

## **Utilizing palm frond-derived activated carbon to remove Trihalomethane from city water**

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### **Abstract:**

Trihalomethanes (THMs) known as undesirable contaminants which are obtained through the pre-chlorination method for water in water treatment processes done in stations. This study prepared low cost activated carbon produced by treatment of palm fronds by phosphoric acid. The activated carbon used to eliminate Trihalomethane (THM). There are different variables were studied like pH, residence time, adsorbent dose, temperature and initial concentration. The results show that removal percentage of Trihalomethane and capacity of adsorption decreased with increased of pH. Kinetic studies showed that pseudo-second-order reaction model is greatest describe the adsorption process where the values of correlation coefficient,  $R^2$ , for the pseudo-second order adsorption model is relatively high ( $>0.9979$ ). The study show  $\Delta G^\circ$  has a negative value that referred to the feasibility and spontaneity of adsorption process. The study also

showed that activated carbon produced from palm frond is a good efficiency as low cost adsorbent for removal of Trihalomethane.

**Keywords:** Trihalomethane, adsorption process, activated carbon, Palm fronds, City Water.

## 1. Introduction

The need for water has increased because of the growing population. Changes to the environment's natural cycles as a result of global warming. Water scarcity, which is a serious issue for the survival of living things, is caused by industrial chemicals, agricultural practices, and commercial products contaminating the environment and drinking water supplies. <sup>[1]</sup> In the drinking water distribution systems, disinfectants such chlorine, chloramines, and chlorine dioxide are most frequently employed. <sup>[2]</sup> Chlorination is one of the most used ways of water purification. Because it can be disinfected inexpensively before being distributed to consumers and because it is the most crucial phase in the water processing process, chlorine is referred to as the principal disinfectant. Although the chlorination of drinking water has many advantages, it can also result in toxic byproducts that raise health concerns for people. <sup>[1]</sup> Trihalomethanes (THMs) and halo acetic acids (HAAs) are byproducts of the disinfection use of chlorine or chloramines. Trihalomethanes are formed when halogen atoms such as iodine, fluorine, astatine, chlorine, and bromine react with the hydrogen atoms present in methane. Halo acetic acids are produced when the hydrogen atoms in acetic acids react by exchanging for halogen atoms. Chloroform (CHCl<sub>3</sub>), dibromochloromethane (CHBr<sub>2</sub>Cl), and bromodichloromethane (CHBrCl<sub>2</sub>) are examples of trihalomethanes (THMs), <sup>[2]</sup>

The 80 mg/L limit for THM pollution was established. However, numerous nations have calculated the highest THM concentrations in drinking water and discovered values ranging from 50 to 250 mg/L. for consumers: Long-term exposure to THMs can result in a variety of issues, including gastrointestinal malignancies, damage to the genital system, and unfavourable effects on fertility. Additionally, it makes the bladder more susceptible to malignancy. THM removal from water is therefore

essential. Through various physicochemical and biological processes, it is possible to either stop the synthesis of these molecules or remove them from aqueous solutions. [1]

For the purpose of purifying water, scientists employ a variety of techniques, such as Distillation, electrolysis, ion exchange, reverse osmosis, and membrane filtration for water purification. , precipitation [3], membrane filtration [4], ion exchange [5- 6], coagulation/flocculation [7], electrochemical operation [8] and adsorption [9].

Adsorption is suggested as a practical method for removing THMs from wastewater. There are several different types of adsorbents used to attract THM, including resins used in ion-exchange, carbon nanotubes, and activated carbon. Carbon nanotubes or activated carbon are efficient adsorbents to remove THM molecules. [1]

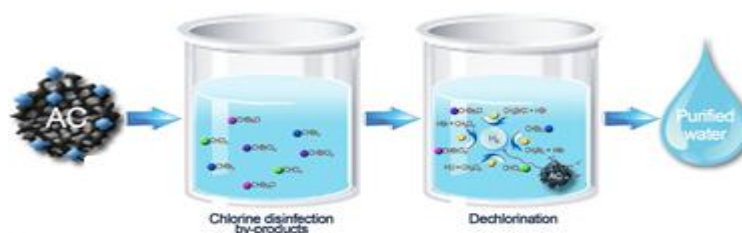


Figure (1) adsorption of chlorination by products using activated carbon [10]

The removal of Trihalomethane via adsorption over many solids use as adsorbents as shown in Figure (1), e.g. activated carbons and others, is one of the majority convenient methods used. Activated carbon obtained from agriculture waste still the excellent adsorbents for many toxic materials present in many application of water. This ability to catch different pollutants is mainly attributed to its very high specific surface area. We can prepare Activated carbon from many organic materials which having a high content of carbon like coal [11], wood [12], lignite [13] coconut shells [14- 15] and recently there are many agricultural by-products such as walnut shells [16], palm shells [17], pecan shells [18- 19], date stones [20-21] almond shells [22], sugar cane bagasse [23,-24] and cotton stalks [25]

This study aiming to prepare activated carbon from palm fronds by different techniques and make a comparison between the two methods used, then the activated carbon obtained from palm frond was used to remove Trihalomethane as adsorbent in adsorption process. Removing of Trihalomethane will studied at different variables like pH, residence time, temperature, initial concentration and adsorbent dose. While the pseudo first-order and pseudo second-order models were used to analyze the kinetic data and thermodynamic parameters were studied

## **2. EXPERIMENTAL parte**

### **2.1 Materials:**

#### **2.1.1 Trihalomethane**

A stock solution of Trihalomethane of concentration 1mg /ml was made by transfer 0.1ml of mixture fixed of Trihalomethane into 1ml of methanol and dilute to 40, 80µg/l done by using methanol under dilution law and real sample have known concentration of THM (62PPB).

### **2.2 Adsorbent Material**

#### **2.2.1 Adsorbent Preparation:**

The Palm fronds have been activated by different activating agents such as zinc Chloride ( $ZnCl_2$ )<sup>[26]</sup>, and phosphoric acid ( $H_3PO_4$ )<sup>[27]</sup>.

#### **2.2.2 Adsorbent Preparation of activated carbon by phosphoric acid:**

Palm fronds were catted to samples into pieces of 1 to 3 cm. The pieces were washed first by tap water and then remove the dust, fibers and impurities by washing the pieces with distilled water, drying process done to remove the moistures content at 105°C for 5 h in an oven (lenton). The dried Palm fronds (RDFs) were crushed into powder. Then the activated carbon prepared according the following method as shown in the following flow chart in figure (2).<sup>[28-29]</sup>

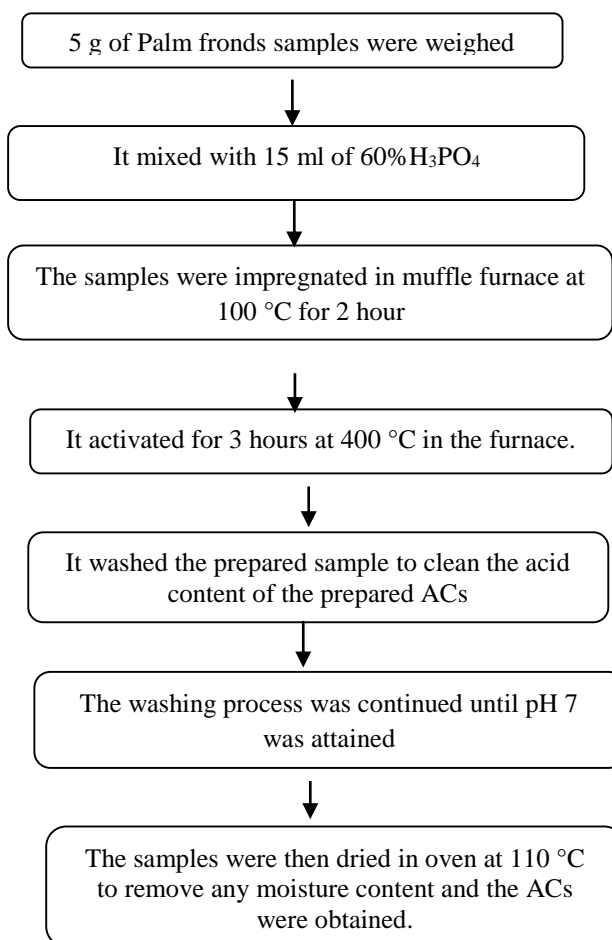


Figure (2): Flow chart for preparation of activated carbon from palm fronds (ACPF) by phosphoric acid

## 2.3 Adsorption Experiment

### 2.3.1 Batch technique

A definite volume of Trihalomethane stock solution with a known initial concentration of THM with a definite amount of activated carbon prepared from palm fronds for the stipulated time in magnetic stirrer using a Teflon stir bar of 2 cm length. pH was determined for the stock solution using pH meter. And experimental work was done in fixed stirring speed of 300rpm

#### 2.3.1.1 Effect of pH:

Add 0.5mg of adsorbent of (ACPF) to 250ml of Real sample (Elmahalla –Elkobra tap of Japanese station) with a known initial concentration of Trihalomethane (62µg/l). By incorporating 0.1 N sodium hydroxide (NaOH) or 0.1 N sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), the pH

can be changed to various values of 2, 4, 6, 7, and 8. The mixture was stirred with a magnetic stirrer (using a Teflon stir bar of 2 cm length) for 1 hour and a half at 300 rpm. 1ml of sample was taken from the reaction solution after certain intervals of time (0, 3, 5,10,40,60 and 90 minutes). And diluted to 10 ml with water .the experiment was done at temperature 25°C

#### **2.3.1.2 Effect of residence time:**

Dilute 1mg/l fixed Trihalomethane to 40 and 80µg/l and there are real sample with a known initial concentration of Trihalomethane (62µg/l). Add 0.5 mg of adsorbent of (ACPF) to 250 ml of THM solution of every concentration at 25°C. the mixture of Trihalomethane was stirred with a magnetic stirrer for one hour and half at 300rpm ,1ml of sample was taken from the reaction solution after 0,3.5,10,20,40,60and 90minute And diluted to 10 ml with water . Residence time of 1 hour and a half is studied by taking samples of the stirred solution at different times.

