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Enhanced removal of trihalomethanes (THMs) from aqueous solutions using activated carbon from Walnut wood (WC) on Equilibrium, thermodynamic and kinetics

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ABSTRACT

In this study, carbon was easily made from walnut wood as a low-cost and non-toxicnatural adsorbent. Walnut wood (WC), an excellent adsorbent, were successfully synthesized by an in chemical vapor deposition method then characterized using after heating. X-ray diffraction pattern, and FT-IR techniques and used for the removal of trihalomethanes (THMs) from aqueous solution. This adsorbent was reused after heating. The trihalomethanes (THMs) removal by the developed adsorbent was investigated using batch adsorption technique and allparameters influencing the removal efficiency such as: dose of adsorbent, pH and initial trihalomethanes (THMs) concentration were considered. The optimal conditions for the trihalomethanes (THMs) removal were found to be 5, 65 min, 10 mg/L, and 50 mg for pH, contact time, initial THMs concentration, and adsorbent dosage, respectively. The rapid adsorption of the THMs is an advantage of this adsorbent. Various isotherm models were used to fit the experimental equilibrium data. The results showed the suitability and applicability of Langmuir model. The maximum sorption capacity qmaxandR^2 in Freundlichisotherm of trihalomethanes (THMs) 3.0 mg/g and 0.995 showed onto Walnut wood (WC). Kinetic models such as pseudo-first-order and pseudo-second-order diffusion models indicated that the second-order equation model controls the kinetic of the adsorption process. Thermodynamic parameters of adsorption process ($\Delta G°$,$\Delta H°$, $\Delta S°$) were also evaluated. The negative ΔG^o value indicates that the process is feasible and the adsorption spontaneous in nature. The negative ΔH^o value indicates the exothermic nature of adsorption and the value of ΔS^o the change in the randomness at the activecarbon from Walnut wood (WC) solution interface during the sorption.The overall adsorption process was exothermic and spontaneous in nature. The results indicated that trihalomethanes (THMs) adsorption onto Walnut wood (WC) might be a physical adsorption.

Keywords: Adsorption; Trihalomethanes; Kinetic; Thermodynamic; Walnut wood (WC).

1. INTRODUCTION

Different countries in the world often use chlorination to disinfect water and supply drinking water. The major concern regarding water disinfection with chlorine is the formation of potentially health-threatening disinfection by products (DBPs). During chlorine disinfection, natural organic material (NOM) reacts with chlorine to form DBPs [1,2]. Since 1974, numerous epidemiological studies have showed the correlation between the consumption of or contact with the chlorinated water and various cancers in humans and animals. Major chlorine disinfection by products are trihalomethanes (THMs) which are toxic, carcinogenic, and mutagenic. THMs cause cancers of bladder, kidney, intestine [3-5],

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and include chloroform (CHCl3), di chloro bromo methane (CHBrCl2), di bromo chloro methane (CHBr2Cl), and bromoform (CHBr3) being the most common. Many studies have reported the incidence of cancer in laboratory animals which were exposed to chloroform as an indicator of THMs. Moreover, some researchers have found a relationship between these compounds and stillbirth [6]. The presence of organic matters in water resources causes a lot of troubles during treatment processes especially the conventional water treatment. NOM are effective in different aspects of water treatment. The most important effect of these compounds is their reaction with chlorine and producing chlorination by products. It has been proved that chlorination by products depend on the concentration of NOM as the main precursor in the formation of these compounds. The conventional water treatment processes remove only 30% of THM precursors [7,8]. Common methods for the removal of THMs and their precursors are the use of activated carbon, membrane processes, advanced flocculation, and air stripping [9-11]. However, as reported in the literature, using these methods poses many limitations such as the high operation cost and initial investment, obstruction, and generation of a large amount of sludge, reduction of water pH, production of corrosive water, and the need for reduction operation [8, 12]. Conventional wastewater treatment protocol based on physicochemical, chemical, and biological processes includes coagulation and ion exchange [13], adsorption [14, 15], ozonation and Air Oxidation [16], Nanofiltration [17], GAC and Air Stripping Columns [18] and biosorption [19]. Among them, adsorption is widely used for large scale biochemical, chemical, environmental recovery, and purification applications [20]. This technique benefits from simple design and ease of operation by efficient non-toxic and low-cost adsorbents. Characteristics and appropriate selection of the adsorbent are based on factors such as removal capacity, treatment cost, and operating conditions [21]. Therefore, it is necessary to apply more appropriate methods for the removal of THMs and their precursors. Among different methods, the adsorption process is a simple and common method for the removal of organic pollutants like THMs and HAs. In theory the activated carbon is a best adsorbent for THMs removal, however in practice it shows low capacity for the removal of high molecular organic compounds such as NOM [22]. Other adsorbents such as volatile ash, bentonite and pumice stone types of biomasses, powder activated carbon, coke, and kaolin are also used in organic pollutants' adsorption [23-25]. However, such adsorbents are expensive, so, recently, the use of cost-effective adsorbents has been attended to and many studies have been done on their feasibility [26].

