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Thermodynamic and kinetic study of the adsorption of Paracetamol drug from aqueous solution using activated Carbon Prepared from Z.SPINA CHRISTI FRUITS NUCLEI

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SUMMARY

In this study,included the preparation of activated carbon from Ziziphus Spina-Christi fruit nuclei,which is locally a vailable in Iraq,the purpose of this study is search for surface that are highly applicable for drug adsorption from aqueous solution . The different variable affecting the adsorption capacity of the activated carbon prepared such as contact time, intial drug concentration in the feed solution,pH of the medium and temperature,were investigated on abatch process mode.the optimum contact time to attain equilibrium is 40 minutes.the maximum percentage removal of (88.96%) occurred at pH (8). Both equilibrium adsorption isotherms and Kinetics were scrutinized in the adsorption research. At various temperatures, the applicability of the Langmuir and Frendlish equations was studied, with the Frendlish isotherms exhibiting the best fit with experimental data. The thermodynamic functions show that the adsorption was automatic operation (ΔGo was negative), that the negative value of (ΔHo) indicates exothermic, and that the negative value of (ΔSo) show non random. The adsorption of drug on activated carbon produced belongs to the Pseudo - second order equation Kinetics, according to the kinetic information.

KEY WORDS: Adsorption, Paracetamol , activated Carbon, Ziziphus Spina-Christi fruit nuclei.

Introduction

The term adsorption is the chemical or physical attachment of the molecules of a substance to the active sites of a surface by forming chemical bonds with the active sites on the surface or by means of weak Van der Waals forces [(1)]. A variety of factors can influence the adsorption process, including the concentration of the adsorbent molecule , pH, temperature ,ionic strength, chemical nature of both

adsorbate and adsorbent molecules [2]. Drugs are substances used to relieve pain, to treat an illness or to improve the state health or well being and control different disease states to make this aim, adequate drug doses must be transfere to the target tissues so that therapeutic , yet nontoxic levels are occured. Most drugs have a number of effects on behavioral and physiological functions and create a wide range of effects, depending on the drug's relative potency and the way it is taken [3] the adrug poisoning regards as a big problems that we face in our time, because of the frequent use of these drugs by the community, in an easy and using the citizens of these drugs, whether one class or more of these medications Known poisoning as a situation caused by swallowing or inhaled or injected, or absorbed by the skin of any Chemical or pharmacological amount higher than usual dose or taken for a long time could lead to poisoning or death, and the main roads to deal with cases of poisoning is dilution with water, vomiting and washing contagious and adsorption[4] . The most extensively used solid surface as an a treatment for poisoning and to inhibit more absorption of the drug was activated charcoal, but patients dislike it due of its color and flavor [5-6]. Activated carbon is an adsorbent used to remove pollutants because of its properties, such as specific surface , pore volume surface chemical group and regeneration possibility [7]. The drug adsorption depends on the characteristics of the carbon surface, pore size distribution and surface Chemistry, from the drug (molecular Size) and from the solution (concentration, temperature and pH)[[8]. paracetamol drug is one of these drugs which cause poisoning if they are taken in large doses, higher Than normal or prescribe dose, which largely available in pharmacies or health centers, parcetamol drug is used to pain killers and for treatment of headaches. The present study is to prepare activated Carbon from locally z.spina-christi fruits stones and to find out the possibility of ysing this activated Carbon as low-Cost adsorbent for the removal of paracetamol drug from aqueous Solution, in vitro as a possible mean for the treatmant of paracetamol poisoning. The equilibrium, kinetic and thermodynamics data of the adsorption were then studied to understand the adsorption. Much of the literature has referred to the use of several types of adsorption surfaces in the fields of medicine, where these adsorbents were used to treat cases of drug poisoning, and activated charcoal was one of the most important of these materials used. Therefore, many researchers were interested in preparing activated carbon from different materials and studying the adsorption process of different chemical compounds, including:

(Ali and her group) [9] studied (in 2019) evaluating the possibility of using pomegranate peel as a low-cost material for the adsorption of metronidazole benzoate (MB). In 2018, (Abd-Alrazak R. and her group)[10] prepared activated

charcoal as an adsorbent from a plant source, pomegranate peels, and studied the efficiency of the prepared activated charcoal in the adsorption of paracetamol from aqueous solution.(Mohamed and his group) [11] in (2017) studied the preparation of activated charcoal from primary plant sources, and its use as a new adsorbent for drug adsorption (amoxicillin). The results also showed that activated charcoal had a high adsorption efficiency of the drug under study, and UV-Vis technology was used To find out the absorbance.. The researcher (T. Darweesh) [12] was able in (2017) to use granular activated charcoal in the adsorption of ciprofloxacin (CIP) and norfloxacin (NOR), as the results showed a decrease in the concentrations of the two drugs as a result of adsorption by granular activated charcoal and with a very high adsorption efficiency.

The goal of the research:

This research aims to study the efficiency of the prepared activated carbon in the adsorption of paracetamol (PC) from aqueous solution, and to explore the ability of the prepared adsorbent to treat cases of drug poisoning.

Experimental

MATERIALS AND METHODS

Materials

Sensitive Balance type (Sartorius AG, Germany,Gottingen), pH Meter (Buchi B190K) ,Burning Oven (Carbolite–England.),Ultraviolet Spectral Measurement type (UV- Vis 2100 Spectrophotometer, SHIMADZ-Japan), (Shaker) Vibrator device type (Adolf Kuhner AG ,Switzerland, Germany),Fourier transformed infra-red type (FT-IR-8400S Japan,SHIMADZU),Scanning electron microscopy type(Scanning electron microscopy-SEM-MIRA3TESCEN) In the laboratories of Tehran / Islamic Republic of Iran,Oven Drying type (Memmert, Germany).

The drug used in this research was obtained from state company for drugs and medicals industry (SDI). This drug is pure and the melting point of this drug was measured practically (172-168 C^{o}).The molecular formula is $C_8H_9NO_2$ withe

molecular weight of (151.16 g/mol) and the maximum absorptian for this drug is (243nm).