#### **2.3.1.3 Effect of initial concentration:**

Dilute 1mg/l fixed Trihalomethane to 40 and 80µg\l and there are real sample with a known initial concentration of Trihalomethane(62µg/l).add 0.5 mg adsorbent (ACPF) to 250ml THM solution with the previously prepared concentrations. the mixture of Trihalomethane were stirred a magnetic stirrer for 1 hour and half at 300 rpm , 1 ml of sample was taken from the reaction solution after 0,3,5,10,20,40,60and 90 minutes and diluted to 10 ml with distilled water .The experiment done at temperature =25° C . Repeat this experiment using initial concentration of Tri Halo Methane (THM) a) 40ppb) real sample (62ppb) c) 80ppb...

#### **2.3.1.4 Effect of adsorbent dose:**

Dilute 1 mg/l of fixed Trihalomethane to 40 and 80 µg\l and there are real sample with a known initial concentration of Trihalomethane (62µg/l). Add 0.5 mg of adsorbent of (ACPF) to 250ml THM solution with the previously prepared concentrations at 25°C. the mixture of Trihalomethane was stirred for 1 hour and a half at 300 rpm , 1 ml of sample was taken from the reaction

solution after 0,3,5,10,20,40,60 and 90 minutes and then diluted to 10 ml with water . Repeat this experiment using 0.1, 0.3, 0.7 and 1mg (ACPF).

### **2.3.1.5 Effect of Temperature:**

Dilute 1mg/l of fixed Trihalomethane to 40 and 80µg\l and there are real samples with a known initial concentration of Trihalomethane (62µg/l). Add 0.5 mg of (ACPF) to 250ml THM solution at 25°C.the mixture of Trihalomethane was stirred with a magnetic stirrer for 1 hour and a half at 300rpm .1 ml of sample was taken from the reaction solution after 0,3,5,10,20,40,60 and 90 minutes and then diluted to 10 ml with water . Repeat this experimental at different temperature 20°C,25°C,30°C,35°C and 40°C also the different Trihalomethane concentration solution (40, real sample(62) and 80µg/l)

### **2.4 Analytical method:**

A technique known as "gas chromatography" (GC) refers to a method of separation in which the mobile phase is a gas.it always done in a column .it separation mixture of gas based on the physical properties of gases or volatile materials and it give both quantitative and qualitative determination . GC can used to determine Trihalomethane by using flame ionization detector.

### **2.5 Data analysis:**

The percentage of adsorption (%) is determined using the following equation:

$$\% \text{ Removal} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

The THM concentration retained in the adsorbent phase ( $q_e$ ) activated carbon prepared by palm fronds is given by the following equation:

$$q_e = \frac{(C_o - C_e)V}{M} \quad (2)$$

Where:

$C_0$ : initial concentration of Trihalomethane (mg/l),  $C_e$ : concentration of Trihalomethane (mg/l) at equilibrium or their final concentration in solution

V: volume (l) , M: weight of adsorbent (g).

### 3. Results and Discussion:

#### 3.1. Trihalomethane (THM) of Gharbiya Water Treatment Plants:

El-Gharbiya Water Company has more than one water treatment plants feed the Gharbiya governorate by the drinking water and receives the raw surface water from the Nile River Damietta, other channels and sub channels (El-bagoria, Bahershebeen, ....etc.), Rosetta branch but not feed with that because highly contaminant which can be affected of water treatment and quality of final product. Feeding of the stations in our Studying can be feeding by raw water from Damietta branch and sub channels as it is :

- Tanta (El- Arida Station) feeding by raw water from El-Melahia Channel.
- El- Mahla El-Kobra (Elyabania station) feeding by raw water from Baher El-Malah.
- Sammanoud Station feeding by raw water from Baher Shebeen.
- Zefta feeding by raw water from Damietta branch directly.
- Kafer elzayate feeding by raw water from El-Bagoria Channel.

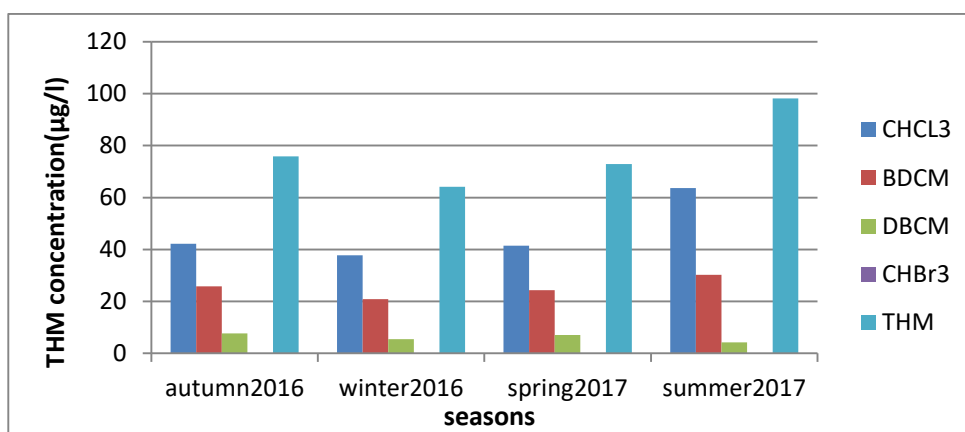
The most important results of parameters during four seasons are collected

##### **3.1.1. Trihalomethane THM of Tanta (El-Arida plant) during the four seasons:**

The information in and Figure (3) demonstrated that disinfection by-products (THM) vary seasonally. Chloroform levels in El-Arida ranged from 37.82 to 63.68 g/l, with the lowest levels recorded in the winter of 2016 and the highest levels recorded in the summer of 2017. In El-Arida, BDCM (Bromodichloromethane) concentrations varied from



20.89 to 30.25 g/l, with the minimum value being recorded in the winter of 2016 and the largest value being recorded in the summer of 2017. The minimum value gained during summer 2017 and the greatest value gained during fall 2016 were 4.24 and 7.66 g/l, respectively, for DBCM in El-Arida .The concentration of bromoform in El-Arida ranged from 0.0 to 0.14 g/l, with the least amount increasing over most months of the year and the highest amount increasing during fall 2016. The physical characteristics of various samples of tape water in Tanta (El-Arida) across the four seasons are shown in table (1). Total THM in El-Arida ranged from 64.15 to 98.17 g/l, with the minimum value recorded during winter 2016 and the largest value observed during summer 2017.



**Figure (3):** THM analysis of Tanta (El-Arida) during the season's period.

The THM levels met the EPA (2012) and WHO (2012) criteria for drinking water, as well as the Egyptian standard (ministerial regulation no. 458/2007). The most elevated THM values and species were seen in the summer, which could be ascribed to the high temperatures.

Table (1): The physical properties of different samples of tape water in the four seasons of Tanta (El-Arida) during the four seasons.

<b>NO</b>	<b>Parameter</b>		<b>Autumn</b>	<b>Winter</b>	<b>Spring</b>	<b>Summer</b>
1	Temperature (°C)		19.21	16.11	21.9	27.6
2	UV254nm	Raw water	0.08	0.08	0.07	0.06
3		Tap	0.05	0.04	0.04	0.03
4	pH		7.5	7.6	7.31	7.32
5	Turbidity (NTU)		0.20	0.90	0.60	0.40
6	Electrical conductivity (µmohs/cm)		388	455	408	354
7	Alkalinity (mg/L)		132	120	140	122
8	TOC (mg/L)	Raw water	4.42	5.46	4.45	5.36
		Tap water	3.60	3.9	3.15	4.74
9	Total alga count (count/ml)	Raw water	1650	2050	3200	1300
		Tap water	5	5	5	0.0
10	Chlorine dose (mg /L)		7.67	7.17	7.83	7.10
11	free chlorine (mg /L)		2.51	2.00	2.50	2.54
12	contact time (hour)		7.67	8.00	7.00	5.33

### 3.2 Effect of pH:

The findings in figure (4) demonstrate that the maximum removal of Trihalomethane take place at pH=2 , pH is very important factor can be affected on the formation of DBPs. <sup>(26)</sup> There have been numerous studies to determine how pH affects DBP production in water supplies treated with chloramines. They found that as pH increases THM levels were increased<sup>(26)</sup>. The result reveals that uptake of Trihalomethane (THM) decreased from 80.83% to 72.33% with increasing the pH from 2 to 8. The % removal and the capacity of adsorption decreased with increasing pH <sup>[30]</sup>

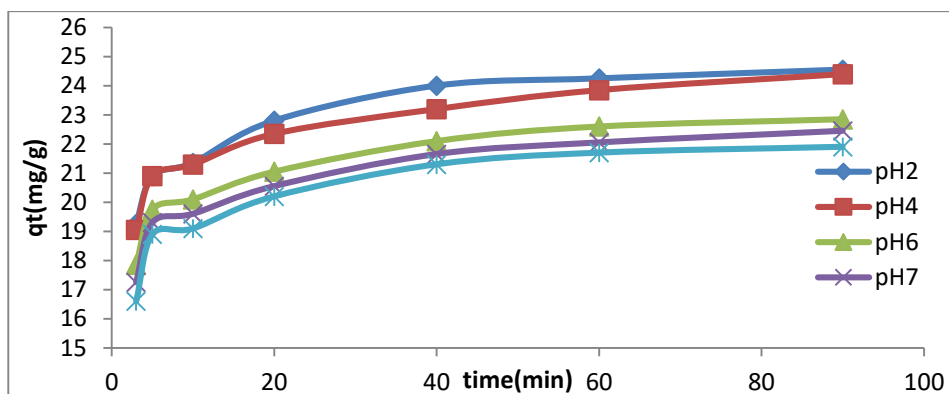


Figure (4) pH effect on capacity adsorption of Trihalomethane onto (ACPF), initial concentration 62 ppb, adsorbent dose: 0.5mg/ 250 ml: stirring speed 300rpm at 25 °C.

