



A THERMODYNAMIC AND KINETIC STUDY OF THE ADSORPTION OF VALSARTAN FROM ITS AQUEOUS SOLUTION USING ACTIVATED CARBON PREPARED FROM WALNUT SHELLS

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Article history:		Abstract:
Received:	October 1 st 2022	The poisoning process resulting from the excessive use of drugs has become a big problem that troubles the society ⁽¹⁾ . Therefore, there must be treatments that make it capable of being excreted from the body, where the phenomenon of adsorption is important to be removed from the study, as it is a cheap and inexpensive research method ⁽²⁾ . The subject of the study included about the possibility of using nut husk powder as an activated carbon with phosphoric acid for the adsorption of Valsartan (C ₂₄ H ₂₉ N ₅ O ₃). The study, changes, and factors affecting the process of blackmail, such as the balance of balance, the acidic sign, and the degree of heat, were studied, and through the results that have been brought up, it shows that the general form of the bodies is raised the firmness (L) the second total in the real estate firmness on the custodian of the custodian (The equilibrium time for the drug solution was (45 minutes) on the surface of activated carbon prepared from walnut shells. The effect of the temperature difference on the amount and capacity of adsorption was also studied at four different temperatures (10, 20, 35, 45 °C) Where the results showed that the adsorption capacity and the amount of Valsartan (C ₂₄ H ₂₉ N ₅ O ₃) adsorption increase when the temperature increases, meaning that the reaction is endothermic ⁽³⁾ . The adsorption isotherms of both the Langmuir isotherm and the Freundlich isotherm were studied, and the results obtained showed that the Freundlich isotherm is more closely aligned. It was also shown through thermodynamic studies that the adsorption process of the studied drug is an automatic process through negative (ΔG) values. The study showed the effect of the acidic function on the percentage of adsorption of the drug solution, as it was found that the highest percentage of adsorption of Valsartan was at PH=6. He also studied the effect of the kinetics of drug adsorption on the surface of activated carbon prepared by applying the first and second-order equations, where the results of the kinetic study showed that the second-order equation of the pseudosigmoidosis of decamine antagonism.
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INTRODUCTION

During the 1950, international statistics said that people who take hypnotics die early by 5-25%, and due to the spread of different medicines, ease of access and frequent use, and the fact that the boundaries between the therapeutic and toxic effect of some medicines are not clear, which is easy to skip, as they have a substance that has A specific toxic effect resulting from the small difference between the therapeutic and toxic effects⁽⁴⁾.of medicines that contain toxins and harmful effects to the body, Valsartan is a white powder that is freely soluble in

methanol, ethanol and water in moderation It is one of the active non-peptide nitrazole derivatives It was discovered in 1997. It has low permeability and is effective in treating children, adolescents and the elderly with mild to moderate hypertension⁽⁵⁾. Valsartan 80 mg is highly effective in patients with congestive heart failure and renal impairment. According to a post-experimental control study of more than 12,881 patients in England, malaise was the most common event 13.7% per 1000 patients as a result of a month of exposure, followed by dizziness 11.7%, migraine 10.3%, fatigue 10%, skin rash 1.1%,



as well as joint stiffness and cramps muscles⁽⁶⁾. Therefore, research studies were conducted to remove the poisoning from drug accumulation in the human body using different surfaces of biomass residues such as husks Plants or their nuclei, in 2012, the researcher (R. Baccar and his group) prepared a low-cost activated carbon from olive kernels (activated with phosphoric acid) for use in the adsorption of ibuprofen, ketoprofen, niroxin and diclofenac sodium⁽⁷⁾. Also, the researcher (Syeda N.F.Ali and his group) prepared carbon in 2019 Activated (AC) from palm fronds and activated with potassium hydroxide KOH and then carbon oxidation with nitric acid HNO₃ to form oxidized activated carbon to produce a surface for adsorption of chlorpheniramine and ibuprofen⁽⁸⁾. In 2013, the researcher (Fatima Mohamaed Abdelwahab) prepared activated carbon from Maryam for the adsorption of a drug and diclofenac sodium (DCF) from its aqueous solution, where the surface area of the carbon was studied by knowing the number of iodine and studying the analysis (SEM) and (FTIR)⁽⁹⁾.