Activated carbon preparation

The Ziziphus Spina-Christi fruit stone used in this stady was collected locally from the Dhi Qar -Iraq marketplace . The nuclei of the fruits used in this study were washed well with distilled water several times to get rid of the remnants of the fruits sticking to it and to get rid of some substances that have the ability to dissolve in water such as dust, salts, etc., after that they were placed in an electric drying oven at a temperature of (120^{o}C) for a period of (24hours), for the purpose of drying it and ridding it of moisture, and then it was crushed and ground to obtain crushed nuclei. A certain weight of the dried material was taken and it was treated with concentrated phosphoric acid in a ratio of (1gm of the dried substance: 1ml of (85% H_3PO_4).The activation process was completed by increasing the temperature to (500°C) for (1 hour) [13]. Then the activated charcoal was washed with an abundant amount of distilled water to purify it from acid residues till the (pH) of the washing solution touched the desired level (6-7), for experimental purposes, the material was dried at (120°C) for (4 hours) [14], crushed, and sieved.

Characterization of Activated Carbon

Chemical function groups were examined by FT-IR apparatuc type Shimadzu using KBr pellet method of room temperature. spectral analysis have been recovered between 400 and 4000 cm^{-1} in the wave number spectrum. The properties of particles (e.g, surface morphology and particle size) of the activated carbon was detected by the scanning electron microscope (SEM).

Adsorption Studies

The adsorption of paracetamol drug was studied using the batch adsorption method on to activated carbon prepared. (0.05gm) of activated carbon particle size (75µm) was added to 50ml of 100 mg / L of medication in a series of 100ml capped conical flasks. All studies were carried out at room temperature after a gentle shake for the necessary amount of time at (190 rpm). the mixture was then Centrifuged and the concentration of the drug determine using uv-vis

spectrophotometer (uv - 2100 spectrometer) with a range (200 - 800 nm). According to the equations, the drug removal efficiency and equilibrium uptake were calculated.

$$R\% = \frac{(C\,i - C_e)}{C\,i} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$Q_e = \frac{V_{sol.}(C\,i - C_e)}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where $R\,\%$ is percentage of adsorption, Ci is concentration of drug prior the adsorption (mg/L) , C_e is equibbrium concentration (mg /L) , M(gm) adsorbent weight and $V_{sol.}$solution volume in liter , Q_e is the equilibrium adsorption capacity (mg/g) .

Kinetic study

The kinetics of paracetamol on activated carbon were determined by transferring (0.05gm) of activated carbon powder into a 100 ml screw cupped conical flask containing 50 ml of the studied medication (25 mg/L), Using an isothermal water-bath shaker, samples were shaken at (190rpm) for (10 ,25,37,50 ^{o}C) and the mixture was taken at different time periods. the mixture was centrifuged then measure the amount of the adsorbed drug spectrophoto metrically at (243 nm) and estimated by equation (2).

Results and Discusstion

Description of the adsorbent the Ft - IR Spectrum as display in fig. (1) and the efficient groups in the activated carbon characteristic bands[15] at table (1).