### 3.3 Kinetics models:

#### 3.3.1 Pseudo – First Order Model:

The pseudo first order equation may be the earliest example of the rate of adsorption being described. Equation (3) proposed a pseudo-first order kinetic model:

$$\ln(q_e - q_t) = \ln(q_e - k_1 t) \quad (3)$$

The form in equation (3) for the border condition of  $t = 0$ ,  $q_t = 0$  and  $t = t$

$$\text{i.e } q_t = \frac{(C_o - C_t)V}{M}, \quad q_e = \frac{(C_o - C_e)V}{M}$$

The initial concentration of the adsorbate, which varies from system to system, affects the value of  $K_1$ . With the initial adsorbate concentration in the bulk phase increasing  $K_1$  usually decreases. <sup>(30)</sup>The plot of  $\ln(q_e - q_t)$  versus  $t$  figures (5 (a, b, c)) will show a relationship in the linear form in which  $k_1$  calculated from the slope and  $q_e$  calculated from intercept of the graph,. The model is presented in figures (5).

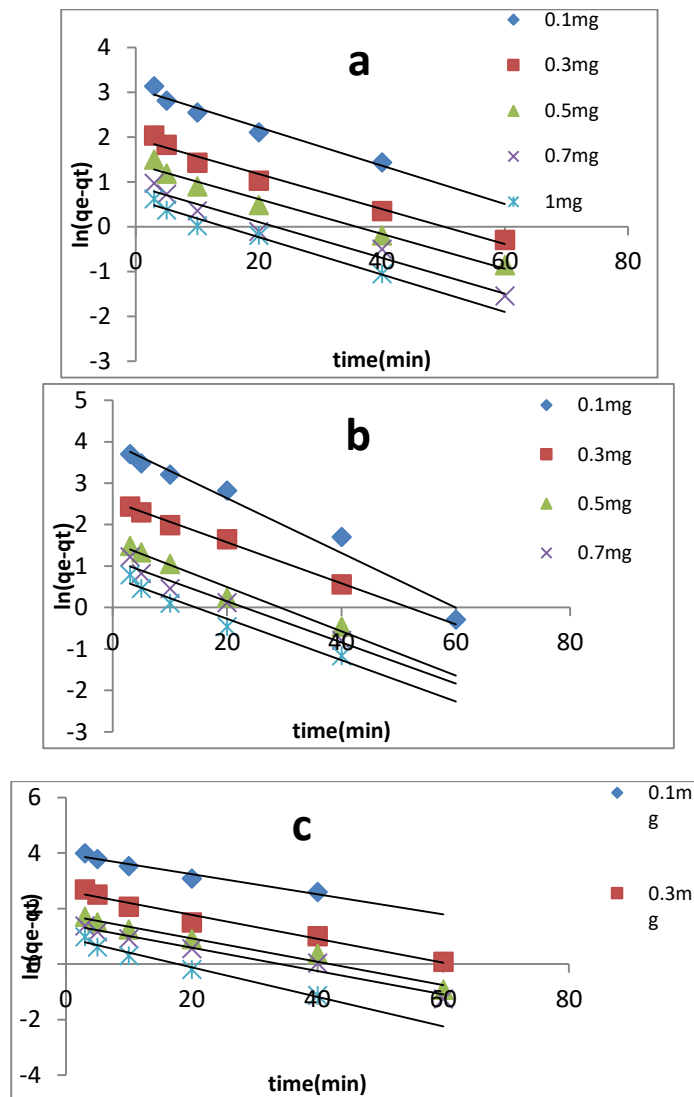


Figure (5) - Pseudo-first order kinetic graphical representations for Tri Halo Methane adsorption at different starting concentrations (THM) a) 40ppb b) 62ppb c) 80ppb. Using different (ACPF)dose (mg/250ml), stirring speed 300rpm, contact time 90 min, pH= 6.5 at temperature 25 °C

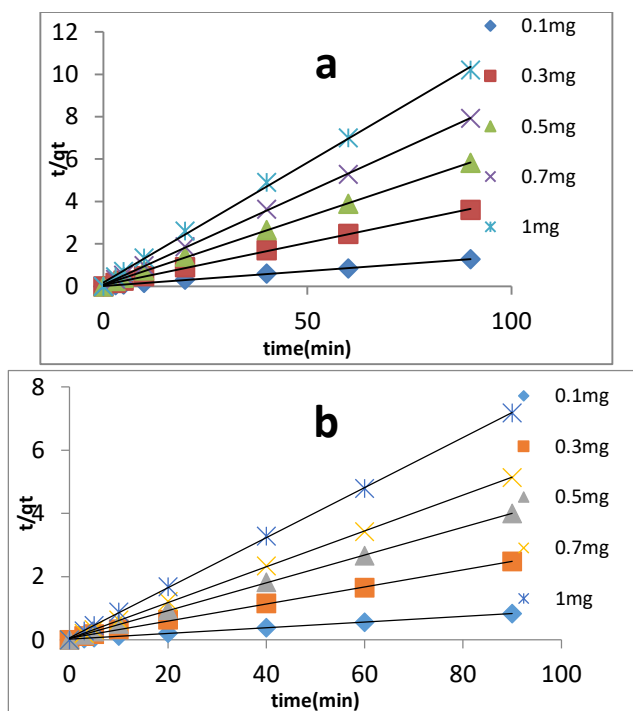
### 3.3.2 Pseudo –Second Order Model:

The second order kinetics is determined from the following equation:

$$\frac{t}{q_t} = \left( \frac{1}{k_2 q_c^2} \right) - \left( \frac{1}{q_c} \right) t \quad (4)$$

the integral form shown in equation (4) predicts that the ratio of the time / adsorbed amount of Trihalomethane ( $t / q_t$ ) should be a linear function of time<sup>(31)</sup>.  $k_2$  depend on the applied condition which are the initial metal concentration ,pH, dose of adsorbent , temperature , rotation speed .... Etc.

The plot of pseudo second order model  $t / q_t$  versus  $t$  found to be a linear relationship from which  $q$  calculated from the slope and  $k_2$  calculated from the intercept of the plot, ( $q = 1/ \text{slope}$  and  $k_2 = (\text{slope})^2 / \text{intercept}$ ). The model is presented in figures (6)



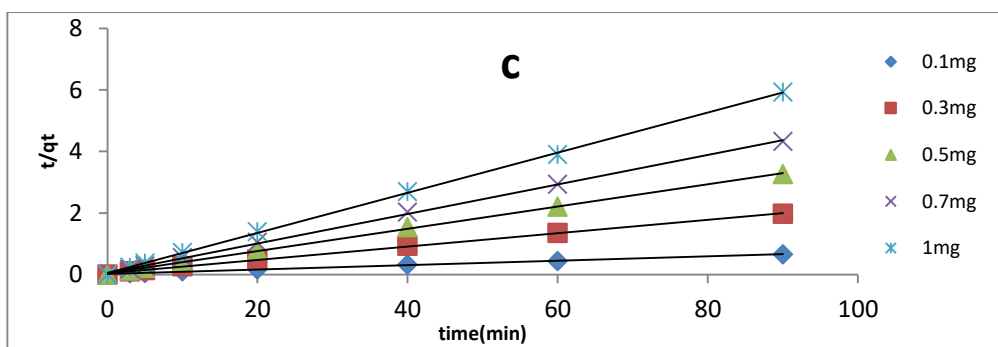


Figure (6) Trihalomethane (THM) initial concentration adsorption pseudo-second order kinetic diagrams a) 40ppb b) real sample(62ppb) c)80ppb using different (ACPF)dose(mg/250ml),stirring speed 300rpm , contact time 90 min ,pH= 6.5 at 25 °C

### 3.3.3 Weber and Morris model:

Because internal diffusion controls the adsorption rate in most liquid systems, the Weber and Morris model, also known as the intra particle diffusion model, is of great relevance. The mass transfer over the boundary layer is represented by the intercept in equation (5), which is a general description of the kinetics. The predicted value of the exponent terms is also shown. 0.5. <sup>(31-32)</sup>

$$q_t = k_m t^{0.5} + c \quad (5)$$

Where  $k_m$  is the intra- particle diffusion rate constant ( $\text{mg/g min}^{1/2}$ ). From Table ( 2 ) Kinetic models and other parameters on adsorption of Trihalomethane (THM) onto activated carbon from palm frond at different initial concentrations(a) 40ppb b) real sample(62ppb) c)80ppb ,contact time 90 min ,at 300 rpm and 25 °C were calculated and figure (7) In accordance with this concept, the plot of  $q_t$  versus  $t^{1/2}$  results in a straight line with a slope of  $k_m$  and an intercept of  $C$  when the intra particle diffusion is involved in the adsorption process. The boundary layer thickness can be roughly estimated by the values of  $C$ ; the higher the  $C$  value, the thicker the boundary layer. if the origin of the drawing lines