THE GOAL OF THE RESEARCH:

Preparing an adsorbent material from the waste of living mass to get rid of the accumulated toxins as a result of the frequent use of medicines.

MATERIALS AND METHODS

Valsartan medication

This drug was used as an adsorbent, as it was supplied by the State Company for the Pharmaceutical Industry and Medical Appliances in Samarra (SDI).

Preparation of activated carbon from walnut shells

Walnut shells were brought from the remnants of the use of walnuts from the local market, where they were cleaned and washed to get rid of dust and loose parts and dried for six hours in the drying oven, then crushed and crushed, and then treated with phosphoric acid at a ratio of 1:1 Which 1 gm of crushed walnut shells with 1 ml of phosphoric acid, then the mixture was dried for eight hours in a drying oven at a temperature of 100 °C and then burned in a combustion oven at a temperature of 550 °C for one hour and then sieved with a laboratory sieve of size (150 μm) and used as an adsorption surface.

Preparation of solutions and determination of the calibration curve

Standard working solutions for each of the three drugs were prepared at a concentration of (50 mg/L) by dissolving 0.05 g of the drug in distilled water in a volumetric bottle of 1000ml and completing the

volume for the mark Then it was determined wave length. Maximize the drug by preparing a diluted standard solution at a concentration (1x10⁻⁴M) of it The measurement was made using a visible-ultraviolet spectrophotometer with a range of (200-800 nm) and using quartz cells (1cm thickness)⁽¹⁰⁾. Then the standard calibration curve was determined by preparing eleven successive concentrations of Valsartan drug solution in the range (5 mg/L- 60 mg/L), and the absorbance values of each of the dilute solutions were measured at (the measured equilibrium between λ_{max} and max) Absorption and concentration , ie the application of a law Beer-Lambert, Beer s, Law $A = \epsilon L C$.

Determining the time to reach equilibrium

To determine the equilibrium time between the surface (prepared activated carbon) and the adsorbent, different times were selected (5, 15, 30, 45, 60, 80, 120) minutes, respectively, at a constant temperature (25 °C) and fixed volumes of carbon dioxide(50 mg / L) and a volume of (50 ml) with the use of a fixed weight of the adsorbent (prepared activated carbon) which is (0.05 gm), the particulate volume of the adsorbent was (150 μm) and a neutral function of Valsartan, and the conical flasks were placed (190 pm) in the incubator at the vibrating incubator (190 rpm) After continuous shaking , the seven solutions were filtered and the absorbance values of the filtrate were recorded by means of visible and ultraviolet spectroscopy, where it was found that the equilibrium time of the drug solution is 45 minutes.

Studying the effect of the acid function on the adsorption process

The effect of the pH function on the adsorption process was studied, as a constant volume and concentration (50 mg/L, 50 ml) of Valsartan was taken, and its acidity function was controlled within the range (1-12) with constant temperature (25 °C) and a fixed amount of adsorbent (0.05 gm),The equilibrium time of Valsartan was (45 minute), the particulate volume of the adsorbent was (150 μm), the acidity function was studied by using (0.1 M) of NaOH and (0.1 M) of HCl and the conical flasks were placed in the vibrating incubator at a speed of 190 rpm. It was left until the specified equilibrium time for each solution was reached, then the solutions were filtered , and the absorbance was measured at the specified wavelength (λ_{max}) of the solution with a visible-ultraviolet spectrophotometer ⁽¹¹⁾.

Temperature Effect

In order to obtain the adsorption isotherms of Valsartan on the adsorbing surface (activated carbon

prepared from walnut shells), solutions of different concentrations of the drug were prepared (mg/L 10, 20, 30, 40, 50), where 50 ml were added from these solutions. The concentrations were transferred to the conical flasks containing a weight of (0.05 g) of the prepared adsorbent surface, and then those flasks were placed inside the vibrating incubator at a speed of (190 rpm) and at different temperatures with a range of (10, 20, 30, 40, 50 °C) on (45 min) packets. The prepared activated carbon, and after the end of the equilibrium time, the solutions were separated by a centrifugal device for (5 min), and after separating the centrifuge, the absorption of the filtrate was measured using a spectrophotometer (Vis-Violet Spectrophotometer, UV-Visible Absorption) for each solution by reference to the standard titration curves.