Chemical treatment and biodegradation procedure are based on expensive and complex processes that generate toxic by products. Walnut wood (WC) is an agricultural tree that grows in different regions. which means that this activated carbon derived from Walnut wood(WC) is very cost effective, energy effective, and a non-toxic material. All these characteristics of this carbon make it more suitable than commercial activated carbon for the removal of water pollution. On the other hand removal (THMs), its based on biological treatment and chemical precipitation is not environmental friendly and has low efficiency [27]. Therefore, we were motivated to prepare activated carbon derived from Walnut wood (WC) as an alternative to expensive or toxic adsorbents for the removal of trihalomethanes

(THMs) from wastewater. FTIR of the activated carbon, were used to characterize this adsorbent. The experimental conditions, such as pH of solution, contact time, initial dye concentration, and adsorbent dosage as well as the dye removal percentage as response, were studied and optimized. The extent to which the experimental factors interact with each other was also investigated. The optimal conditions for the THMs removal were found to be pH 5, contact time 65 min, initial THMs concentration 10mg/L, and adsorbent dosage 50mg. Various isotherm models, such as Langmuir, Freundlich, and Dubinin–Radushkevich were used to fit the experimental equilibrium data. The results showed the suitability and applicability of the Langmuir model. Kinetic models, such as pseudo-first-order and pseudo-second-order diffusion models indicated that the pseudo-second-order model controls the kinetic of adsorption process. It was shown that the activated carbon derived from Walnut wood (WC) can be effectively used to remove of trihalomethanes from wastewater.

2. MATERIALS AND METHODS

2.1. Preparation of Stock Solution

All chemicals were of reagent grade and used without further purification. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for the pH adjustment. THM solutions were prepared synthetically by diluting a 2000 mg/L analytical grade THM solution (Supelco Inc. Bellefonte, USA), which contains equivalent concentrations of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$, and $CHBr_3$, into deionized water to obtain the desired THM concentration [28].

2.2. Preparation of Activated Carbonfrom WC

First, the walnut wood was chopped into small pieces (about 1 cm) and rinsed with distilled water. Then, the pieces were dried in an oven at a temperature of 105˚C overnight. Afterwards, they were placedin a metal container with a small opening for theexhaust, and the container was heated with gas flamefor one hour at a temperature above 400 ˚C. The produced coal was then slowly cooled to room temperature. The product was washed again with distilledwater. The WC was pulverized after drying and sieving with a mesh sieve 50, and then it was characterized by FTIR [29].

2.4. Batch adsorption experiments

Batch adsorption experiments were carried out to determine the trihalomethanes (THMs) adsorption isotherm onto active carbon from Walnut wood (WC) and its thermodynamic properties: 100 mL solution having 10 mg/L concentration of trihalomethanes (THMs) was prepared and Initial pH of the solution was adjusted with the help of 0.01N HCl / 0.01N NaOH aqueous solution without any further adjustments during the experiments. 10 samples of 100 mL solution were taken in ten 250 mL flasks containing fixed adsorbent dose of 10mg/L. These flasks were agitated at a constant rate of 200 rpm in a temperature controlled orbital shaker maintained at 25^oC temperatures. One of the sample flasks was withdrawn from orbital shaker after fixed time intervals (5, 10, 20, 30, 40, 50, 60, 70, 80 min) and analyzed for remaining metal ions present in the adsorbate solution. Active carbon from Walnut wood (WC) was separated from aqueous solution by filtration through Whatman No. 42 filter paper. The concentration of the trihalomethanes (THMs) in solution samples were analyzed by using a “ U-Visible Shimadzu 160 Spectrophotometer” equipped with an air-acetylene flame. The metal removal (%A) or removal efficiency of metal ion is evaluated by using the equation:

$$\%A_t = \frac{A_0 - A_t}{A_0} \times 100 \qquad (1)$$

Where C_0 and C_e are the initial and final concentration of trihalomethanes(THMs) in solution(mg/L), respectively. The amount (mg/g) of trihalomethanes(THMs) adsorbed at equilibrium was calculated by using the following equation:

$$q_t = \frac{(C_0 - C_t)V}{w} \qquad (2)$$

where, C_o and C_t are initial ion concentration and concentration of trihalomethanes (THMs) at any time'''t', while V is volume of solution in litters and W is adsorbent dosage in mg/L. To evaluate the thermodynamic properties of the adsorption process, 50 mg of activecarbon from Walnut wood (WC) was added into 100 mL initial trihalomethanes (THMs) concentration ranging from 2 to 12 ppm in each experiment. Each solution was shaken continuously for 65 min at 25^{oC}.

After the solutions reached equilibrium, the trihalomethanes (THMs) concentrations were measured and the desorption results were then obtained. Each experiment was carried out in triplicate and the average results are presented in this study.

3. RESULTS AND DISCUSSION

3.1. Characterization FTIR of WC

The characteristic functional groups of the adsorbent were investigated using XRD and FTIR spectra as the most powerful and well-stabilized instrument Fig. (1, 2). For the XRD and FTIR of WC. Stretching vibration band around 1,700 $cm^{-1}$is assigned to carbonyl C=O group present in aldehyde, ester, ketone, and acetyl derivatives. The strong band at 1,500 cm^{-1}may be due to C=C bond. The peaks appearing between 423 and 634 cm^{-1}areassigned to metal–oxygen (M–O) stretching mode in the structure of WC [30].