Table (2) : the adsorption kinetics data for 250 ml solution contain different concentration of Trihalomethane(THM) onto activated carbon from palm fronds , contact time 90min at 300 rpm , 25°C and pH = 6.5

<b>Initial concentration of THM (40ppb )(a)</b>						
Kinetic models	parameters	activated carbon prepare by palm fronds doses				
		0.1mg	0.3mg	0.5mg	0.7mg	1mg
Pseudo 1 <sup>st</sup> order equation	q <sub>e</sub> (EXP.)(mg/g)	70.5	24.92	15.85	11.61	8.5
	q <sub>e</sub> (calc.)	21.75	7.099	4.05	1.82	1.82
	R <sub>2</sub>	0.96	0.976	0.97	0.97	0.967
	K <sub>1</sub> (min <sup>-1</sup> )	0.43	0.039	0.039	0.04	0.04
Pseudo 2 <sup>nd</sup> order equation	q <sub>e</sub> (calc.)	71.4	25	16.67	11.49	9.09
	R <sub>2</sub>	0.999	0.999	1	1	0.998
	K <sub>2</sub> (g/mg. min)	0.01	0.003	0.05	0.09	0.07
Weber and Morris model	C	46.99	16.9	11.3	8.9	6.43
	R <sub>2</sub>	0.9	0.9	0.9	0.9	0.96
	K <sub>m</sub> (mg g <sup>-1</sup> min <sup>-1</sup> )	2.83	0.93	0.53	0.32	0.27

<b>Initial concentration of THM (62ppb) (b)</b>						
Kinetic models	parameters	activated carbon prepare by palm fronds doses				
		0.1mg	0.3mg	0.5mg	0.7mg	1mg
Pseudo 1 <sup>st</sup> order equation	q <sub>e</sub> (EXP.)(mg/g)	108.5	36.33	22.475	17.52	12.53
	q <sub>e</sub> (calc.)	51.93	12.81	4.76	3.12	2.05
	R <sub>2</sub>	0.97	0.99	0.97	0.96	0.95
	K <sub>1</sub> (min <sup>-1</sup> )	0.06	0.05	0.05	0.049	0.05
Pseudo 2 <sup>nd</sup> order equation	q <sub>e</sub> (calc.)	111.11	37.03	22.73	16.67	14.28
	R <sub>2</sub>	0.998	1.0	1.0	1.0	1.0

	$K_2$ (g/mg. min)	0.004	0.014	0.045	0.072	0.082
Weber and Morris model	C	64.9	23.4	17.66	14.26	10.35
	$R_2$	0.92	0.93	0.89	0.86	0.86
	$K_m$ (mg g <sup>-1</sup> min <sup>-1</sup> )	5.25	1.55	0.59	0.4	0.27

Initial concentration of THM (80ppb) ( c )						
Kinetic models	parameters	activated carbon prepared by palm fronds doses				
		0.1mg	0.3mg	0.5mg	0.7mg	1mg
Pseudo 1 <sup>st</sup> order equation	$q_e$ (EXP.)(mg/g)	136.5	45.5	27.5	20.79	15.18
	$q_e$ (calc.)	52.45	13.87	5.87	4.22	2.586
	$R_2$	0.95	0.97	0.97	0.97	0.976
	$K_1$ (min <sup>-1</sup> )	0.04	0.04	0.03	0.04	0.05
Pseudo 2 <sup>nd</sup> order equation	$q_e$ (calc.)	142.86	50	25	20.83	15.38
	$R_2$	1.0	0.999	0.999	0.999	1.0
	$K_2$ (g/mg.min)	0.003	0.01	0.04	0.05	0.08
Weber and Morris model	C	77.29	30.16	21.46	16.47	12.5
	$R_2$	0.93	0.88	0.95	0.95	0.86
	$K_m$ (mg g <sup>-1</sup> min <sup>-1</sup> )	7.01	1.82	0.69	0.5	0.33



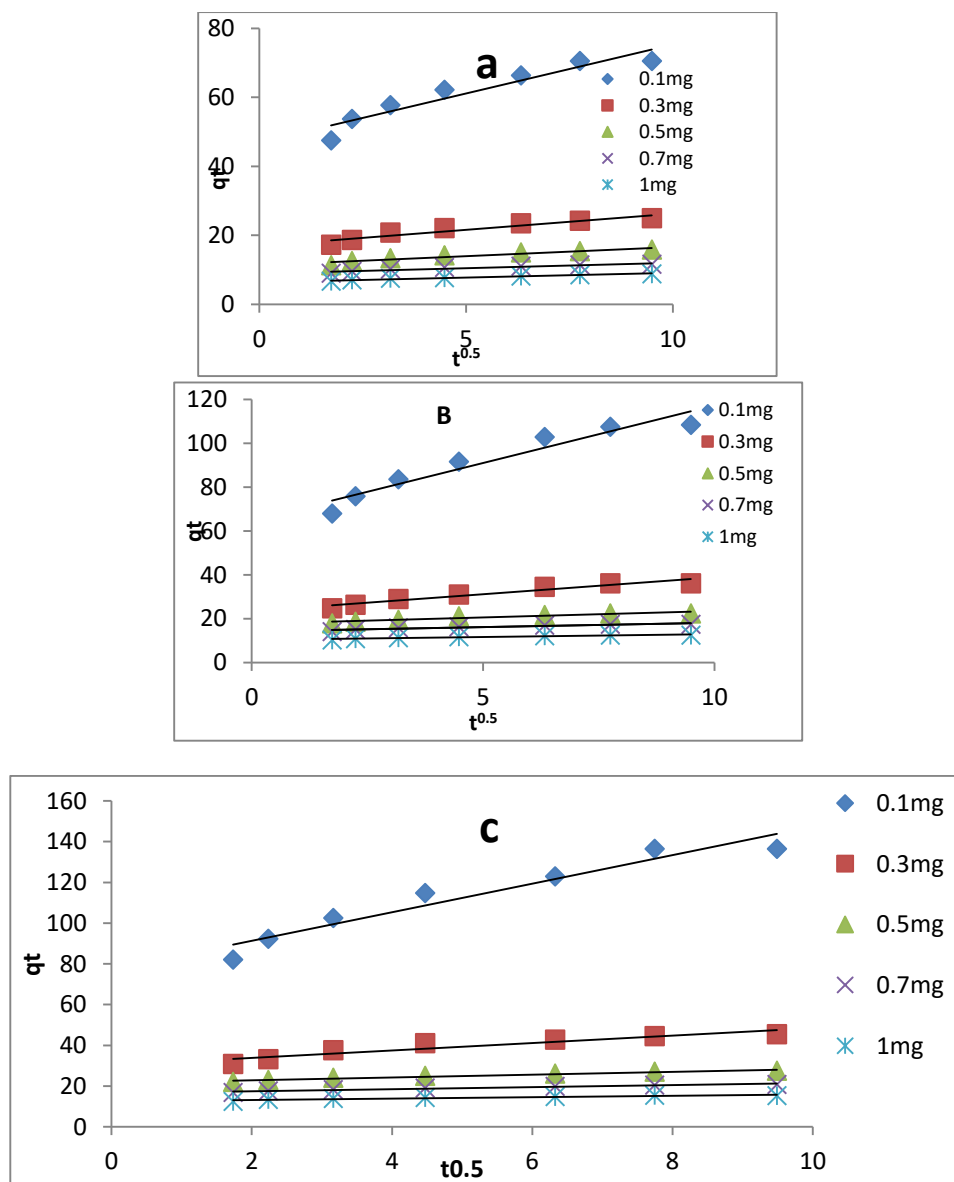


Figure (7): the Weber model for the adsorption of initial concentration of Trihalomethane (THM) a) 40ppb , b) real sample (62ppb) , c) 80ppb, using different (ACPF) dose (mg/250ml), stirring speed 300rpm , contact time 90 min , pH= 6.5 at 25 °C

Trihalomethane (THM) solutions with concentrations of (40, 62, and 80 ppb) at pH = 6.5 are used to study the fluctuation in adsorption capacity ( $q_t$ ) with time. The results shown in figures (8) & (9) revealed that Trihalomethane (THM) uptake was very rapid during the first ten minutes. After twenty-minute adsorption rates slowly declined and reach equilibrium in the range of 60 to 90 minutes, It is evident that as the amount of time increased, so did the percentage of THM elimination.

Trihalomethane (THM) elimination increased over time, reaching equilibrium after about 60 minutes.