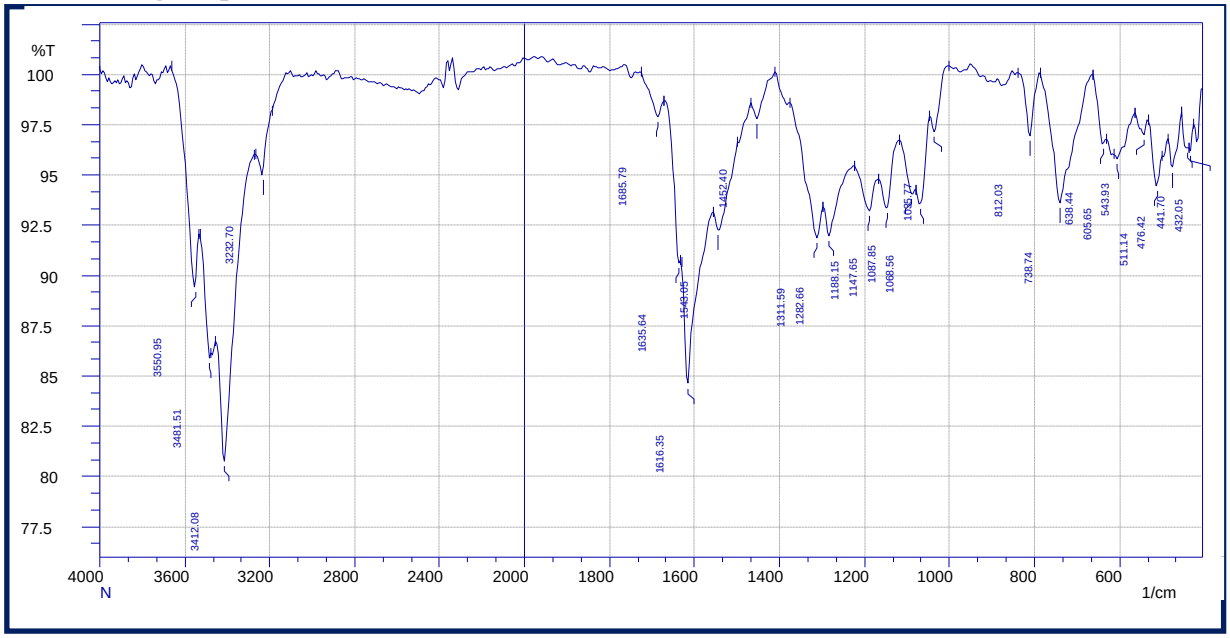


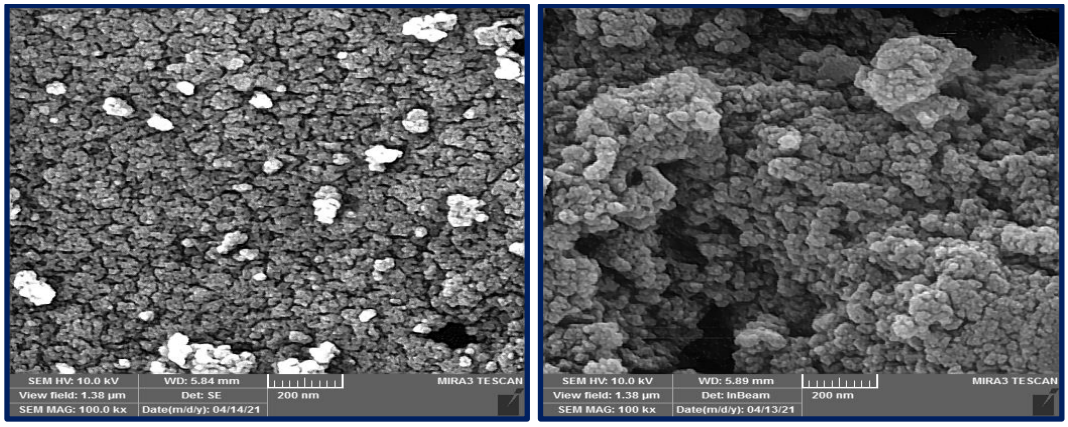
Figure (1): FT-IR of Activated carbon prepared

Type of bond	frequency(cm^{-1})
(O-H) Stretching	3412.08
(N-H) Stretching	3232.70
(N-H)Bending	1616.35
(C=C) Stretching	1543.05
(C-N) Stretching	1282.66
(C-O) Stretching	1147.65

Table(l): FT-IR spectroscopy for the chemical functional groups in the activated carbon prepared

SEM Analysis

The surface morphology of AC is carried out using SEM, this is because the SEM images enables us to directly observe to the changes in the surface microstructure of the AC due to the modification[16].Also,the surface morphology before and after adsorption are comparable [17] Figure 2 (a and b) represent SEM images of AC, it is notice in the SEM image (200nm) of AC that the surface of similar to the masses interspersed with holes and this gives it the characteristic of porosity that the distribution of these hunks and holes in this surface is relatively homogenous , as it shows the morphology of the surface and its porosity before and after adsorption, it is clear that drug particles cover the AC surface (Figure 2(b)) indicating that adsorption has occurred.

(b) 

(a)

Figure(2):image of SEM for PC surface(200nm)
(a)before and (b) after drug adsorption.

Effect of Contact Time

The effect of contact time on the amount of drug adsorbed was investigated at different period (5-60 min)at 25°C. Figure (3) shows that the percentage of drug removed increased with increasing equilibrium time before reaching equilibrium.

The rate of drug removal is higher at the begining because ther is. an abundance of active sites available for the adsorption process and Then gradually slows down until the equilibriun is stabilize [18] .Equilibrium time was attained at (40min).

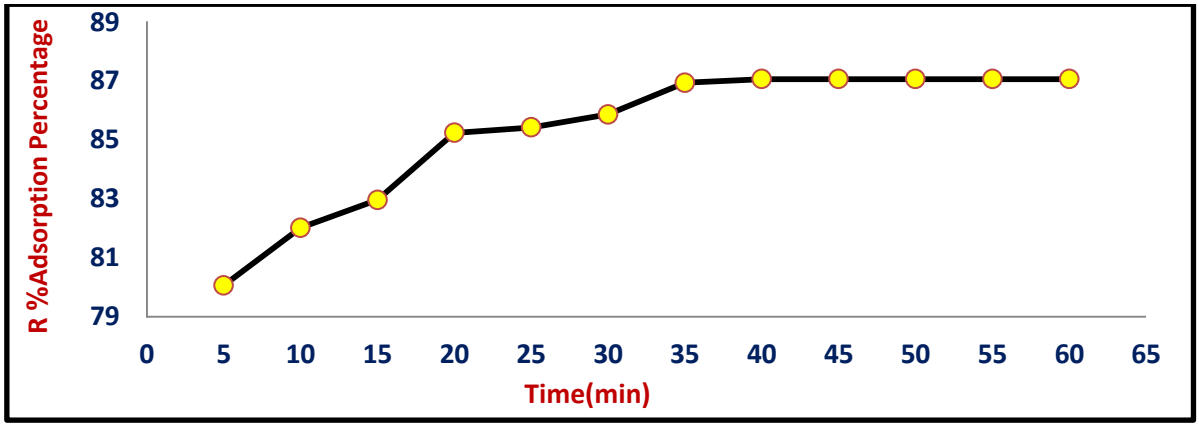


Fig.(3): The effect of contact time on adsorption of PC drug

Effect of initial concentration

The effect of initial concentration of drug solution on the adsorption was carried out for different concentration of drug solution in the range (5-30 mg/L) at 25°C.These samples were shaken at (190rpm) for (40min) after equilibrium. A quantity of the solution was taken and separated by the centrifuge then the drug residue was determined spectrophotometrically, Hence the amount of adsorbed is calculated.the outcomes revealed that the percentage of drug adsorption decreased with initial concentration raised. the number of free adsorption sites reduces hence the removal percentage decreases by increasing the initial drug concentration[19]. the figure(4) revealed that the C_i (25mg/L) was the ideal initial concentration of drug.