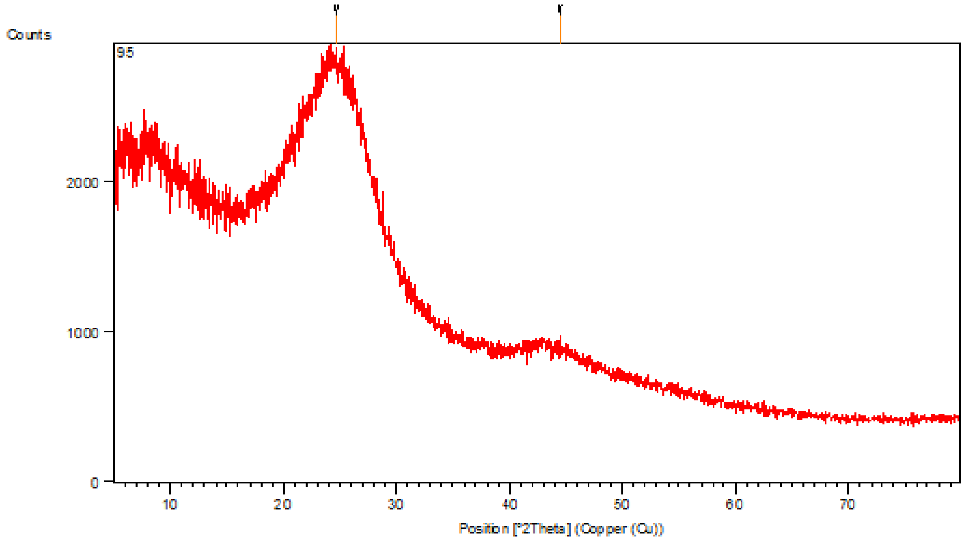

Fig. 1. X-ray diffraction of walnut carbon.

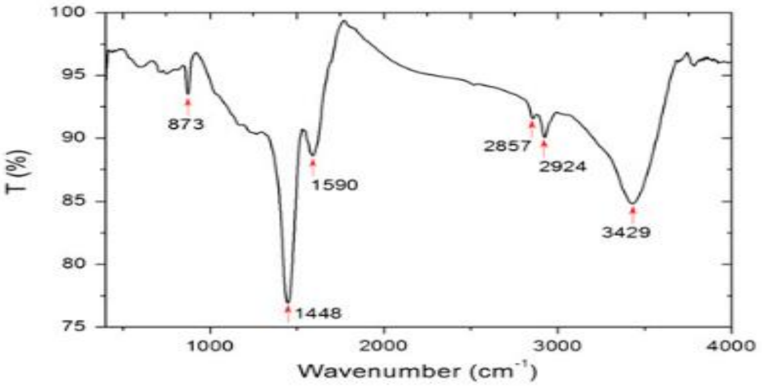

Fig. 2. FTIR spectrum of walnut carbon.

3.2 Effect of pH

The pH has been identified as one of the most important parameter that is effective on trihalomethanes (THMs) sorption. It is directly related with competition ability of hydrogen ions with THMs to active sites on the biosorbent surface. The effect of pH on the biosorption of trihalomethanes (THMs) onto activecarbon from Walnut wood (WC) was studied at pH 3.0–10.0, Fig.3. The maximum biosorption was observed at pH 5.0 for trihalomethanes (THMs). Therefore, the remaining all biosorption experiments were carried out at this pH value [31]. The biosorption mechanisms on the activecarbon from Walnut wood (WC) surface reflect the nature of the physic chemical interaction of the solution. At highly acidic pH, the overall surface charge on the active sites became. positive and THMs and protons compete for binding sites on activecarbon from Walnut wood(WC), which results in lower uptake of THMs. The biosorbent surface was more negatively charged as the pH solution increased from 5.0. The functional groups of the activecarbon from Walnut wood (WC) was more deprotonated and thus available for the THMs. Decrease in biosorption yield at higher pH=5 is not only related to the formation of soluble hydroxylated complexes of the (THMs), but also to the ionized nature of the activecarbon from Walnut wood (WC) of the biosorbent under the studied pH. Previous studies also reported that the maximum biosorption efficiency of trihalomethanes (THMs) on biomass was observed at pH 5.0.

