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Article

Removal of Oleandrin from aqueous solutions using activated charcoal from pomegranate peel and date pits surfaces

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Abstract

In this search, pomegranate peel and date pits were used to prepare activated charcoal for the adsorption of oleandrin from an aqueous solution. KOH was used as the activated agent, and the charcoal was activated at 700°C for an hour, with a particle size of 600µm. The results were analyzed using UV-Visible technique. The effects of several parameters, such as temperature, PH, adsorbent quantity, and contact time, on the extraction of oleandrin were investigated. Langmuir, Freundlich, Temkin, Elovich, Harkins-Jura, and Dubinin-Radushkevich all examined the isotherm data.computation of several thermodynamic parameters, including Gibb's free energy altered (ΔG), entropy (ΔS), and enthalpy (ΔH),. For

both surfaces, the endothermic nature of the process can be seen by the positive values of (ΔH) and the negative values of (ΔG), which suggest that the oleandrin adsorption process is spontaneous in nature. Pseudo first order and pseudo second order rate equations were fitted using adsorption kinetics, and pseudo second order performed better than pseudo first order.

Keywords: adsorption ,kinetic,extraction,isotherm, thermodynamic parameters

introduction

Much dangerous material, including hazardous chemicals and prescription drugs, is adsorbed onto the surface of activated charcoal preventing their absorption of the digestive system secondary to a purifying process, It stops the possible flow of blood through the liver and/or the stomach. [1-3]. In order for activated charcoal to effectively remove poison, it needs to come into touch with the material in question. It needs to be supplied right away as a result. When given within one to two hours of intake, clinically significant adsorption can be expected[4,5].Activated charcoal (AC) is made up of small pieces of carbon organized in a quasi-graphitic shape. It is a tasteless, porous substance that is separated from elemental carbon by the oxidation of the carbon surface and the elimination of all noncarbon contaminant [6].AC has a special adsorption capacity due to its incredibly huge surface area, volume, and extremely fine network of pores [7].

Adsorption has been demonstrated to be a dependable technique .It has a significant ability to remove a wide range of contaminants and is both economical and environmentally benign. The most popular use of activated carbon as an adsorbent is the removal of biologically resistant organic pollutants from aqueous solutions..The need to find an inexpensive alternative adsorbent was prompted by the high cost of commercial activated charcoal [8,9].

The most practical and popular technique for figuring out the equilibrium in an adsorption system is to use the adsorption isotherm. The magnitude of the enthalpy of adsorption and the relative adorability of an adsorbate on a particular adsorbent in relation to a selected standard are both revealed by the adsorption isotherm. The literature provides many isotherms that can be used to depict the adsorption data. The most important which being used in this research are Langmuir, and Freundlich, isotherms.[10]. Nerium oleander has long been considered dangerous because of various compounds that could be detrimental when took in in high quantities, especially by animals. Among these are the cardiac glycosides

oleandrigenin and oleandrin, which have a low therapeutic index and could be hazardous if consumed in excess [11].

Nerium oleander is a member of the Apocynaceae family. It is indigenous to Europe and Africa's Mediterranean areas. This stunning shrub has evergreen leaves, and its flowers are a variety of colors, from deep red to pink to white [12].The primary toxin in oleander is oleandrin (C32H48O9), a glycoside. In plant tissues, oleandrin is present in concentrations of about 0.08% [13]. Oleandrin shows promise as an anti-cancer medication. Research revealed a possible in vitro impact on prostate, pancreatic, non-small cell lung, leukemia, and colon malignancies.[14]C

Materials and Method:

Charcoal Derived from pomegranate peels (PPC)and date pits(DPC) were used in this research . Before being used, the samples were dried at 100°C in an oven after being repeatedly cleaned, and they were then crushed into a fine powder). Oleandrin extracted from oleander leaves.

Storage and Crushing Samples:

Oleander leaves were gathered from the Najaf area of Iraq, the leaves were washed and then left to dry and grind to be ready for water extraction.