Adsorption kinetics study

took place Impact study temperature on me kinetics Adsorption at four temperatures (10, 25, 37, 50 °C) and at a constant volume (50 ml) and a constant

concentration (50 mg/l) for Valsartan, a constant weight of the adsorbent surface (0.05 g) and a particulate volume of the adsorbent (150 µm), Then the conical flasks were placed in the incubator vibrating at a speed of (190 rpm) and at different times (5, 15, 30, 45) on the surface of the activated carbon prepared from the shells of the walnut after that, Centrifugal device for a period of (5 min) and after separation, the absorption of the filtrate was measured using UV-visible spectrophotometer.

RESULTS AND DISCUSSION

(Figure 1) illustrates the morphology of the micropores of the prepared activated carbon, which has a large number of pores, which appear in black color. While after adsorption, these particles appeared in the form of clumps as a result of the accumulation of layers of Valsartan on their surface in the form of white spherical-shaped particles Adsorption Studies⁽¹²⁾.

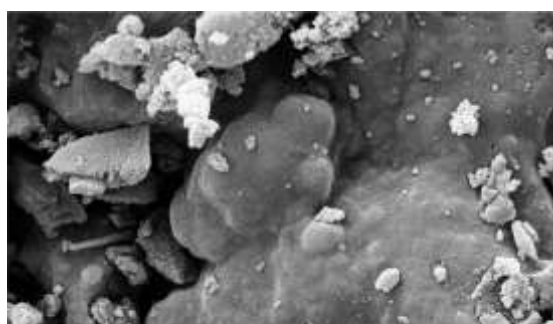
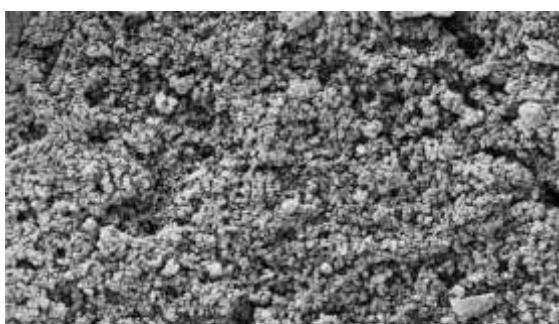


Figure (1) A - Before adsorption

B - After adsorption

The time required to reach the equilibrium state was also determined at the (λ_{max}) value of Valsartan, which is 242 nm. The results showed in Table (1) and Figure (2) that the adsorption process reaches equilibrium within (45 min)

Drug	Time (min)	Equilibrium concentration C_e (mg/L)	adsorption capacity Q_e (mg/g)	Adsorption %	Equilibrium Time (min)
VTN	5	5	45	90	45 minute
	15	3.94	46.06	92.12	
	30	2.89	47.11	94.22	
	45	2.36	47.64	95.28	
	60	2.36	47.64	95.28	
	80	2.36	47.64	95.28	
	120	2.36	47.64	95.28	

Table (1) Effect of equilibrium time on the percentage of Valsartan adsorption .