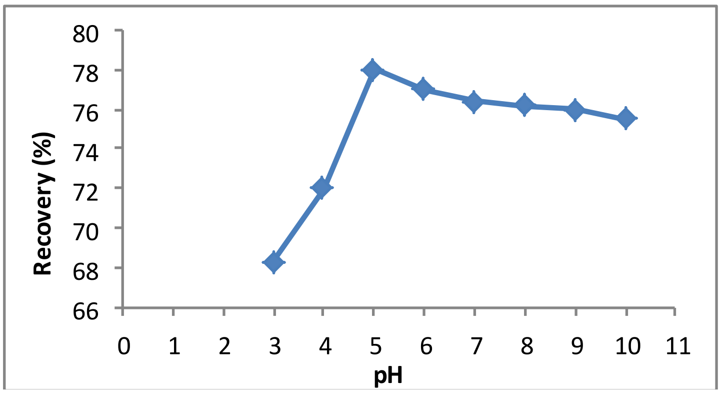

Fig. 3. Effect of pH on removal of (THMs) (conc = 10 mg/L; adsorbent dose = 50 mg, contact time = 65 min; stirring speed =200 rpm; temp = 25^{oC})

3.3. Effect of Initial trihalomethanes (THMs) Concentration

The adsorption uptake of trihalomethanes (THMs) was examined for initial concentration range 2 to 12 mg/L and shown inFig.4. An increasein the initial concentration of trihalomethanes (THMs). leads to increase in the adsorption capacity of these trihalomethanes (THMs) by activecarbon from Walnut wood (WC). The initial concentration provide the necessary driving force to overcome the resistance to mass transfer of adsorbent between aqueous and solid phases.

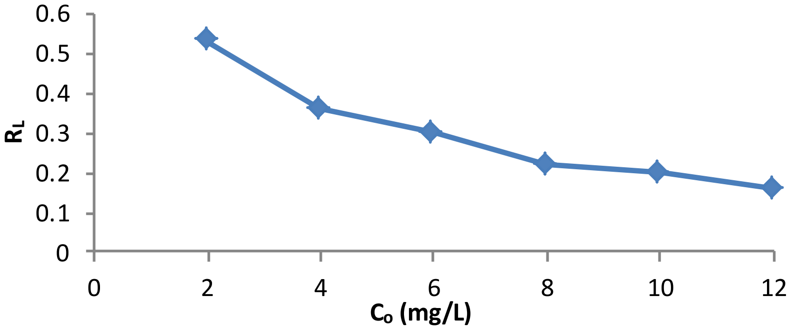

Fig. 4. Effect of Initial (THMs) Concentration on Metal Uptake of Adsorbent; Adsorbent dosage=50mg, pH of solution = 5.0, contact time = 65 min.

3.4. Effect of Contact Time

The uptake of trihalomethanes (THMs) was studied over a time range 5 to 80 minutes and the effect of contact time on removal efficiency presented in Fig. 5.It was observed that almost (THMs) was removed in first 65 minutes. So 65 minutes for trihalomethanes (THMs) is assumed to be sufficient to attain the equilibrium.

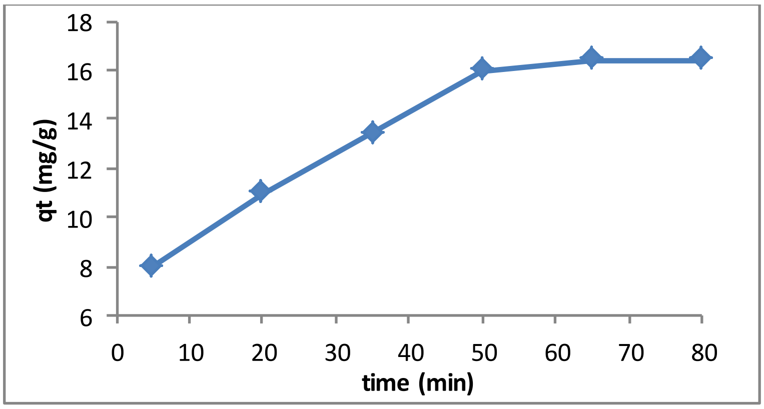

Fig. 5. Effect of contact time on removal of (THMs) by active carbon from Walnut wood (WC); Initial (THMs) concentration=10 mg/L, adsorbent dosage=50 mg, pH of solution = 5.0.

3.5. Effect of Temperature

The adsorption of trihalomethanes (THMs) on activecarbon from Walnut wood (WC) was investigated as a function of temperature and maximum uptake was obtained at 25^{o}C. Experiments were performed at temperatures of 25, 35, 45 and 55^{oC} for the initial (THMs) concentration of 10 mg/L and at constant adsorbent dose of 50mg and pH of 5.0. The adsorption decreased from 80.0 to 60.0 % for the initial (THMs) concentration of 30 mg/L with an increase in temperature from 25 to 55°C (Fig. 6). This is mainly due to the decreased surface activity, suggesting that adsorption between trihalomethanes (THMs) and activecarbon from Walnut wood (WC) is an exothermic process.

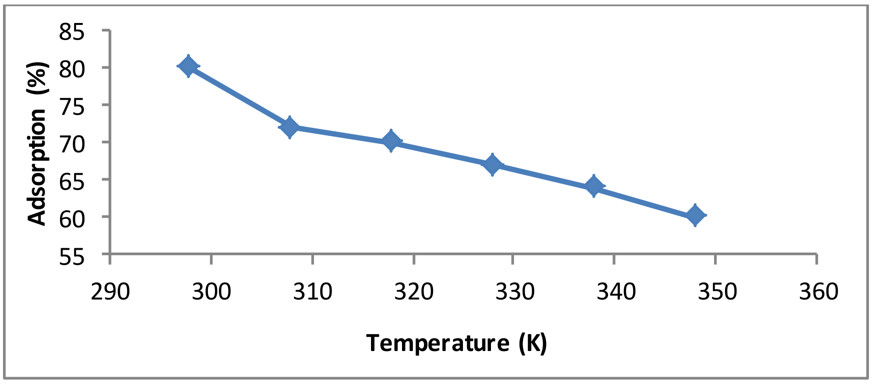

Fig. 6. Effect of temperature for adsorption of (THMs) by active carbon from Walnut wood (WC), Initial metal ion concentration=10 mg/L, adsorbent dosage=50mg, pH of solution = 5.0.