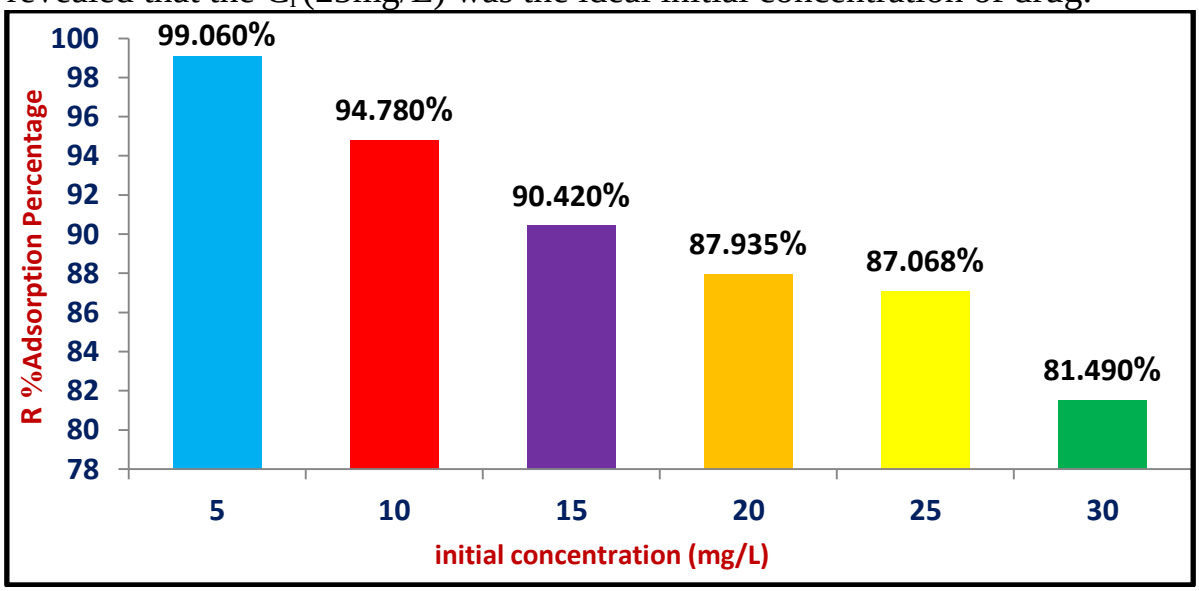
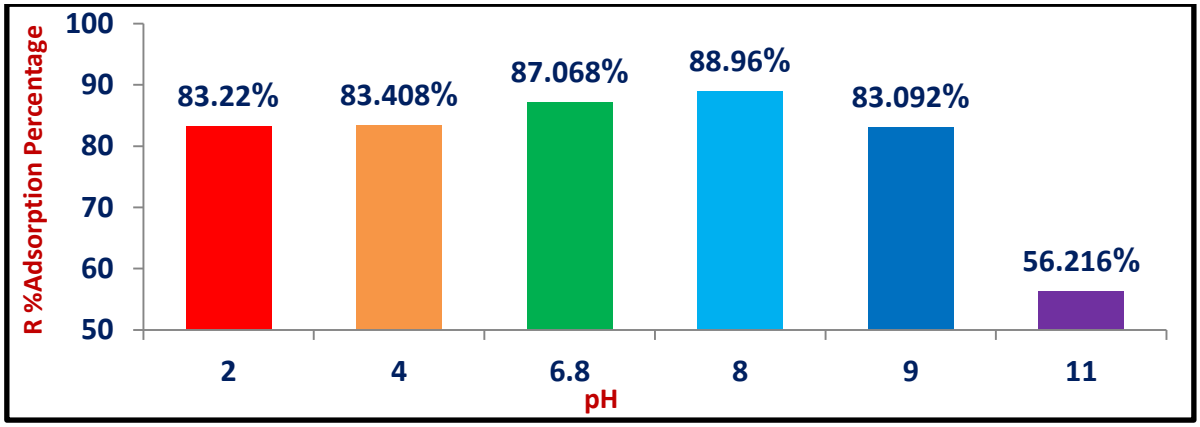


Fig.(4): The effect of initial concentration on adsorption of PC drug.

Effect of pH

The adsorption of drug from aqueous solution is highly dependent on the pH of solution which affect the surface charge of the adsorbent and the degree of ionization and speciation of the adsorbate species [20].pH studies were carried out at various pH values in the range of (2-11).Figure (5) shows the Percentage removal of drug had an increasing trend with increasing the pH. the results showed that the maximum removal of drug a observed at PH value (8).on the other hand the increase in adsorption uptake of the drug with increasing pH of solution could be attributed to the possible changes in properties of the Surface [21].



Figare(5): The effect of pH on adsorption of PC drug

Effect of adsorbent amount

The effect of different (AC) weights on drug percentage removal at contact time (40 min) was examined by the (AC) amount range from (0.0125-0.4gm)in 25mg/L drug solution, figure (6) shows a raised in percentage removal of drug with raising of activated carbon amount and that was because large surface area requires more adsorbent sites by increasing the activated carbon weight [22].

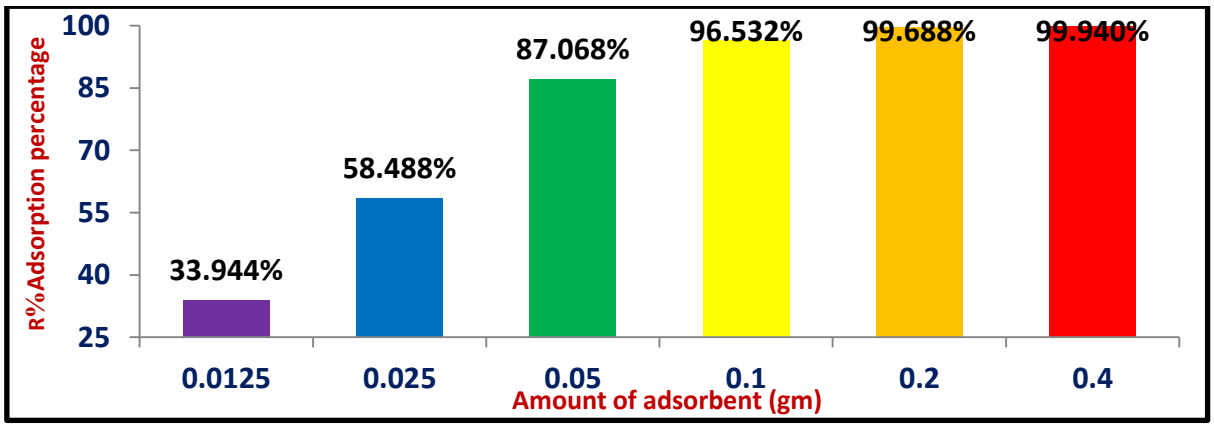


Fig. (6): The effect of adsorbent amount on adsorption of PC drug

Adsorption isotherm

Adsorption isotherm is the relation ship between the amount of substance adsorbed and its concentration in the equilibrium solution at constant temperature. the

adsorption isotherm is important for both atheoretical and apractical point of view, because the application of adsorption isotherms facilitate describing the interaction between the adsorbate and the adsorbent of any system. the parameters obtained from the different models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent [23]. the adsorption of drug from aqueous solution on activated carbon has been studied at different temperatures (10,25,37and 50°C) the general shap of drug adsorption isotherm are show in figure(7)where the quantities adsorbed on AC (Q_e) are plotted as afunction of equilibrium concentration (C_e) at (10,25,37and50 °C).