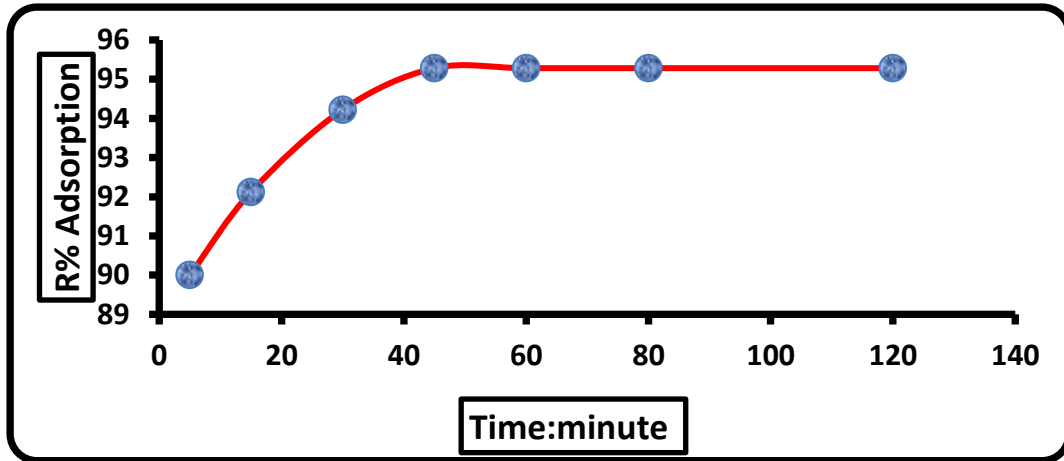


Figure (2): Relationship of the adsorption percentage to the equilibrium time of Valsartan.

The results show in Table (2) and Figure (3) that the percentage of adsorption increases in the acidic medium and then gradually decreases in the neutral and basic medium. The reason for the decrease is due to the increase in the molecular interactions in the adsorption medium and thus weakens the adsorption efficiency⁽¹³⁾.

Drug	PH	Equilibrium concentration C_e (mg/L)	adsorption capacity Q_e (mg/g)	Adsorption%
VTN	2	2.815	47.185	94.370
	4	2.551	47.451	94.902
	6	2.131	47.869	95.738
	7	2.440	47.561	95.122
	9	4.572	45.432	90.864
	12	24.7	25.301	50.602

Table (2): The effect of the acid function on the percentage of adsorption of Valsartan.

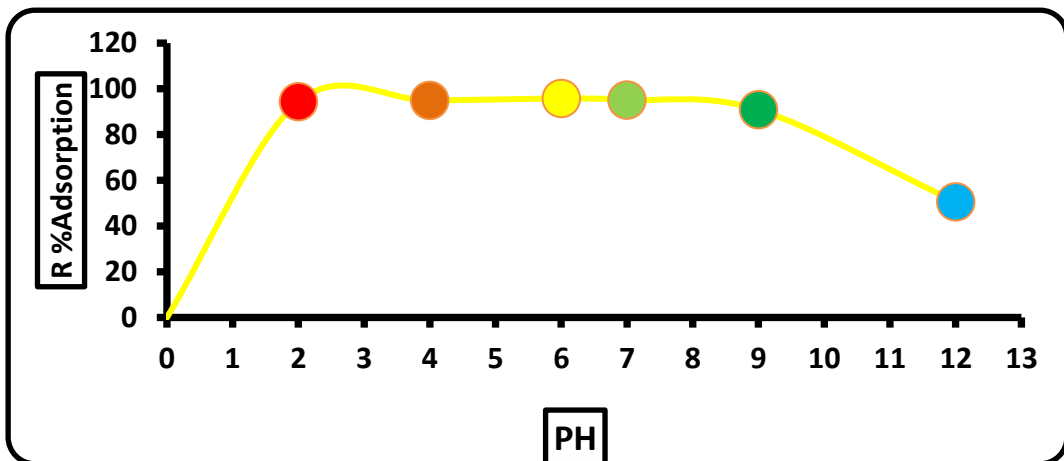


Figure (3) Relationship of the percentage of adsorption to the pH of Valsartan.



The values of the equilibrium constant for the adsorption process (K_{eq}) were calculated at different temperatures at equilibrium, through the ratio between the concentration of the adsorbent and the residual concentration of the drug solution according to equation (1), and the value of ΔH^0 was calculated from the graph of the temperature ratio of $\ln K_{eq}$ According to the Vant-Hoff Equation No (2) (3), therefore, we will get a straight line with a slope equal to $(-R / \Delta H^0)$ and from it we get ΔH^0 , and the values of ΔG^0 and ΔS^0 were calculated according to equation (4) and (5) Respectively, below are the equations for calculating the thermodynamic functions using a concentration of 50 mg/l of the drug solution and a constant acidity function of the drug .