3.6. Kinetics Study

Parameters from two kinetic models, pseudo-first-order and pseudo-second-order, were fit to experimental data to examine the biosorption kinetics of trihalomethanes (THMs) uptake onto activecarbon from Walnut wood (WC).

3.6.1. Pseudo-first-order kinetics

The pseudo-first-order equation of Lagergren [32] is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \qquad (3)$$

Where qe and qt are the sorption capacities at equilibrium and at time t, respectively (mg/g), and k_1 is the rate constant of pseudo-first-order sorption (1/min). After integration and applying boundary conditions, qt=0 to qt=qt at t=0 to t=t, the integrated form of equation becomes [33]:

$$\ln(q_{e/\exp} - q_t) = \ln q_{e/cal} - \frac{K_1}{2.303}t \qquad (4)$$

The equation applicable to experimental results generally differs from a true first-order equation in two ways: the parameter k_1(qe-qt) does not represent the number of available sites; and the parameter ln qe is an adjustable parameter which is often not found equal to the intercept of a plot of ln (qe - qt) against t, whereas in a true first-order sorption reaction log qe should be equal to the intercept of ln(qe - qt) against t. To fit the equation to experimental data, the equilibrium sorption capacity, qe, must be known.

In many cases is unknown and as chemisorption tends to become unmeasurably slow, the amount sorbed is still significantly smaller than the equilibrium amount. In most cases in the literature, the pseudo-first-order equation of Lagergren does not fit well for the whole range of contact time and is generally applicable over the initial 5–50 min of the sorption process. Furthermore, one has to find some means of extrapolating the experimental data to t = ∞ on treating qe as an adjustable parameter to be determined by trial and error. For this reason, it is therefore necessary to use trial and error to obtain the equilibrium sorption capacity, to analyze the pseudo-first-order model kinetics.

The pseudo-first-order rate constant can be obtained from the slope of plot between log (qe-qt) against time (t), Fig. 7. The calculated values and their corresponding linear regression correlation coefficient values are listed in Table 1. R^2 Was found to be 0.8331, which shows that this model cannot be applied to predict the adsorption kinetic model.

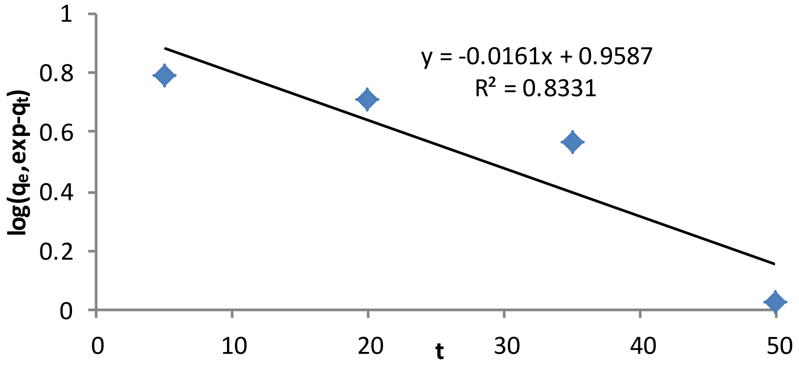

Fig. 7. Pseudo-first-order kinetics for (THMs) onto activecarbon from Walnut wood (WC).

3.6.2. Pseudo-second-order kinetics

The pseudo-second-order rate expression, which has been applied for analyzing chemisorption kinetics rate, is expressed as [34]:

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \qquad (5)$$

Where qe and qt are the sorption capacity at equilibrium and at time t, respectively (mg/g), and k is the rate constant of pseudo-second-order sorption, (g/mg min). For the boundary conditions to qt=0 to qt=qt at t=0 to t=t, the integrated form of Eq. (12) becomes [35]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{e/cal}^2} + \frac{t}{q_{e/cal}} \qquad (6)$$

where t is the contact time(min), qe(mg/g) and qt(mg/g) are the amount of the solute adsorbed at equilibrium and at any time, t. If pseudo-second-order kinetics is applicable, the plot of t/q t versus t of Eq. (13) should give a linear relationship, from which qe and k_2 can be determined from the slope and intercept of the plot, Fig. 8.

The pseudo- second-order rate constant k_2, the calculated e value and the corresponding linear regression correlation coefficient value are given in Table 1. At all initial metal concentrations, the linear regression correlation coefficient R^2Was found to be0.9814, values were higher. The higher values confirm that the adsorption data are well represented by pseudo-second-order kinetics.