Preparation of water extract

200 gm of oleandrin per 1 liter of distilled water, a volumetric flask was placed in magnetic stirrer for 24 hours, 700 rounds per hour, after that put in the centrifuge(5000rounds an hour) for 0.5hour, then a medical monitor was filtrated by using what –man NO.1., and the accelerator dried up in the dry oven 40^0 C for a two day , and the amount recovered was 50 gm[15].

Making the Oleandrin Solution:

Accurately weighted oleandrin was dissolved to a concentration of 1000 mg/L in distilled water to create the stock solution.. The oleandrin stock solution was diluted in precise amounts to produce the experimental solutions at various starting concentrations.

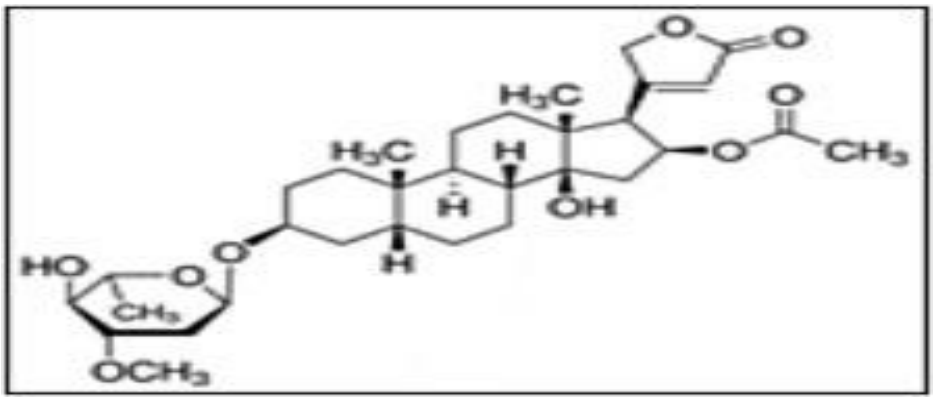

Fig.1: Structure of Oleandrin

Preparation of Charcoal created from pomegranate peel(PPC) and date pit (DPC) (by two steps):

1-physical activation: the peel and pit are washed with distilled water, and then we let it dry, and then we put it in the oven for 2h at 50^0C, and then it's grinding the burned coal with the palms, and after which it is repeatedly cleaned with distilled water, and then it's dry at 80^0C. (40min)

2- Chemical activation of prepared charcoal with phosphoric acid at a concentration of 5M by a ratio of 1:1 for 24 hours

Sorption Studies:

1-Analysis of oleandrin:

The UV-Visible spectrophotometer was used to measure the amount of oleandrin in the supernatant solution before and after adsorption at a wavelength of 229 nm.It was discovered that demonstrating the calibration curve's great reproducibility and linearity increasing concentrationrange utilized in the experiment (50-300 ppm) and that the supernatant from the charcoal showed no absorbance at this wavelength.

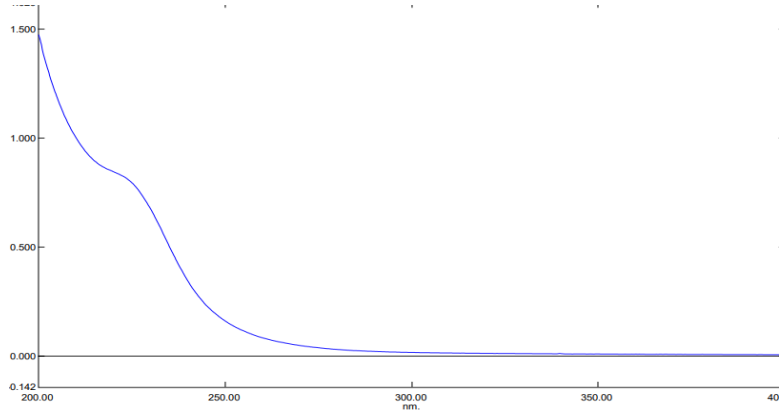

Fig.2 : Wavelength for adsorption oleandrin on activated charcoal at 298K

2-Effect of adsorbent dose :

(0.05,0.1,0.2,0.3,0.4, and 0.5)g of sorbent mass were used to examine the impact of sorbent dose on the equilibrium absorption of oleandrin. the experiments were carried out through the addition a known weights of PPC and DPC to six volumetric flask of (25) ml containing 10ml of 300ppm solution in pH=6. The ideal contact period was achieved by shaking the flasks at 200 rpm and 25 °C, and the spectrophotometric equilibrium concentration of the residual oleandrin was found.