Due to the large number of free molecules that were initially available for the sorption operation, extremely high adsorption rates were seen, and adsorption equilibrium then gradually developed [33]

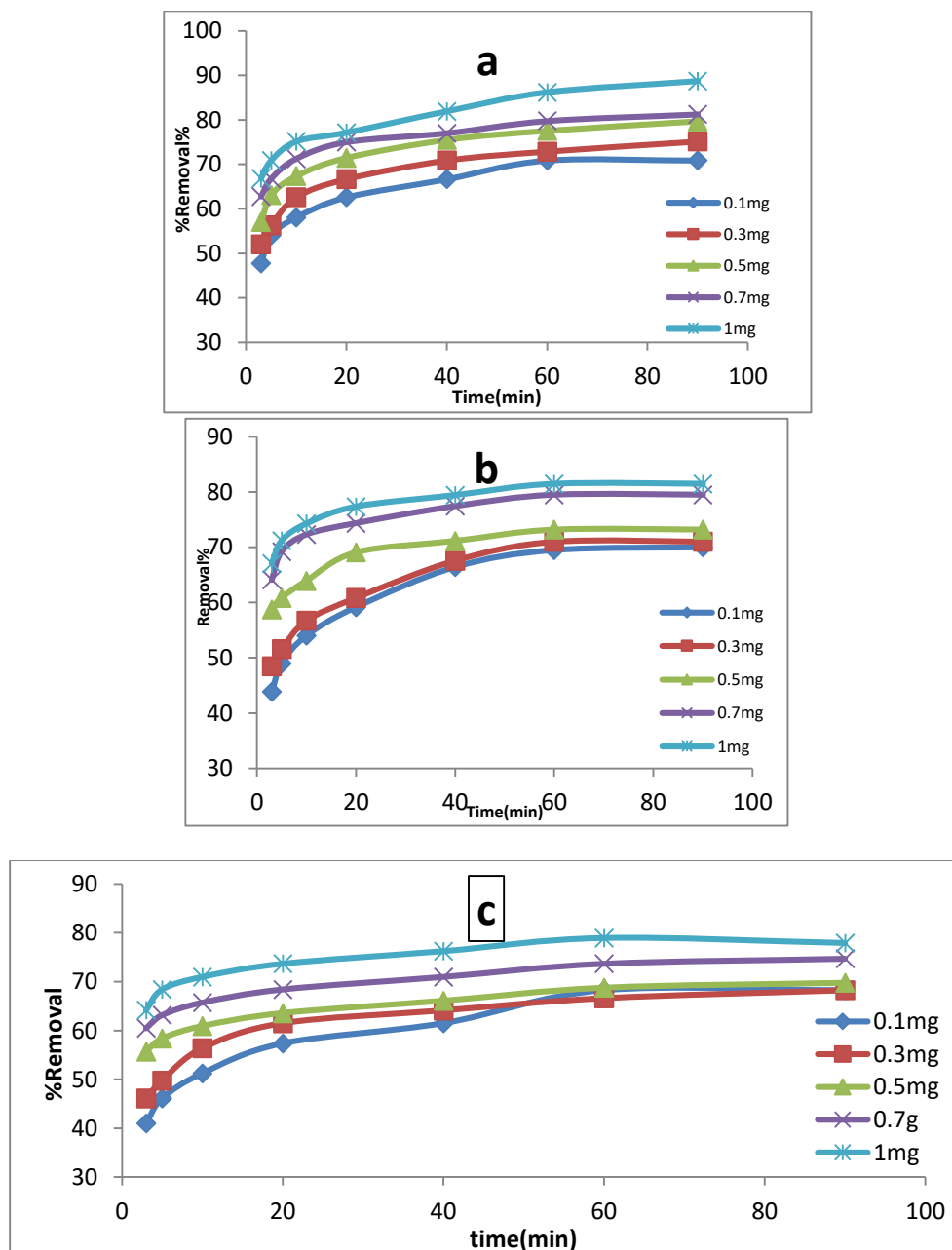


Figure (8) contact time (min) effect on %removal of different initial concentrations on Trihalomethane (THM): a) 40ppb b) 62ppb c) 80ppb. Using different (ACPF) doses (mg/250 ml): stirring speed 300 rpm; contact time 90 min; PH =6.5 at 25 °C.

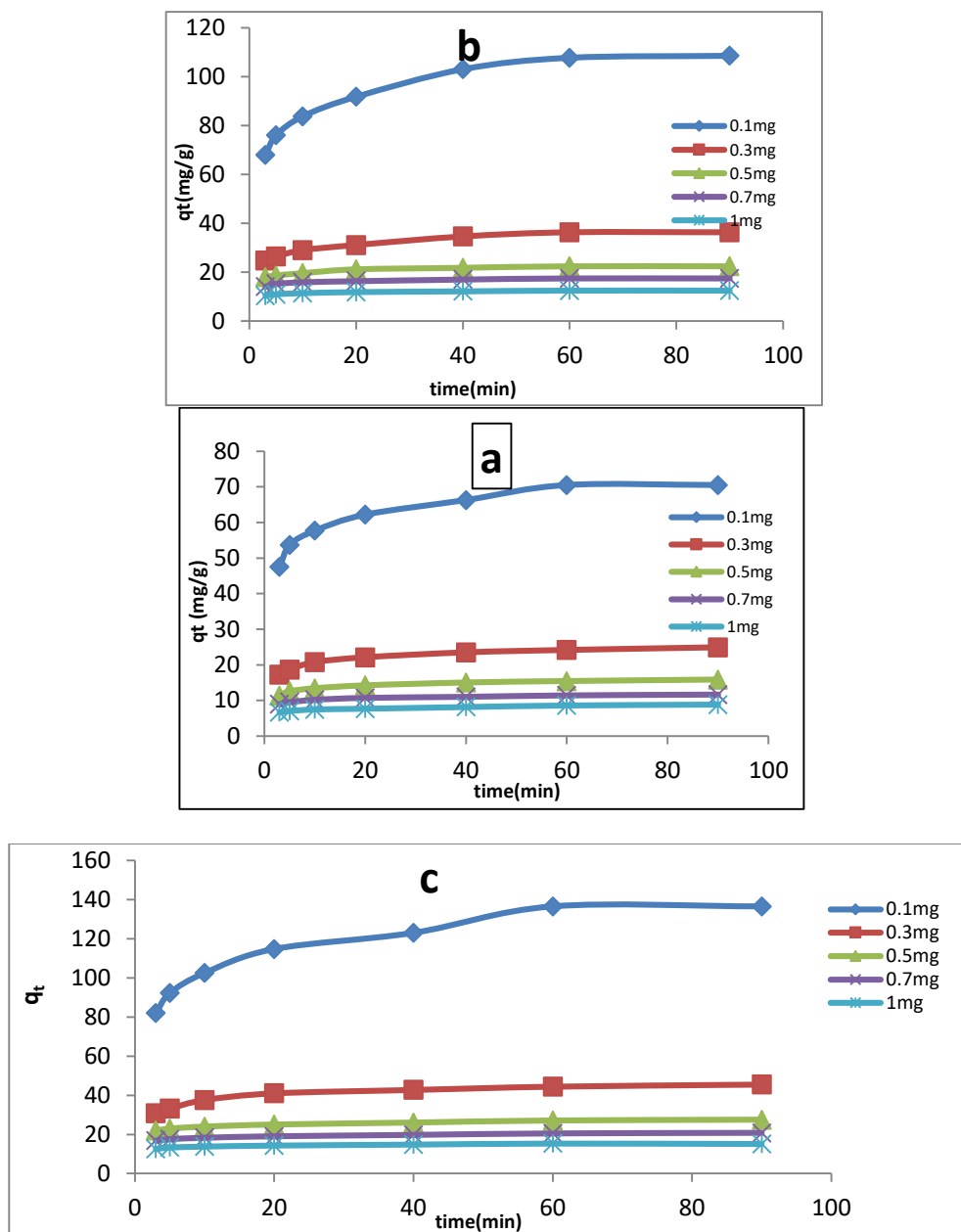


Figure (9) Effect of contact time on the adsorption capacity of THM onto activated carbon prepared by palm fronds at different initial Trihalomethane (THM): a) 40ppb , b) 62ppb , c)80ppb using different (ACPF) doses (mg/250 ml): stirring speed 300 rpm; contact time 90 min ; pH =6.5 at 25 °C

### 3. 4 Effect of Initial Concentration:

The capacity of the (ACPF) to adsorb trihalomethane was studied at contact duration (20 min), pH = 6.5, stirring speed (300 rpm), and 25 °C. Figures (10, 11) demonstrate that as trihalomethane concentration increases, the capacity of adsorption  $q_e$  (mg/g) and removal % change,

respectively. This drop in removal percentage results from a lack of activated carbon active sites, or from the saturation of activated carbon made from palm fronds sites, which indicates that THM may form in monolayers on the activated carbon's outer surface [34].

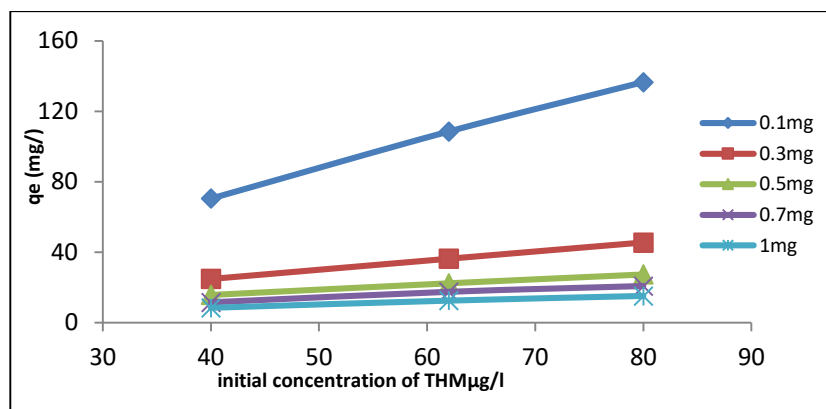


Figure (10) Effect of initial Trihalomethane (THM) concentration on  $q_e$  (mg/g) of Trihalomethane (THM) by different adsorbent (ACPF) doses (mg/250 ml); stirring speed 300rpm; pH =6.5, contact time 90 min at 25 °C.