3.7. Adsorption Isotherm

Linear plots of the Freundlich, Langmuir, Temp kinamd Dubinin - Radushkevich (DR) models for adsorption of trihalomethanes (THMs) on activecarbon from Walnut wood(WC) are shown in Fig. 9 to 12 and parameters of these models are given in Table.2.

3.7.1. Langmuir Isotherm

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites [36]. Once a site is filled, no further sorption can take place at that site. As such the surface will eventually reach a saturation point where the maximum adsorption of the surface will be achieved. The linear form of the Langmuir isotherm model is described as [37]:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\left(\frac{1}{C_e}\right) + \frac{1}{q_m} \qquad (7)$$

The plots of C_e versus C_e/q_e for trihalomethanes(THMs) are shown in Fig. 9 and the linear isothermparameters qmax, b_L and the correlation coefficient are given in Table. 2. The maximum sorption capacityq_{max} of trihalomethanes (THMs) 3.0 mg/g showed onto activecarbon from Walnut wood(WC).

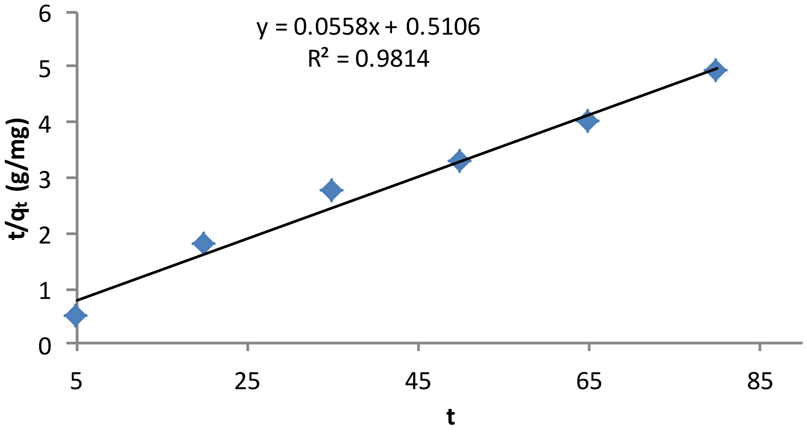

Fig. 8. Pseudo-second-order kinetics for (THMs) onto activecarbon from Walnut wood (WC).

Table 1. Adsorption rate constants by kinetic equation

Kinetic Model ion	Pseudo first - order kinetic			seudo second-order kinetic		
	q_e(mg g^{-1})	K_1(1/min)	R^2	q_e(mg g^{-1})	$K_2 \times 10^{-3}$ (g/mg min)	R^2
Trihalomethanes (THMs)	9.1	0.04	0.8331	18.0	6.1	0.9814

Table 2. Adsorption isotherms parameters and correlation coefficients

Isotherms	parameters	Values
Langmuir	q_m (mg/g)	3
	K_L (L/mg)	0.45
	R^2	0.9679
Freundich	n	0.4
	$K_F(mg)^{1-n}\ L^n\ g^{-1}$	2.6
	R^2	0.995
Tempkin	A_T (L mg^{-1})	1.07
	B_T	21.441
	R^2	0.8906
Dubinin - Radushkevich (DR)	q_d (mg/g)	42
	$K_D \times 10^{-6}$ $(mol/J)^2$	1
	E (kJ/mol)	-700
	R^2	0.9714

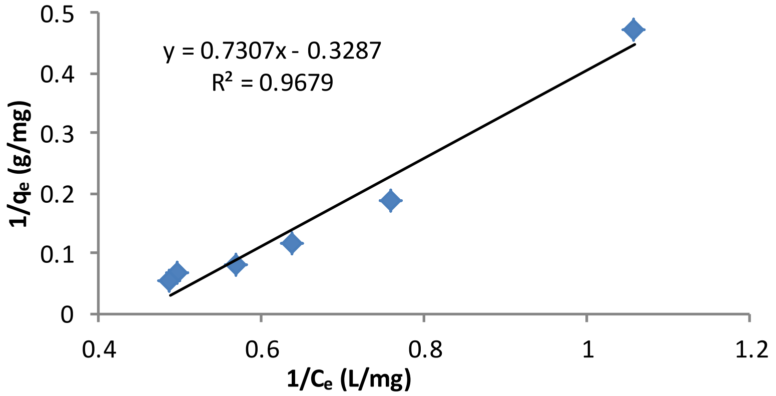

Fig. 9. Langmuir plot for adsorption of(THMs)by active carbon from Walnut wood(WC) adsorbentdosage=50mg, pH of solution = 5.0, contact time =65 min.

3.7.2. Freundlich Isotherm

Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [38, 39]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{8}$$

Where K_F is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n (g/L) is a measure of the deviation from linearity of adsorption [40].

The 1/n and k_F are slope and intercept of the plots ln (C_e) versus ln (q_e) (Fig. 10), the values of N_f and k_F are given in Table. 2. The value of 1/n < 1, for both metal ions indicates favourable adsorption. For higher k_F value sorption intensity will be higher. Therefore, activecarbon from Walnut wood (WC) is times good sorbent for trihalomethanes (THMs) is 2.6. The Freundlich isotherm bestfitted for adsorption of trihalomethanes (THMs) on active carbon from Walnut wood (WC) with corelation coefficient R^2 0.995, respectively.