$$K_{eq} = C_{ad}(mg/L)/C_e(mg/L) \dots \dots \dots (1)$$

$$K_{eq} = K_0 e^{-H^0/RT} \dots \dots \dots (2)$$

$$\ln K_{eq} = \ln K_0 - H^0/RT \dots \dots \dots (3)$$

$$\Delta G^0 = -RT \ln K_{eq} \dots \dots \dots (4)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \dots \dots \dots (5)$$

The results shown in Table (3) showed that increasing the temperature leads to an increase in the adsorption efficiency, and this indicates that the adsorption process is endothermic on the surface of the prepared carbon from knowing the positive ΔH^0 values, and the positive ΔS^0 values also indicate an increase in randomness on the surface of the prepared carbon and that the adsorption process is Automatically from knowing negative ΔG^0 values.

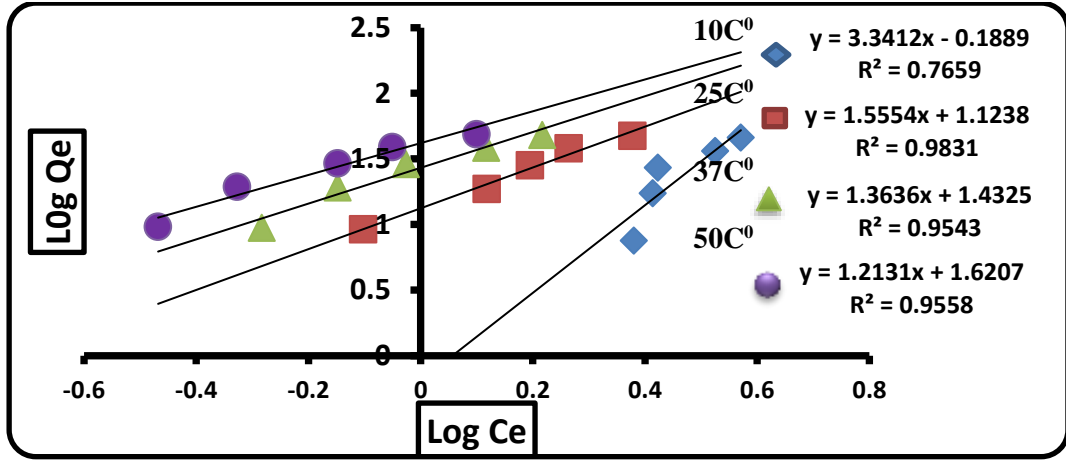
Drug	C _o mg/L	Temp. K°	Equilibrium Constant K _{eq}	Ln K _{eq}	ΔH° KJ.mol ⁻¹	ΔG° KJ.mol ⁻¹	ΔS° J.mol ⁻¹ .k ⁻¹
VTN	50	283 K	12.404	2.518	21.804	-5.924	97.931
		298 K	19.920	2.991		-7.410	98.921
		310 K	29.303	3.377		-8.703	98.534
		323 K	38.682	3.655		-9.815	97.618

Table (3): values of equilibrium constants and thermodynamic functions at equilibrium for adsorption of Valsartan on the surface of activated carbon prepared at different temperatures.

The Freindlich equation (6) and (7) was also applied, where it gave a linear relationship and correlation coefficient (R^2) , which is greater than it in the Lankmeier model as in Figure (4) and Table (4), where the Freindlich model indicates that the process of the solution in the case of surfaces is not The homogeneity is more responsive to this model compared to the Lankmeier model, and here the adsorption is in multiple layers.

$$Q_e = K_f C_e^{1/n} \dots \dots \dots (6)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \dots \dots \dots (7)$$



Figure(4):represents the linear relationship of the Freundlich isotherm for adsorption of Valsartan on coal

Drug	Temperature (°C)	N (L/mg)	K _f (mg/g)	R ²
VTN	10	0.300	0.647	0.7659
	25	0.647	35.01	0.9831
	37	0.733	27.07	0.9543
	50	0.824	41.74	0.9558

Table (4): shows the values of the Freundlich constants and the correlation root (R²) for adsorption of the drug on activated charcoal .