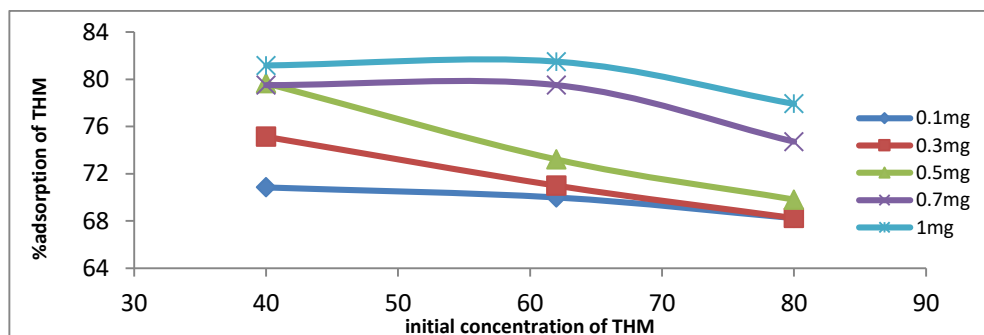


Figure 11 Effect of initial Trihalomethane (THM) concentration on % removal of Trihalomethane (THM) concentration by different adsorbent (ACPF) doses (mg/250 ml); stirring speed 300rpm; pH =6.5, Contact time 90 min at 25 °C.

### 3.5 Effect of adsorbent dose:

At a contact time of 20 min at an initial concentration of 62 ppb of trihalomethane (THM) at a temperature of 25 °C, the influence of adsorbent dosage on the adsorption of THM was investigated. Palm fronds were used to prepare activated carbon in amounts ranging from 0.1 to 1 mg.

Figure (12) illustrates how the amount of adsorbent used increases the removal percentage of trihalomethane when the initial concentration of sorbate is fixed. The increased amount of adsorbent also increases the availability of exchangeable sites, which results in increased uptake of trihalomethane (THM). Table 3 indicates that the sorption capacity ( $q_t$ ) does, however, drop due to the overlap of active sites at high dosages. Consequently, the effective surface area of the aggregate of exchanger particles decreases. Many studies have typically found that the amount of adsorbed material per mass of adsorbent decreases <sup>[35]</sup>. This could result from two factors:

1. As a result of the effective reduction in the formation of adsorption sites caused by large adsorbent quantities, very less adsorption occurs at higher adsorbent amounts due to the decrease in the number of sites per unit mass.
2. Using a lot of adsorbent leads to particle aggregation, which reduces the overall surface area and lengthens the diffusion channel, both of which result in less adsorption per unit mass <sup>[36]</sup>.

Table (3): Effect of adsorbent dose on trihalomethane (THM) adsorption

activated carbon prepare by palm fronds		0.1mg	0.3m g	0.5m g	0.7mg	1mg
Trihalomethane (THM)	%adsorption	59.19	60.8	69.1	77.37	74.36
	$q_t$	91.75	31.1	21.21	11.89	16.39

capacity in  $q_t$  (mg/g) and percent removal at 20 minutes, 25 °C, and pH = 6.5

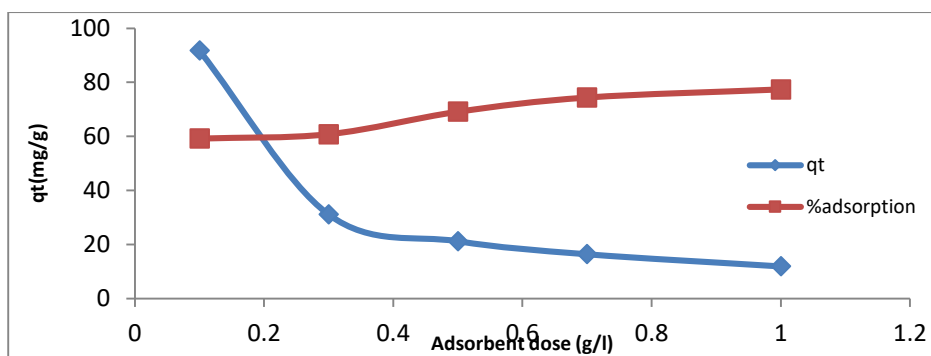


Figure (12) Effect of adsorbent dose of (ACPF) on % removal and  $q_t$  of THM compounds with initial concentration 62ppb at contact time 20 min , Stirring speed 300rpm, 25 °C and pH =6.5.

### 3.6 Effect of temperature:

Trihalomethane (THM) removal effectiveness was shown to be affected by temperature in Figures (13, 14), from water using (ACPF) . Different temperature were used in the study at (20, 25, 30,35and 40°C) with 62ppb initial concentration of Trihalomethane (THM) in presence of (0.5mg/250ml) for activated carbon prepare by palm fronds. The figure showed that in 20min, the efficiency of removal increased By raising the temperature, it is because

- Firstly , higher temperatures activate the Trihalomethane for enhancing adsorption at the coordination sites of the adsorbent , and Trihalomethane(THM) become more faster
- Secondly , On the adsorbent surface, new activation sites are created and certain previously sluggish steps are accelerated [37-38]

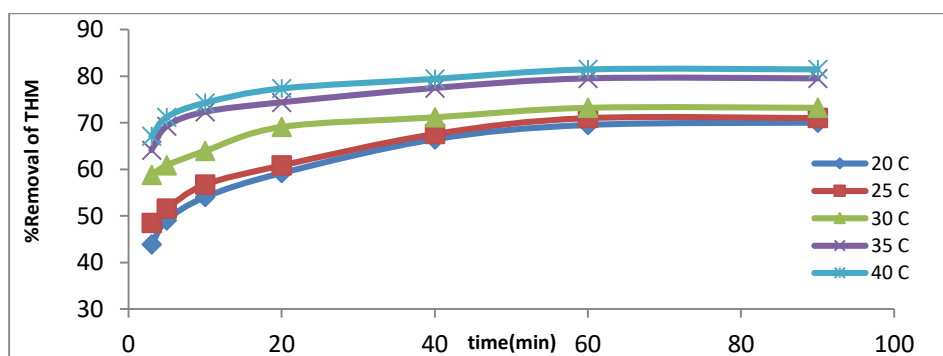
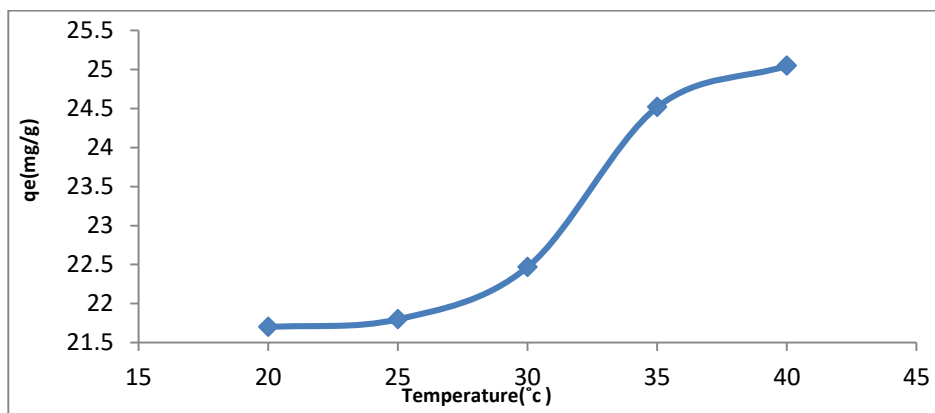


Figure (13) Effect of time on % removal of Trihalomethane(THM) at different temperature (ACPF), initial Trihalomethane(THM)

concentration 62ppb , adsorbent dose : 0.5 mg\250ml stirring speed 300rpm , contact time 1 h and pH =6.5.



Figure( 14) Effect of temperature on adsorption capacity of Trihalomethane(THM) onto (ACPF), initial real sample(Tap of Japanese - Elmahalla- Elkobra) Trihalomethane (THM) concentration 62 ppb , adsorbent dose : 0.5 mg\250ml stirring speed 300rpm , contact time 1 h and pH =6.5

### 3.7 Thermodynamic Parameters:

The standard Gibbs free energy ( $G^\circ$ ), standard enthalpy change ( $H^\circ$ ), and standard entropy change ( $S^\circ$ ) were calculated using the adsorption equilibrium data collected at various temperatures. Equation (6) was used to determine the THM adsorption's standard Gibbs free energy ( $G^\circ$ )

$$\Delta G^\circ = -RT \ln K_e \quad (6)$$

The adsorption equilibrium constant,  $K_e$  was calculated at each temperature using the equation (7).

$$K_e = \frac{q_e}{c_e} \quad (7)$$

Where  $q_e$  (mg/g) is the amount of Trihalomethane adsorbed onto activated carbon prepared by palm fronds from the solution at equilibrium  $C_e$  (mg/l) the equilibrium concentration of THM in the solution,  $R$  (j/mol.k) the gas constant 8.314,  $T$  (°k) the absolute temperature.

$$\ln K_e = \left( \frac{-\Delta H^\circ}{RT} \right) + \left( \frac{\Delta S^\circ}{R} \right) \quad (8)$$

$\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the slope and intercept respectively, of the van't Hoff's plot<sup>(39-40)</sup> of  $\ln(k_{eq})$  versus  $1/T$ ; equation (8) as shown in figure (15) and for THM.

The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  from table (4) show that, the positive value of  $\Delta H^\circ$  reveal that considerable energy is required for the exchange of the divalent Trihalomethane. The positive value of  $\Delta S^\circ$  suggests and adsorbate and adsorbent .A negative value of  $\Delta G^\circ$  indicate the feasibility and spontaneity of adsorption processes.