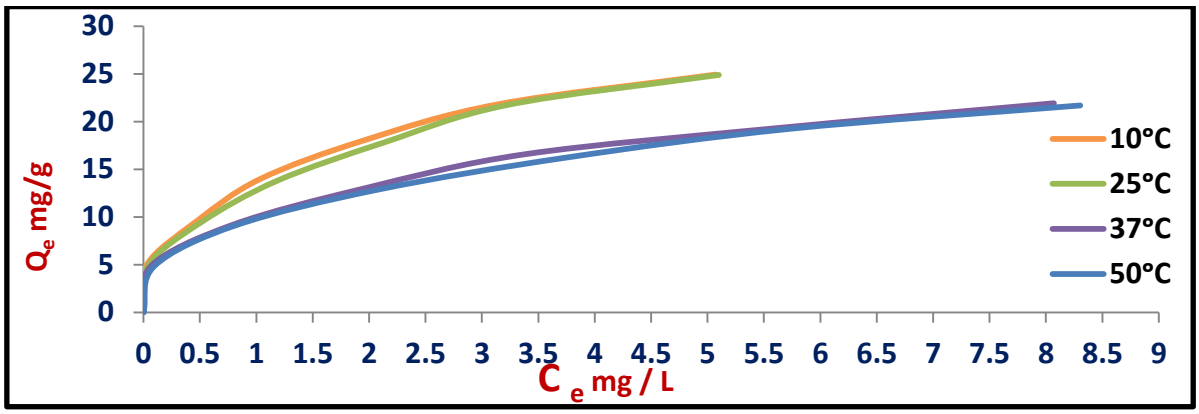


Fig.(7): Adsorption isotherms for a drug at different temperatures.

The adsorption isotherm type of drug on AC corres ponding to (L2 type)in the classification Giles. this type, indication of horizontal orientation of adsorbed in which the adsorbed molecules are parallel to the adsorbent surface [24]. The adsorption data from the experiments were extended to both the theoretical.

The empirical Freundlich equation and the Langmuir equation isotherm. The outcomes of Langmuir (equation 3) and Freundlich (equation 4) were extended.

$$Ce / Qe = (1/ b\, Qm) + Ce / Qm \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

Where: (Qm) represents the maximum theoretical adsorption capacity (mg/g) and (b) represents the strength of the bond between the drug and the adsorbent surface.

$$log\, Qe = log\, kf + 1 / n\, log\, Ce \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

where : n,kf is equal to the Freindlich isotherm constants.

Drug	Temp. (C°)	Langmuir			Freundlich		
		Q_m (mg/g)	b (L/mg)	R^2	K_f (mg/g)	n (L/mg)	R^2
PC	10	27.252	1.445	0.9682	14.288	3.153	0.9780
	25	27.036	1.250	0.9590	13.632	2.902	0.9829
	37	23.740	0.923	0.9724	11.084	3.038	0.9778
	50	23.700	0.831	0.9706	10.332	2.940	0.9956

Table (2) : Results of application of Langmuir and Freundlich isotherm on the system studied.

The isotherm Langmuir and Freundlich was extended on experimental data on the adsorption of drug on activated carbon by plotting (Ce/Qe) versus (Ce) and (log Qe) versus (log Ce) consequently, (Figure 8 and 9). the results of table (2) show that the value of (Qm) decreased with decreasing in the temperature because the adsorption was exothermic,the results also indicate that the Freundlich isotherm is better fitted on this than the Langmuir isotherm as show by the linear relation ship of (log versus (log Qe) Ce) Figure (8).

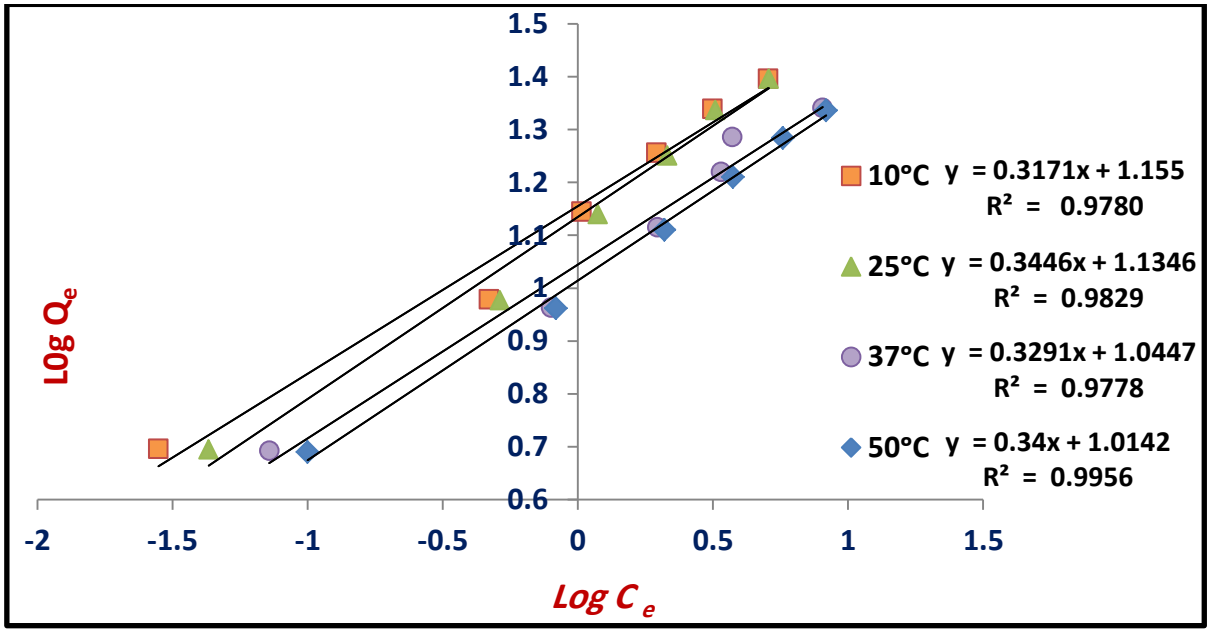


Figure (8): linear form of Freundlich isotherm of PC drug on AC at different temperature.