Then I used a model of the first and second adsorption kinetics equations in order to verify the mechanism and rate of adsorption how to control the steps .

The adsorption kinetics is similar to that of the adsorption n isotherms at equilibrium and the difference between them is that the adsorption solution was measured at predetermined time intervals, and the adsorption was measured as mg/l (mg/l) of the adsorption solution (mg/t) after the Turkish adsorption solution. The value of (Ct) The value of the weighty capacity for adsorption (Qe) at time (t) is calculated from the following equation:

$$Q_e = \frac{V_{sol} \cdot (C_0 - C_t)}{m} \text{-----(8)}$$

Q_e = the weight capacity of the adsorbent (mg/g)
 C_t = concentration at time t of the adsorbent solution in units (mg/l)
 V = total volume of the adsorbent solution (L)
 m = weight of the adsorbent (g)

False first order equation

The adsorption rate of the first-order equation is expressed by the Lagergeen equation as follows:

$$dq/dt = K_1 (q_e - q_t) \text{-----(9)}$$

q_e and q_t represent the amount of adsorbent on the adsorbent surface at equilibrium and at time t respectively in units (mg/g) and K₁ is the adsorption rate constant of the first order (hr⁻¹) after incorporating and applying the boundary conditions to (t=t) And (q=0) to (q_e=q) the model becomes after integrating equation (9) as follows:

$$\ln (q_e - q_t) = -\ln q_e - K_1 t \text{-----(10)}$$

And by plotting Ln (q_e-q_t) against time (t) a linear relationship is given if the kinetic model is applicable, and the real value of the adsorption capacity at equilibrium can be obtained (q_e), where the value of (hr) is -1 units, where the value of (hr) is -1 It represents the value of Ln q_e from which q_e is calculated in units (mg/g) as in Figure (5) and Table (5).

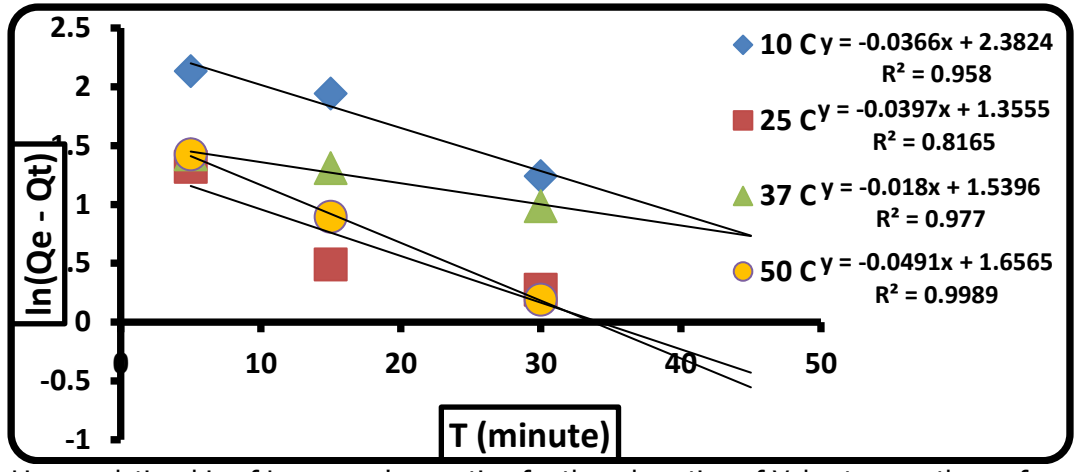


Figure (5) Linear relationship of Lagergren's equation for the adsorption of Valsartan on the surface of activated carbon prepared at different temperatures.

Drug	Temperature (°C)	Q _e (exp.) mg/g	Q _e (CalC.) mg/g	K ₁ min ⁻¹	R ²
VTN	10	45.009	10.830	0.036	0.958
	25	46.316	3.878	0.039	0.816
	37	47.887	4.660	0.017	0.977
	50	48.338	5.243	0.049	0.998

Table (5): shows the values of the velocity constants and adsorption capacity, experimental and theoretical at equilibrium. At different temperatures for the drugs under study by the false first order equation Lagergren.

