (3.4) indicate that the process followed pseudo-second-order kinetics. The data listed in Table (3.3) indicate that the half-time for photodegradation alone was considerably greater than that observed for the combination of photodegradation /adsorption and for the combination of photodegradation/adsorption /TiO_2. The apparent THM removal rate, k_{app}, showed a considerable and rapid increase in the case of photodegradation/adsorption /TiO_2 hybrid relative to the individual processes.

Table (3.4) Apparent Pseudo-second-order Kinetic Rate Constants, k_{app}, and Correlation Coefficient Values, R^2, for the Removal of THMs by Different Processes

Sorbate	Photodegradation			Photodegradation /adsorption			Photodegradation /adsorption /TiO_2		
	10^4k_{app} (min^{-1})	$t_{0.5}$ (min)	R^2	10^4k_{app} (min^{-1})	$t_{0.5}$ (min)	R^2	10^4k_{app} (min^{-1})	$t_{0.5}$ (min)	R^2
$CHBr_3$	175	29.3	0.997	256	23.01	0.989	422	33.27	0.989
$CHCl_3$	230	36.02	0.999	312	17.4	0.989	569	18.2	0.997
$CHBr_2Cl$	163	38.06	0.994	275	25.3	0.997	398	36	0.999
$CHBrCl_2$	118	34.44	0.999	146	33.22	0.997	266	24.07	0.999

Table (3.4) indicating the presence of a synergistic effect. Thus, the addition of olive stone activated carbon and olive stone activated carbon with TiO_2 in the presence of UV illumination accelerates the removal of THMs and decreases the decay time. Active carbon and with TiO_2 itself contributes in two ways to the process: (i) it acts a catalyst promoting the degradation of THMs and (ii) as an adsorbent removing the intermediates and by-products arising from the degradation of the THMs[31].

CONCLUSION

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 R%) 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:

OS P_{60}-2500 : $CHBr_3$; OS P_{80} -2500 : $CHCl_3$;
OS P_{80} -2500 : $CHBr_2Cl$ and 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 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 (104). The formation of water clusters on these groups would block the access of THM molecules to the adsorption sites and lead to a smaller adsorption of THMs.

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 (R%) of each THM increases too. This is occurred from 5 ml solution containing 100 ug/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 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 THM 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 (%) 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.

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