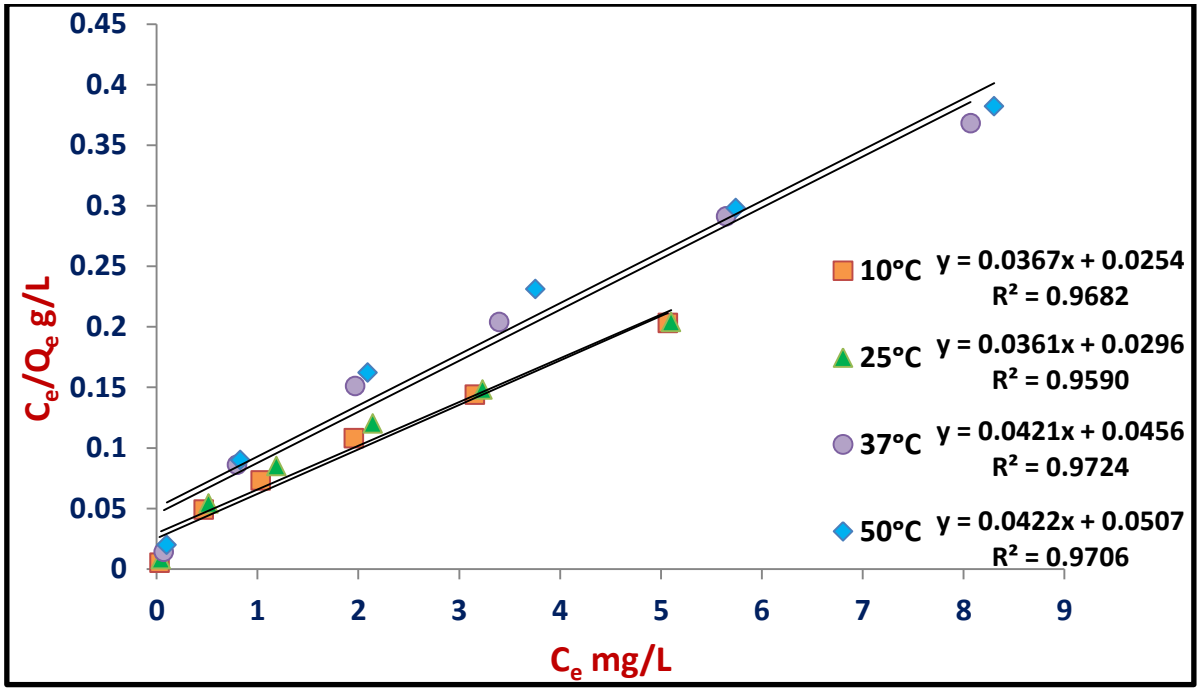


Fig. (9): linear form of Langmuir isotherm of PC drug on AC at different temperature.

Thermodynamic study

The influence of heats on drug adsorption on activated carbon was tested for heats ranging from (10 to 50°C)using varying starting concentrations as well as the thermodynamic variables The following mathematical relations can be used to calculate free energy (ΔG°) , enthalpy adsorption (ΔH°) , and entropy change (ΔS^{o}) , which are crucial in understanding the feasibility, spontaneity, and nature of adsorbate-adsorbent interactions.

$$LnK_{eq}=\Delta S^{o}/RT-\Delta H^{\circ}/RT \ldots\ldots\ldots\ldots\ldots \quad (5)$$

$$K_{eq}=C_{ad}(mg/L)/C_{e}(mg/L) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (6)$$

$$\Delta G^{\circ}= -RT\ lnK_{eq} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (7)$$

where (K_{eq}) represents the equilibrium constant, and (C_{ad}) is the concentration of the adsorbent (mg/L). (C_e) is the concentration of the residue (mg/L), (T) is the kelvin heat ,and (R)is the general constant of gases(0.008314 k $J.mol^{-1}.K^{-1}$), The negative sign of the (ΔG°) obtained suggests that the adsorption process was spontaneous , and the slope and intercept of the van'tHoff plot fig.(10) ,(ΔH°)and(ΔS^{o})are has been calculated Table(3)summarizes the thermodynamic results and indicates.The exothermie character of the adsorption process is shown by a negative value of (ΔH°),whereas the negative worth of (ΔS^{o}) indicates that the decreased haphazardness at the solid solution interface [25].

Table (3):Thermodynamic function for adsorption of stadied drug.

العقار Drug	C_i (mg/L)	Temp. K^o	Equilibrium Constant(K_{eq})	Ln K_{eq}	ΔH^o ($KJ.mol^{-1}$)	ΔG^o ($KJ.mol^{-1}$)	ΔS^o ($J.mol^{-1}.k^{-1}$)
PC	5	283 K	177.571	5.179	-25.005	- 12.185	- 45.300
		298 K	115.279	4.747		- 11.861	- 44.107
		310 K	68.444	4.226		- 10.891	- 45.529
		323 K	49.000	3.891		- 10.448	- 45.068
	10	283 K	20.367	3.013	-12.955	- 7.089	- 20.727
		298 K	18.417	2.913		- 7.217	- 19.255
		310 K	11.562	2.447		- 6.306	- 21.448
		323 K	11.077	2.404		- 6.455	- 20.123
	15	283 K	13.548	2.606	-16.554	- 6.131	- 36.830
		298 K	11.636	2.454		- 6.079	- 35.151
		310 K	6.621	1.890		- 4.871	- 37.687
		323 K	6.166	1.819		- 4.884	- 36.130
	20	283 K	9.224	2.221	-15.776	- 5.225	- 37.282
		298 K	8.332	2.120		- 5.252	- 35.315
		310 K	4.891	1.587		- 4.090	- 37.696
		323 K	4.326	1.464		- 3.931	- 36.671
	25	283 K	6.926	1.935	-15.978	- 4.552	- 40.374
		298 K	6.732	1.906		- 4.722	- 37.771
		310 K	3.427	1.231		- 3.172	- 41.309
		323 K	3.354	1.210		-3.249	- 39.408
	30	283 K	4.918	1.592	-13.877	- 3.745	- 35.802
		298 K	4.880	1.585		- 3.926	- 33.392
		310 K	2.717	0.999		-2.574	- 36.461
		323 K	2.612	0.960		- 2.578	- 34.981