False second-order equation

The second-order equation model also describes the kinetics of adsorption, as it shows how the adsorption rate depends on the adsorption capacity of the adsorbent material, but not on the concentration of the adsorbent. Adsorption and surface adsorbents. The second-order equation model for adsorption kinetics is expressed by:

$$dq/dt = K_2(q_e - q_t)^2 \dots \dots \dots (11)$$

Where K₂ (g. mg⁻¹. hr⁻¹) is the adsorption rate constant of the second order. The linear model after integrating equation (11) becomes the following:

$$t/q_t = 1/K_2Q_e^2 + (1/Q_e) t \dots \dots \dots (12)$$

By graphing t/q_t against time (t) a linear relationship is given if the kinetic model of the second-order equation is applicable and the calculated value of the adsorption capacity at equilibrium is expressed as (q_e exp.) and Table (6).

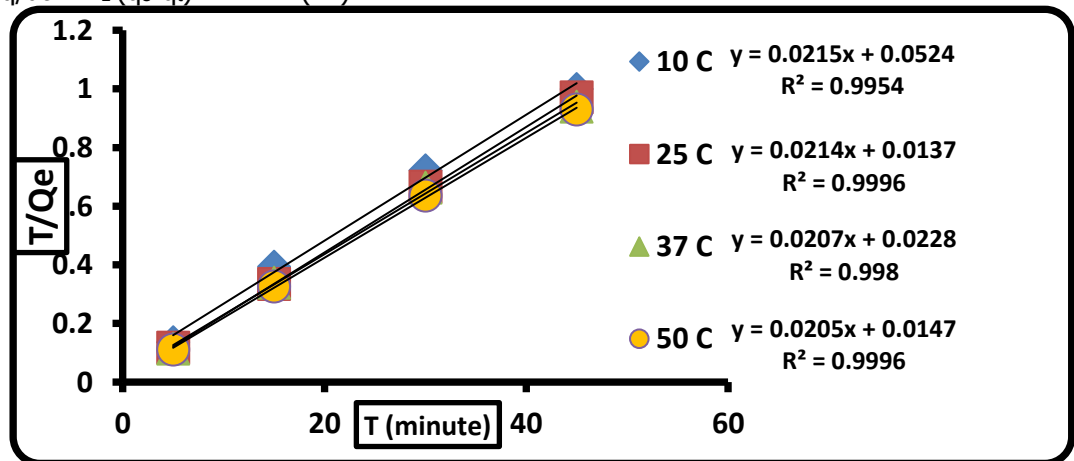


Figure (6) Linear relationship of the pseudo-second-order equation for adsorption of Valsartan on the surface of activated carbon prepared at different temperatures.



Drug	Temperature (°C)	Q _e (exp.) mg/g	Q _e (CalC.) mg/g	K ₂ min ⁻¹ .g.mg ⁻¹	R ²
VTN	10	45.009	46.533	0.008	0.995
	25	46.316	46.704	0.033	0.999
	37	47.887	48.379	0.018	0.999
	50	48.338	48.875	0.028	0.999

Table (6): shows the experimental and theoretical values of velocity and adsorption constants at equilibrium at different temperatures for the drugs under study by pseudo-second-order equation.

Looking at the results listed in Table (5) and Table (6) above, the application of the second-order equation model gave excellent linear relationships, and this indicates the values of the correlation coefficients (R²) for Valsartan, in addition, the values of the calculated straight adsorption capacity were the calculated linearity. More in agreement with the practical values, which indicates that the adsorption process of the system is subject to the pseudo-second-order kinetic equation model, and these results are consistent with a number of previous studies.

CONCLUSION

The study showed that activated carbon prepared from walnut husks has a great ability to adsorption, as it was used to adsorption of Valsartan from its aqueous solution, where the time to reach equilibrium was 45 minutes and the adsorption rate reached 95% at a range of pH equal to 6, as the thermodynamic process was studied. Adsorption occurs spontaneously, and it is an endothermic process, and the Freundlich model is more applicable to the adsorption process, and this adsorption system is subject to the false second-order model by studying its kinetics.

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