3- Impact of pH:

There was an evident effect of pH on the adsorption of oleandrin. To do this, various pH values for oleandrin were obtained. With the ideal weight surface in the experiment, 10 ml of an oleandrin solution with a variable pH (between 2 - 10) was introduced to several HCl and NaOH solutions.

4-Adsorption experiments in batches :

Sorption studies were conducted using 25 ml shaking flasks holding 10 ml of various concentrations and initial pH values of oleandrin solutions in a rotary shaker operating at 200 rpm and 25°C. A pH meter was used to initially modify the solution's pH values using diluted NaOH or HCl. All flask was filled with varying amounts of charcoal made from date pits and pomegranate peels, after that, the flasks are sealed to avoid the volume of the solution from changing while the tests were being conducted. Following the flasks' predefined periods of shaking,after the samples were taken out of the flasks, centrifugation was used to separate the sorbent and oleandrin solution.

Using the mass balance equation, the amount of oleandrin absorbed by charcoal made from pomegranate peel and date pit was determined. [16]:

$$Qe=(Co-Ce)Vsol/m.....(1)$$

Results & Discussions

1-Contact time impact on oleandrin elimination:

Equilibrium time is one of the most important design parameters for a wastewater treatment system that is economical. The adsorption of oleandrin on date pits and pomegranate peel was examined to calculate the required adsorption time to equilibrium in a function of contact time.

Equilibrium time establishment indicate an adsorbent's effectiveness when used in wastewater treatment. As shown in Figure (3A) displays how pomegranate peel and date pit adsorb oleandrin in relation to contact time., Adsorption progresses until equilibrium is attained, and it was demonstrated that the adsorption rate increases rapidly at first and then progressively.[17]

The positively charged surfaces of the pomegranate peel and date pit are responsible for the fast adsorption during the first contact time, whereas the sluggish rate of oleandrin adsorption is most likely caused by the solute's slow pore diffusion into the majority of the adsorbent.[18]

2-Effect of pH on oleandrin adsorption:

pH levels in effluent from textile industry typically vary widely. thus, the system's pH has a significant impact on how textile wastes are treated. The adsorbents' surface binding sites and aqueous chemistry are both impacted by the pH value.

The effects of initial pH on oleandrin adsorption were investigated in the range of (2 to 10) at 298K at initial oleandrin concentrations of 300 mg/l, 0.2 g of adsorbent, and contact times of 30 min for PPC and 2 hours for DPC. The corresponding findings are shown in Figure (3B). As may be shown, the highest oleandrin absorption on PPC and DPC is obtained at pH of 2 ,.It was observed and shown that the pH had a substantial impact on the amount of oleandrin that is adsorbed over the adsorbent and that this value also causes a decline in adsorption efficiency. Lower removal efficiency results from greater competition between H+ and

oleandrin for accessible adsorption sites because many sites on PPC and DPC may become positively charged at extremely low pH[19,20]

3- Impact of an adsorbent dosage at a fixed concentration of oleandrin:

Using sorbent masses of 0.05,0.1,0.2,0.3,0.4, and 0.5g, the impact of sorbent dose on the equilibrium absorption of oleandrin was examined.. In order to conduct the tests, known weights of PPC and DPC were added to six 25 ml conical flasks holding 10 ml of a 300 ppm solution at the ideal pH.The flasks were shaken for 0.5 hours of PPC and 2 hours of DPC at 200 rpm and 298 K. Spectrophotometric analysis was used to estimate the equilibrium concentration of the remainder oleandrin.. The greatest degree of oleandrin removal was found to be achieved for adsorbent masses of at least adsorbent[21], This might be the result of aggregation of CDB at higher doses or the quick rise with in surface plus number of accessible active sites for oleandrin adsorption [22] From the point, the optimum weight for the decrease adsorption process occurred at 0.2 and 0.3 gm for pomegranate peel also 0.5 gm for date pit because a further increase in the weight would not lead to enhancing the adsorption capacity (i.e., a steady state equilibrium will be obtained)[23] .As shown in Figure(3C).