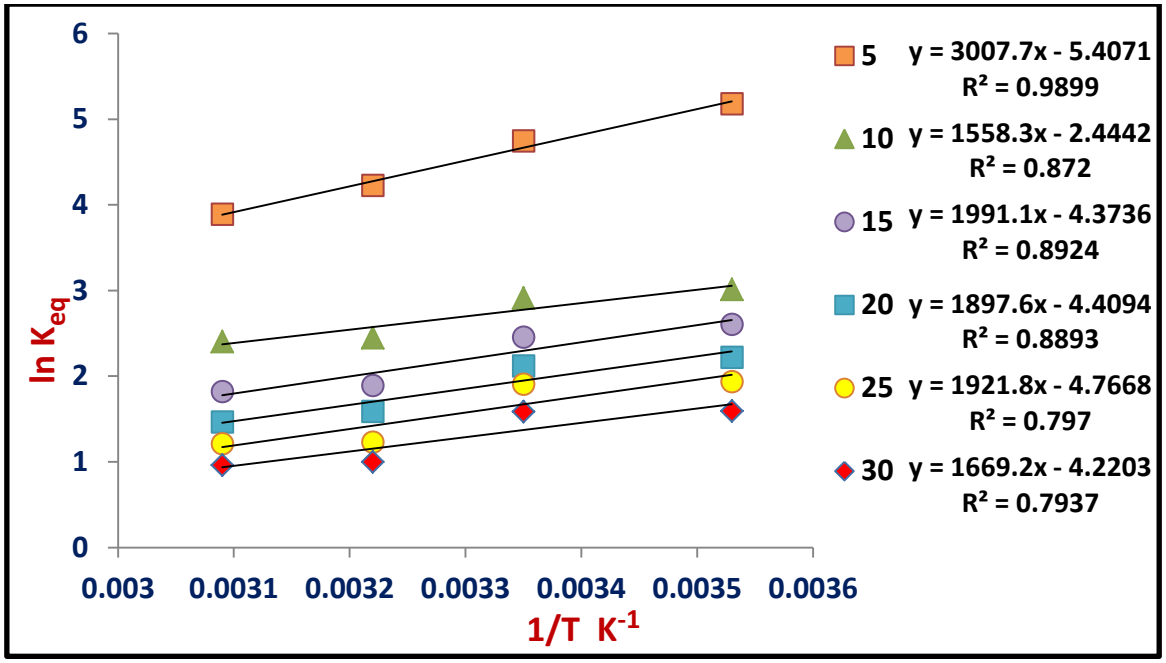


Fig.(10): van't Hoff relation ship between $\ln K_{eq}$ and 1/T

Kinetic study of adsorption

In order to choose the appropriate mechanism in which the adsorption process occurs, and to determine the forces that control the occurrence of the adsorption process, which can be facilitated by a chemical reaction or through the forces that control diffusion or mass transfer. To achieve this goal, the effect of changing the temperature on the adsorption kinetics of the (PC) drug was studied through the application of typical false first order and false second order kinetic equations on the practical data for adsorption of the drug under study on the prepared activated carbon surface.

The following pseudo-first-order equation model known as Lagergren's equation has been applied to the experimental data for adsorption of the drug under study.

$$\ln(Qe - Q_t) = \ln Q_e - k_1 t \ldots\ldots\ldots \quad (8)$$

Which depends on changing the difference between the weight capacity of the adsorbent at equilibrium (Qe) and its weight capacity at time (t) (Qe) by plotting the relationship between ln(Qe-Qt) versus time t (minute) to get linear relationships with slope of (- k_1) and the (lnQe) segment from which the values of (k_1 and Qe) can be calculated respectively, using the pseudo-first-order (Lagergren) rate equation (8). Table (4) presents the findings, which are depicted in Fig. (11).

The following pseudo-second-order equation model was also applied to the practical data for adsorption of the drug under study.

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad \ldots\ldots\ldots\ldots \quad (9)$$

By plotting the relationship between (t/Q_t) versus time t (minute). The values of slope and section of the straight lines obtained from the graph were used to calculate the values of the velocity constant (K_2) ($g.mg^{-1}.min^{-1}$) and the equilibrium adsorption capacity (mg/g) Q_e , respectively. using the pseudo -Second-order rate equation (9) . Table (4) presents the findings , which are depicted in Fig.(12).