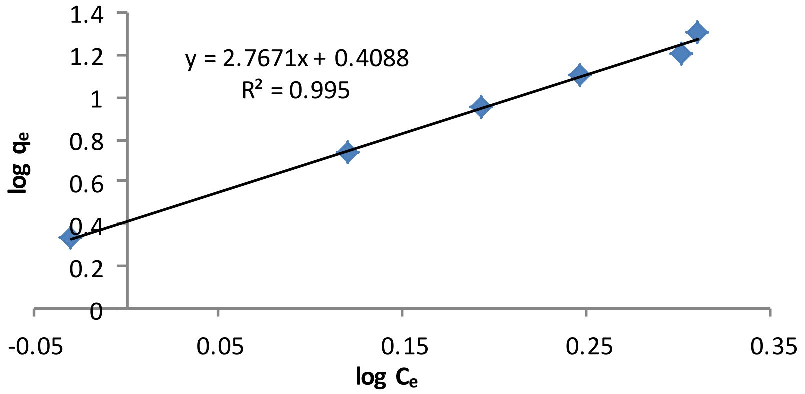

Fig.10. Freundich plot for adsorption of (THMs)by active carbon from Walnut wood(WC) adsorbent dosage= 50 mg, pH of solution =5.0, contact time= 65 min.

3.7.3. Temkin Isotherm

Temkin isotherm equation [41] assumes that the heat of biosorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions and that the adsorption is characterized by a uniform distribution of the binding energies up to some maximum binding energy[42]. The Temkin isotherm has been used in the linear form as follows:

$$\log(\frac{1}{q_e}) = \log(\frac{k_L+1}{k_L q_m}) + \frac{1}{n}\log\frac{1}{C_e} \qquad (9)$$

The plots of ln (C_e) versus q_e for trihalomethanes(THMs) are shown in Fig. 11 and the linear isothermparameters b_T, KT and the correlation coefficient aregiven in Table. 2. The b_T constant related to heat ofsorption for trihalomethanes (THMs) is 21.441 J/mol, showed ontoactivecarbon from Walnut wood(WC).

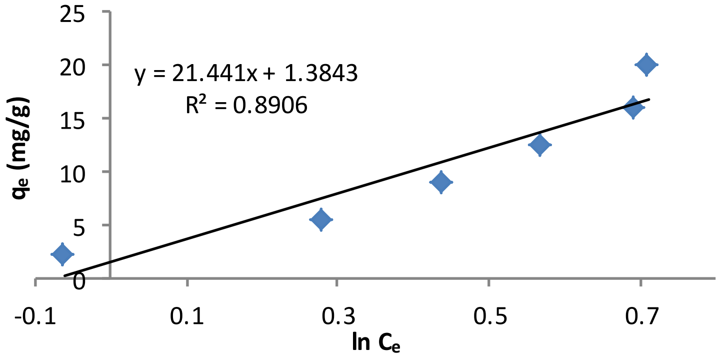

Fig. 11. Tempkin plot for adsorption of (THMs) by active carbon from Walnut wood(WC) adsorbentdosage=50 mg, pH of solution = 5.0, contact time = 65 min.

3.7.4. Dubinin - Radushkevich (DR) Isotherm

The Dubinin–Radushkevich isotherm [43] describes the biosorption nature of the sorbate on the biosorbent and to calculate the mean free energy of biosorption.

$$Lnq_e = Lnq_d - K_D\varepsilon^2 \qquad (10)$$

Where e can be correlated

$$\varepsilon = RTLn(1+\frac{1}{C_e}) \qquad (11)$$

where R is the gas constant (8.314 J/mol K). T is the absolute temperature (K). The D–R isotherm constants b and qmax were obtained from the slope and intercept of the plot of ln qe against e^2, Fig.12. The calculated values are listed in Table 2. The mean free energy of biosorption, E, defined as the free energy change when 1 mol of ion is transferred to the surface of the solid from infinity in solution and calculated from the b value from:[44].

$$E = -0.7K_D^{-0.5} \qquad (12)$$

The plots of RT ln (1+1/C_e) versus ln(q_e) for trihalomethanes (THMs) are shown in Fig. 12and the linear isotherm parameters q_D, B_D and the correlation coefficient are given in Table.2.