4-Thermodynamic studies and temperature effects:

The adsorption studies were carried out between temperatures (298-328) ^{0}K. Figure (3D,3E) results show that, in each case, adsorption decreases as temperature rises. The results show that the adsorption of oleandrin on both surfaces decrease with raise in temperature it demonstrates the endothermic spontaneity of the adsorption process explains the endothermic nature of the process. The sorption mechanism's enhanced desorption step is the cause of the temperature-dependent drop in sorption capacity, indicating an endothermic reaction[24]

It is well known that the weakening of sorption forces in between the active sites on PPC, DPC, along with oleandrin species, as well as between neighboring oleandrin molecules on the sorbed phase, is the primary cause of the diminishing sorption capacity with increasing temperature.An rise in temperature typically speeds up the approach to equilibrium for a standard physisorption system, but lowers the equilibrium capacity[25].

Equation [26,27]. is used to compute thermodynamic characteristics of oleandrin adsorbed by the CDB, like change in Gibbs free energy (ΔG), charge in enthalpy (ΔH), and change in entropy (ΔS).

$$lnKd = ln\frac{qe}{Ce} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots\dots\dots (2)$$

$$\Delta G = \Delta H - T\Delta S \dots\dots\dots (3)$$

where Ce(mg/L) is the oleandrin equilibrium concentration at time t, R(8.314 J/mol.K) is the ideal gas constant, and Kd is the distribution coefficient of the adsorbate. Qe(t)(mg/g) is the oleandrin adsorption capacity of the PPC,DPC at time t.The thermodynamic parameters are displayed in Table (1), and the values of ΔG are obtained using Gibb's equation. The slopes and intercepts of the linear plots of log Kd vs 1/T are used to determine the values of ΔS and ΔH, as seen in Figure(3F). The presence of a weak interaction between PPC, DPC, and oleandrin is shown by the positive ΔH value, which verifies that the adsorption process is endothermic for oleandrin.The non-spontaneous character of the adsorption process was confirmed by the positive value of ΔG. The negative value of ΔS suggests that there were few degrees of freedom by the solid-liquid interface when oleandrin was adsorbed onto PPC and DPC. This observation the affinity of PPC and DPC for oleandrin in aqueous solutions and could not potentially imply structural alterations in the adsorbents [28].

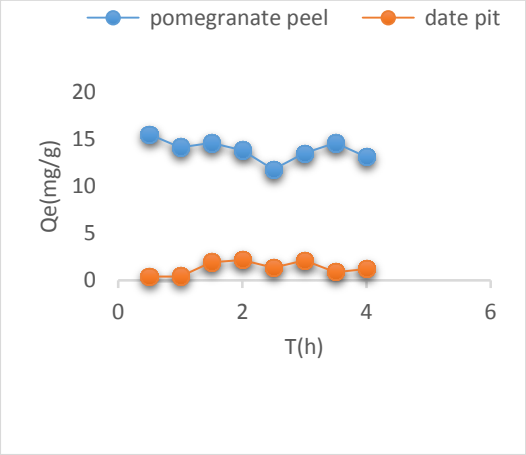

Fig.3A: Effect of contact time for adsorption oleandrin on different surfaces at 298K and pH=6

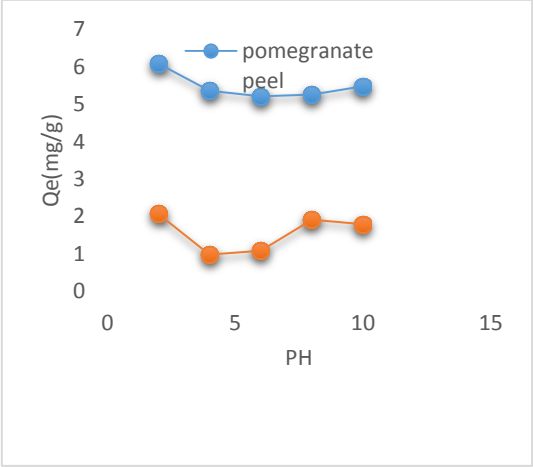

Fig.3B:Effect of PH for adsorption oleandrin on different surfaces at 298K and pH=6