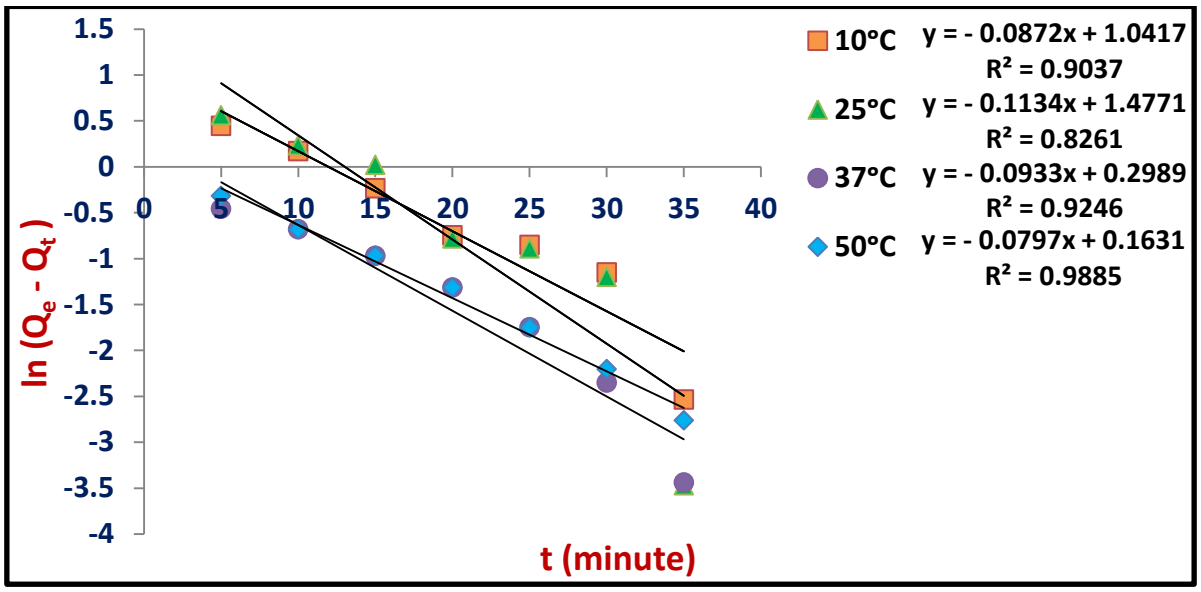


Fig.(11): Linear relationship of the pseudo-first-order equation for adsorption of paracetamol on the surface of activated carbon prepared at different temperatures

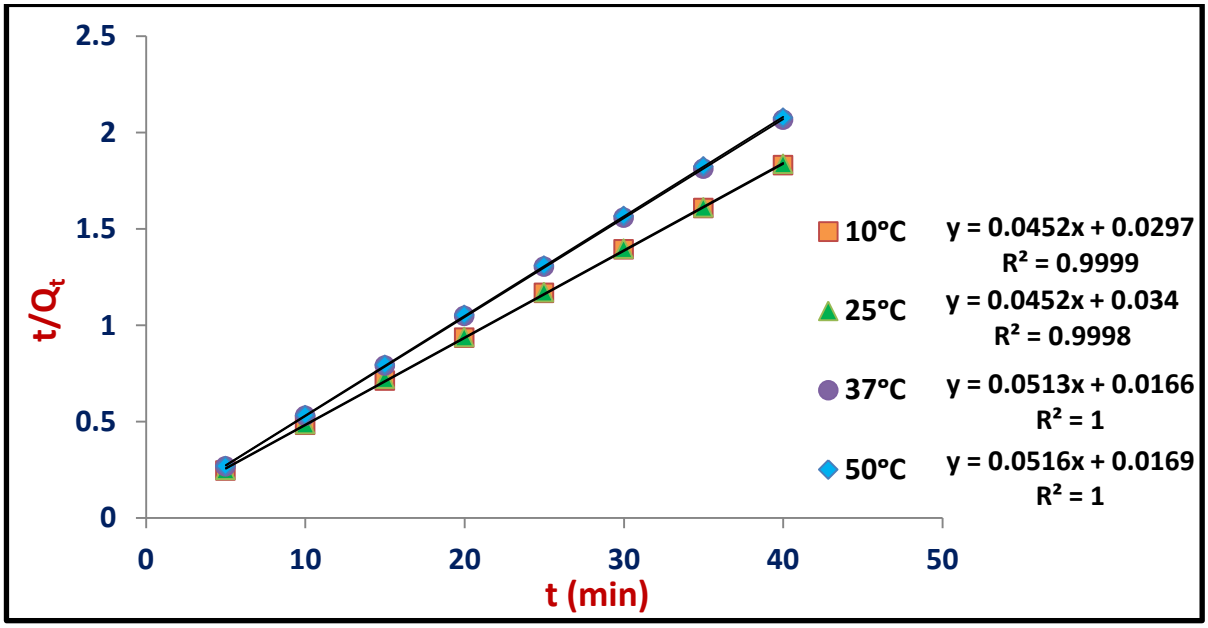


Fig.(12): Linear relationship of the pseudo-second-order equation for adsorption of paracetamol on the surface of activated carbon prepared at different temperatures

Drug	Temp.	Pseudo first order equation	Pseudo second order equation

	(C^o)	Q_e (exp.) mg/g	Q_e (cal.) mg/g	K_1 min^{-1}	R^2	Q_e (exp.) mg/g	Q_e (cal.) mg/g	K_2 $min^{-1}.g.mg^{-1}$	R^2
PC	10	21.846	2.834	0.0872	0.9037	21.846	22.125	0.068	0.9999
	25	21.767	4.380	0.1134	0.8261	21.767	22.119	0.060	0.9998
	37	19.354	1.348	0.0933	0.9246	19.354	19.485	0.158	1
	50	19.259	1.177	0.0797	0.9885	19.259	19.380	0.157	1

Table (4): Results of application of Pseudo first order equation and Pseudo second order equation on the system studied.

From the observation of the lines shown in Figure (11) above, we find that they represent weak linear relationships, and this is indicated by the values of (R^2) listed in Table (4) above. In addition, the values of Qe (calc.) calculated from the segments of the obtained straight lines do not match the calculated values. Experimentally Qe (exp.) Therefore, this adsorption process cannot be considered a first-order reaction. When look closely at the results listed in Table (4) above, find that, contrary to what was observed when applying the first false equation model, the application of the second-order equation model gave excellent linear relationships as in Figure (12) above. This is indicated by the values of the correlation coefficients (R^2) for the drug (PC) whose valuesranged between (1-0.9998), in addition, the values of the adsorption capacity calculated from the slope of the flat lines were more in line with the practical values, which indicates that the adsorption process of the system under study is subject to the kinetic equation model of the second order false [(26)].

Conclusion

The current study showed that the (AC) prepared was used as an adsorbent for (PC) drug from the aqueous solution. It was found that the highest percentage of (PC) removal was (88.96%) at (pH = 8). The results indicated that the studied system is subject to the degree equation the second false. The thermodynamic study of the drug also showed that the adsorption process is spontaneous and exothermic.The results showed that the Freundlech isotherm is more applicable to the studied system. It can be concluded that (AC) prepared from plant raw materials is a promising, cheap and highly efficient adsorbent material for removing the drug from the aqueous solution.

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