Table(4): Thermodynamic parameters ( $\Delta G^\circ$ (kJ/mol) ,  $\Delta H^\circ$ (kJ/mol),  $\Delta S^\circ$ (kJ/mol. K)) for solution contain initial THM concentration of 62PPB , adsorbent dose 0.5m g /250 ml activated carbon prepare by palm fronds at 300 rpm , pH =6.5 for Trihalomethane(THM) contact time 90 min.

Concentration ( 62PPB) of THM (Tri Halo methane)	T( K)	293	298	303	308	313
	$1000/ T( K^{-1})$	3.41	3.35	3.29	3.24	3.19
	$q_e$	21.6	21.95	22.15	22.1	22.55
	$C_e$	18.6	17.8	16.9	16.1	15.2
	$K_e$	1.16	1.23	1.31	1.37	1.48
	$\ln K_e$	0.15	0.2	0.27	0.31	0.39
	$\Delta G^\circ$ (kJ/mol )	-	-	-	-	-
	$\Delta H^\circ$ (kJ/mol)	0.365	0.496	0.680	0.794	1.015
	$\Delta S^\circ$ (kJ/mol. K)	8.89				
	31.49					



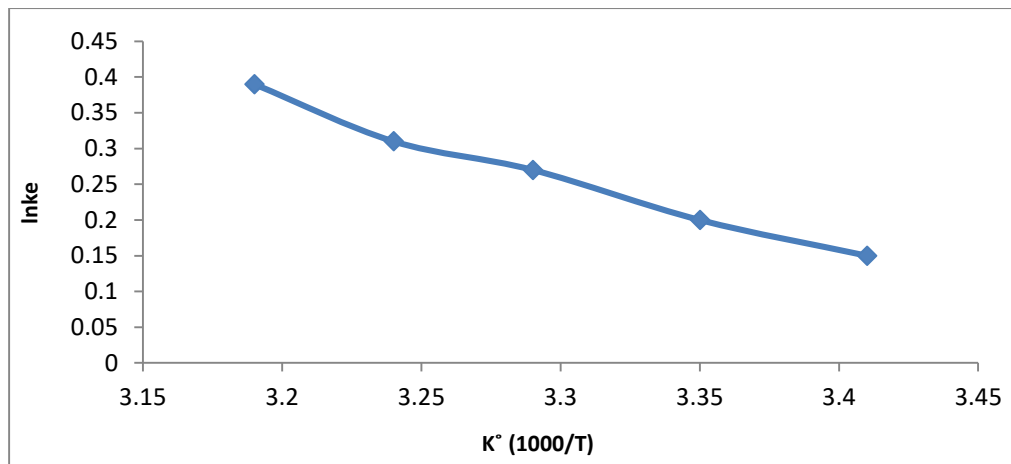


Figure (15) : van't Hoff's plot of adsorption equilibrium constant  $k_e$  for solution of initial Tri Halo Methane (THM) concentration 62ppb at pH = 6, adsorbent dose 0.5 mg /250 ml (ACPF) at 300 rpm, contact time 90 min at different temperatures..

### 3.8 Isothermal models:

Analysing equilibrium data is crucial and plays a significant part in figuring out the maximum capacity of adsorbents. It is crucial for figuring out the maximum capacity of adsorbents. It's crucial to create an equation that accurately captures the outcomes and can be applied to design. The two equations that have been reported the most commonly for the equilibrium modelling of an adsorption system are Freundlich and Langmuir.<sup>[41]</sup>

#### 3.8.1 Langmuir adsorption Isotherm:

According to the Langmuir model, there is no interaction between the sorbed species and Trihalomethane absorption takes place on a homogeneous surface by monolayer adsorption. The following is how the Langmuir equation (9) is written :<sup>[42-43]</sup>

$$\frac{c_e}{q_e} = \left( \frac{1}{q_{max} \times b} \right) + \left( \frac{c_e}{q_{max}} \right) \quad (9)$$

Where:

$q_e$  :is the equilibrium Trihalomethane (THM) on the adsorbent (mg/g),  
 $C_e$ : the equilibrium Trihalomethane (THM) concentration in the solution,  
 $q_{max}$ : the monolayer adsorption saturation capacity of the adsorbent , b: is Langmuir constant.

A plot of  $C_e/q_e$  versus  $C_e$  gives straight line and the values of slope ( $1/q_{max}$ ) and intercept ( $1/q_{max}.b$ ) at initial Trihalomethane (THM) concentration of 62ppb, as illustrated in figure (17) for Trihalomethane (THM). i.e:  $q_t = \frac{(C_o - C_t)V}{M}$  ,  $q_e = \frac{(C_o - C_e)V}{M}$

The Langmuir adsorption constant and the regressing correlation coefficient are shown in table (5), and the linear plot in figure (16) demonstrates how the adsorption confirms the Langmuir isotherm. The separation factor, dimensionless number constant, or equilibrium parameter can all be used to express the basic properties of the Langmuir equation <sup>[44]</sup> ( $R_L$  given by Equation. (10)):

$$R_L = \left( \frac{1}{1 + bc_o} \right) \tag{10}$$

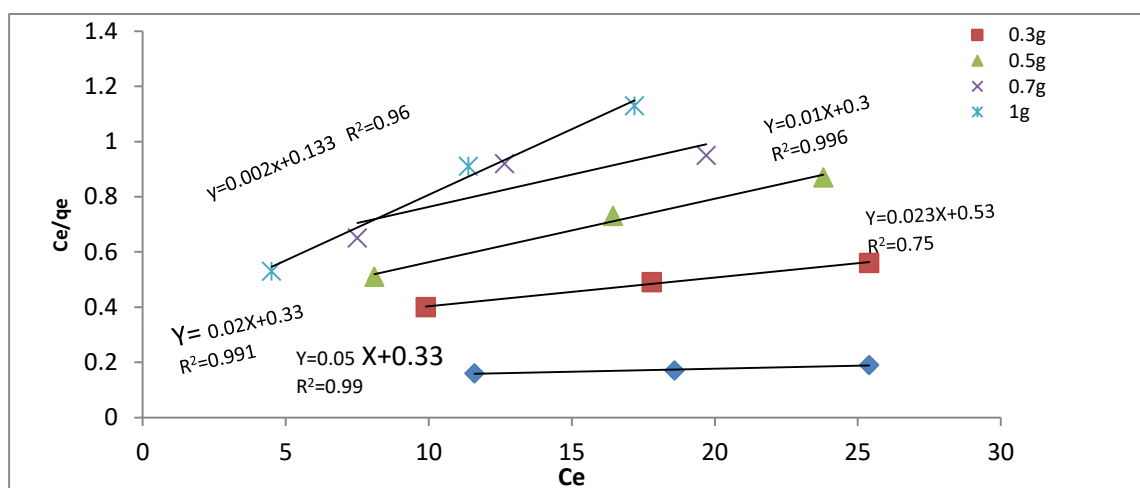


Figure (16): Langmuir adsorption isotherm for Tri Halo Methane (THM) adsorption with different dose (ACPF) (mg/250 ml) at pH =6.5, 300rpm and contact time 90 min.

### 3.8.2 Freundlich Adsorption Isotherm:

This isotherm provides an expression that considers the exponential distribution of active sites' energy and surface heterogeneity. The Freundlich model's nonlinear form is given as <sup>[45-46]</sup>:

$$q_e = K_f (C_e)^{\frac{1}{n}} \tag{11}$$

The linear form of Freundlich model is expressed as:

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e \quad (12)$$

Where:

$K_F$  : is Freundlich constant representing and adsorption capacity ,  $n$  : is a constant related to the sorption intensity, which varies with the heterogeneity of the adsorbents. A plot of  $\log q_e$  versus  $\log C_e$  gives a straight line with a slope(1/n) and intercept ( $\log K_f$ ) as shown in figure(17) for Tri Halo Methane(THM) and table(5)

If the value of (1/n) less than 1 represent of favorable sorption for Trihalomethane (THM). And also confirm the heterogeneity of the adsorbent. Moreover, it indicates that the bond between Trihalomethane (THM) and activated carbon prepare by palm fronds are strong [46].