3.8. Adsorption thermodynamics

Thermodynamic parameters for adsorption of trihalomethanes (THMs) onto activecarbon from Walnut wood (WC) were obtained at various temperatures of 25, 35, 45, and 55°C. This was performed to investigate the spontaneous nature of the adsorption process. Theequation used is expressed as [45]:

$$\Delta G_{ads} = -RTLnK \qquad (13)$$

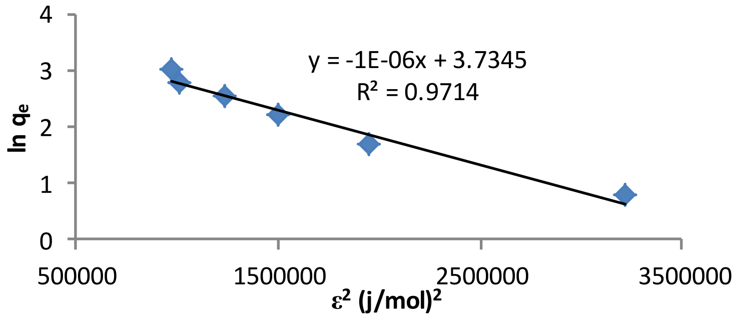

Fig. 12. Dubinin – Radushkevich (DR) plot for adsorption of (THMs) by active carbon from Walnut wood(WC) adsorbent dosage=50 mg, pH of solution = 5.0, contact time =65 min.

Aplotofln Keagainst 1/Tgives a graph (Fig. 13), from theslope of which Δ Gcan be obtained. Thermodynamic parameter results for the adsorption of trihalomethanes (THMs) onto activecarbon from Walnut wood (WC) at various temperatures are reported in Table.3 and 4.

The ΔG^o values were calculated using Equation adsorption of trihalomethanes (THMs) on Walnut wood (WC) decreased when the temperature was increased from 298 to 348 K as shown in Fig. 13. The process was thus exothermic in nature. The plots were used to compute the values of the thermodynamic parameters (Table 3,4) [45]. The values of the enthalpy change (ΔH^o) and the entropy change (ΔS^o) found in this work were -15.0 kJ/mol and -40.0 J/mol.K, respectively. The negative ΔG^o value indicates that the process is feasible and the adsorption spontaneous in nature. The negative ΔH^o value indicates the exothermic nature of adsorption and the value of ΔS^o the change in the randomness at the active carbon from Walnut wood (WC) solution interface during the sorption. It has been reported that ΔG^o values up to -2.25 kJ/mol are consistent with electrostatic interaction between sorption sites and the (THMs) (physical adsorption). The ΔG^o values obtained in this study for trihalomethanes (THMs) are <-5 kJ/mol, which indicates that physical adsorption is the predominant mechanism in the sorption process [46].

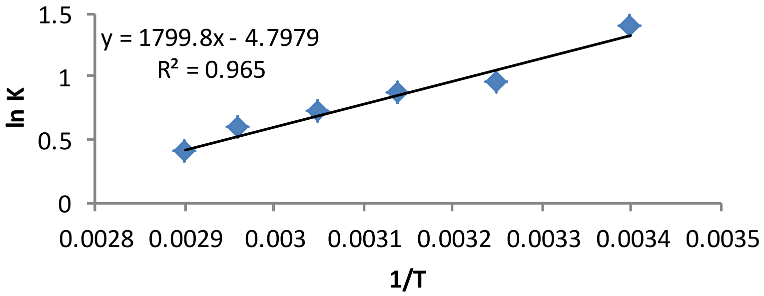

Fig. 13. Plot of lnKcvs. 1/Tfor the estimation of thermodynamic parameters.

Table 3. The distribution coefficients at different temperature

Trihalomethanes (THMs) concn. (mg/L)	R^2	K_d					
		298K	308K	318K	328K	338K	348K
10(mg/L)	0.936	4.0	2.6	2.33	2.03	1.87	1.5

Table 4. The thermodynamic parameters for the adsorption of trihalomethanes (THMs) on Walnut wood (WC) adsorbent.

Trihalomethanes(THMs) concn. (mg/L)	ΔH^o(kJ/mol)	ΔS^o(kJ/mol K)	ΔG^o(kJ/mol)					
			298K	308K	318K	328K	338K	348K
10(mg/L)	-15.0	-40.0	-3.44	-2.40	-2.25	-1.94	-1.63	-1.16

4. CONCLUSIONS

The activated carbon was prepared from Walnut wood (WC) as a low-cost and non-toxic natural adsorbent and used as an effective adsorbent for the removal of trihalomethanes (THMs) from aqueous solutions. The effects of adsorbent dosage, pH, contact time, and initial (THMs) on the removal of (THMs) were investigated through batch experiments. Isotherm models such as Freundlich, Langmuir, Tempkinand Dubinin - Radushkevich (DR) models for the adsorption process were evaluated and the equilibrium data were best described by the Freundlich model. The maximum sorption capacity qmaxandR^2 in Langmuir isotherm of trihalomethanes (THMs) 3.0 mg/g and 0.995 showed onto Walnut wood (WC). The process kinetics was found to be successfully fitted to the pseudo-second-order kinetic model. Adsorption of (HAs) was found to be spontaneous at the temperatures under investigation. The negative ΔG^o value indicates that the process is feasible and the adsorption spontaneous in nature. The negative ΔH^o value indicates the exothermic nature of adsorption and the value of ΔS^o the change in the randomness at the activecarbon from Walnut wood (WC) solution interface during the sorption. The goal for this work is to develop inexpensive, highly available, effective trihalomethanes (THMs) adsorbents from natural waste as alternative to existing commercial adsorbents.Walnut wood (WC), has a high adsorption capacity when compared to other adsorbents for trihalomethanes (THMs) removal from an aqueous medium.

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