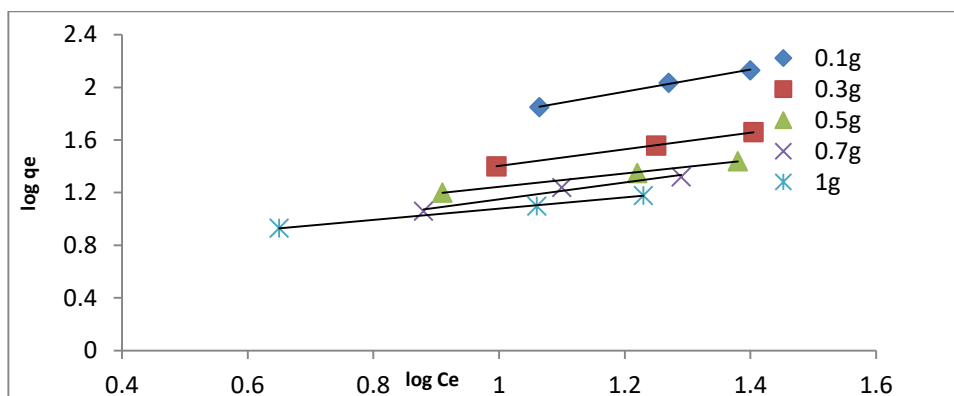


Figure (17): Freundlich adsorption isotherm for Trihalomethane (THM) adsorptions with different dose (ACPF) (mg/250 ml) at pH =6.5, 300rpm and contact time 90 min

Table (5) show Langmuir vs. Freundlich isotherm constant

THM	activated carbon prepare by palm fronds(0.5g/250 ml)	Langmuir Isotherm constants			Freundlich Isotherm Constants		
		$q_{max}$ (mg/g)	$b$ (L/mol)	$R^2$	1/n	$K_f$ (mg/g)	$R^2$
	0.1mg	500	0.015	0.96	0.84	0.96	0.997
	0.3mg	97.08	0.03	0.996	0.635	0.77	1

	0.5mg	43.478	0.07	0.99	0.51	0.74	0.99 8
	0.7mg	50	0.09	0.75	0.63	0.51	0.96 9
	1mg	21.05	0.14	0.98 9	0.43	0.65	0.99 9

### 3.9 FT-IR studies:

FT-IR analysis was performed on two samples of activated carbon made from palm fronds, each containing around 1 mg, one before and one after the heavy metals were removed. The sample was grinded and milled with 100 mg KBr to form a fine powder. After the sample was ground and milled with 100 mg of KBr to create a fine powder, it was analyzed with a spectrometer, and the spectrum's 400–4000  $\text{cm}^{-1}$  spectral range was recorded. Then the sample was analyzed using spectrometer and the spectrum was recorded in a spectral range of 400-4000. Figures (18) (a) & (18) (b) show differences in FT-IR configuration between activated carbon prepared from palm fronds by using phosphoric acid before and after adsorption of Trihalomethane (THM)

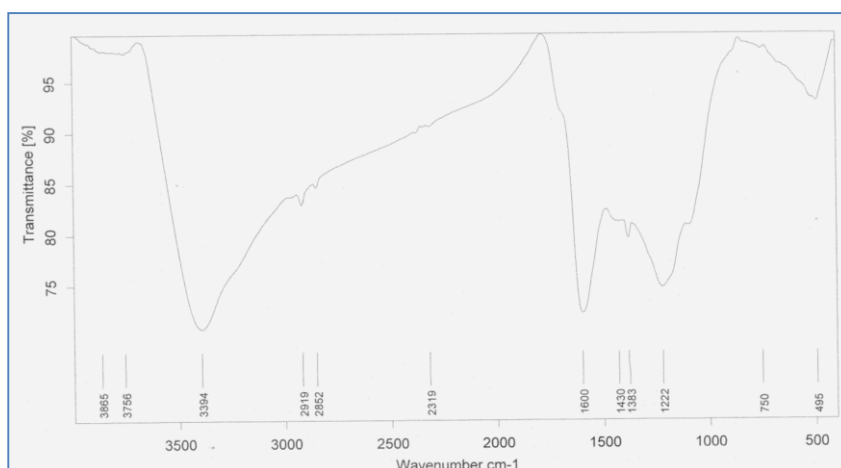


Figure (18): FT-IR characterization of (ACPF) before adsorption process

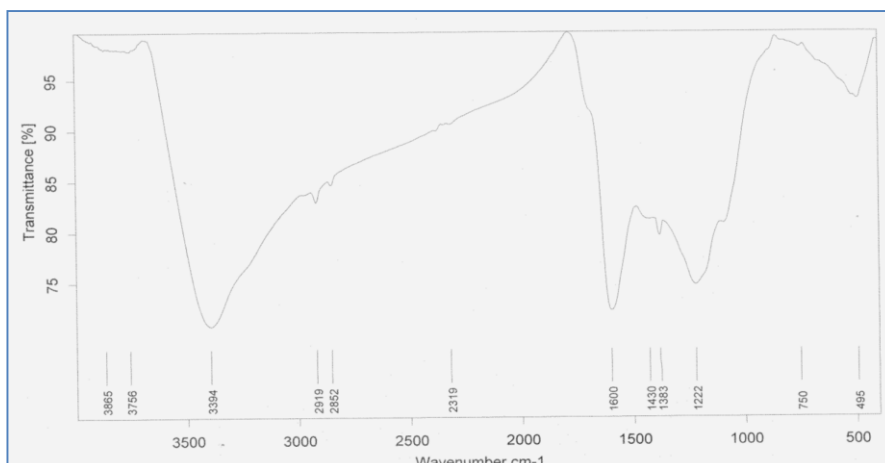


Figure (19): FT-IR analysis of (ACPF) after adsorption of Trihalomethane (THM).

Assignment	Wave number ( $\lambda$ )	
	activated carbon before adsorption ( $\text{cm}^{-1}$ )	activated carbon after adsorption Trihalomethane (THM) ( $\text{cm}^{-1}$ )
Free O-H out of plane (bending)	495	495
Di-substituted ring(stretching) and C-H out of plane	882 992	750 .....
C-O-C in polysaccharides (asymmetric)	1170	1222
Methyl group (symmetric)	1383	1383
Methyl group (asymmetric)	1406	1430
CH <sub>3</sub> (scissoring)	1452	.....
Carboxyl group in COOH-COOCH <sub>3</sub> (stretching)	1614	1600
Carbon dioxide(CO <sub>2</sub> )	2312	2319
	2347	.....
	2396	.....

CH <sub>3</sub> and CH <sub>2</sub> groups (stretching)	2853	2852
	2921	2919
O-H (stretching)	3420	3394

Table (6): Assignment of FT-IR bands of (ACPF) show some functional groups before and after adsorption Trihalomethane (THM)

By using (FT-IR) in the 400–4500 cm<sup>-1</sup> range, the distinctive functional groups that enable the adsorption were examined. The (FT-IR) spectra of activated carbon prepared from palm frond by using phosphoric acid before and after adsorption Trihalomethane (THM) are shown in figures ( 18 , 19 ) respectively . In the adsorbent, where the infrared spectrum showed a significant number of adsorption peaks, various types of functional groups were found.

The peaks at 2921 and 2853 cm<sup>-1</sup> were caused by the aliphatic C-H stretching vibration of the methyl and methylene groups, respectively. The broad band beak at 3420 cm<sup>-1</sup> was attributed to O-H stretching vibrations due to inter-molecular hydrogen banding of polymeric compounds (macromolecular association). There are three different bands caused by the airborne carbon dioxide (CO<sub>2</sub>) at 2396, 2347, and 2312. The strong band at 1614, which can be attributed to carboxylic acids or their esters, corresponds to the stretch vibration of the bond caused by non-ionic carboxyl group (-COOH, -COOCH<sub>3</sub>). The methyl molecule, asymmetric and symmetric vibrations, and O-H in-plane deformation, respectively, were linked to the weak bands 1452, 1406 and 1383 cm<sup>-1</sup>. The asymmetrical stretching vibration of C-O-C in polysaccharide (cellulose and hemicellulose) is responsible for the band at 1170 cm<sup>-1</sup>. Di-substituted ring stretching and out-of-plane carbon single bonded hydrogen caused the peak at 998 and 882 cm<sup>-1</sup>, respectively. The last reference is Free O-H out of plane bending at 495.

Table (6 ) illustrate the intensity of broad band of the O-H stretching vibration at the wave number 3420 cm<sup>-1</sup> after adsorption was noticeably shifted to 3394 cm<sup>-1</sup> due to adsorption of Trihalomethane (THM) .the stretching vibration bands of CH<sub>3</sub>and CH<sub>2</sub> groups were changed from 2921 , 2853 to 2919 , 2852 cm<sup>-1</sup> the band in Carbon dioxide(CO<sub>2</sub>) change from 2312, 2347 and 2921 to 2319 cm<sup>-1</sup> and the other band 2347 and 2921

$\text{cm}^{-1}$  absent after adsorption. The intensity of strong band at  $1614 \text{ cm}^{-1}$  of carboxyl group noticed it will be decreased to  $1600 \text{ cm}^{-1}$  after adsorption. the band in methyl group (scissoring) is absent after adsorption but the band of methyl group asymmetric the shifted of band will be increased from  $1406$  to  $1430 \text{ cm}^{-1}$  after adsorption and methyl group symmetric is noticed there is no change between before and after adsorption. The absence diminishing of these bands indicate that methyl group and O-H played important role in adsorption process. The band intensity were increased from  $1170$  to  $1222 \text{ cm}^{-1}$  to  $1222 \text{ cm}^{-1}$  and the intensity of peak Di-substituted ring(stretching) and C-H out of plane decrease from  $992,882$  to  $750$  after adsorption process.

Changes in the bonding energies of functional groups including hydroxyl, methyl, methylene carbonyl, carboxyl, aromatic rings, and carbon single-bonded hydrogen groups are reflected in a shift in wave number. FT-IR result indicates that the functional groups in activated carbon prepared from palm frond by using phosphoric acid participated in adsorption process and binding Trihalomethane (THM). finally it can concluded that chemical adsorption occurred in surface of activated carbon prepared from palm frond by using phosphoric acid.<sup>[47]</sup>

#### 4. Conclusion:

From the obtained results, it is indicated that the (ACPF) is a good adsorbent for removal of Trihalomethane. The results of established batch studies demonstrated that the pH, residence time, adsorbent dose, starting concentration, and temperature all affect the adsorption of trihalomethane. This study offers an affordable method for eliminating metal ions from drinking water because palm fronds (agricultural waste) are cheap and easily accessible.

**Funding:** “This research received no external funding”

**Conflicts of Interest:** Declare conflicts of interest or state “The authors declare no conflict of interest.”

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