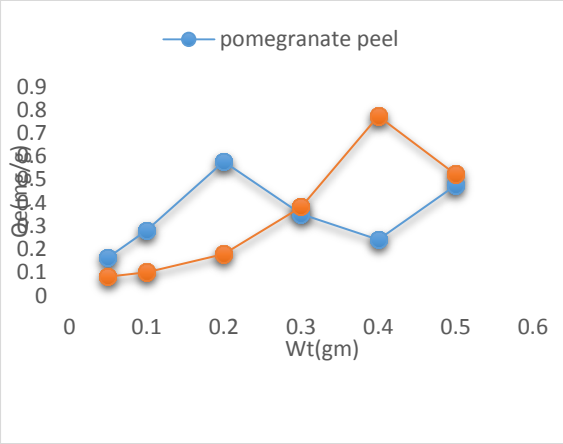

Fig.3C: Effect of weight for adsorption oleandrin on different surfaces at 298K and pH=6

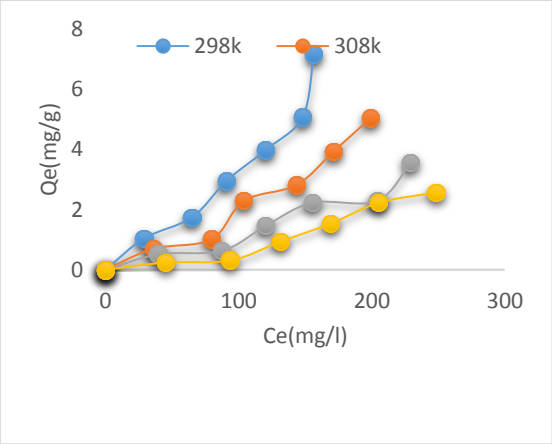

Fig.3D:Effect of Temperature for adsorption oleandrin on activated charcoal from pomegranate peel

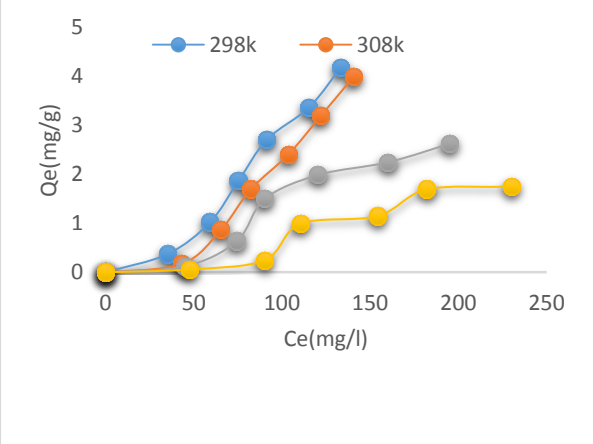

Fig.3E:Effect of Temperature for adsorption oleandrin on activated charcoal from date pit.

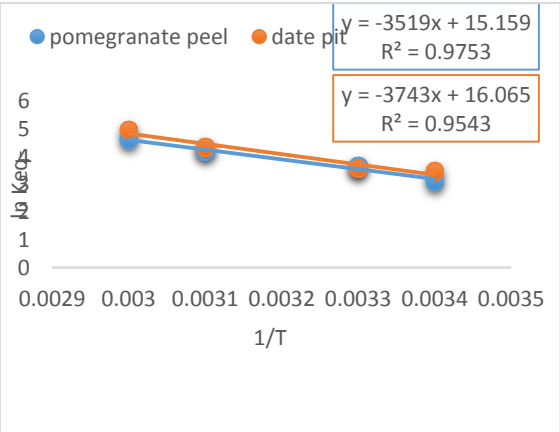

Fig. 3F: The relation ship between 1/T and Ln Keq of oleandrin on different surfaces.

Fig.3: Effects of the adsorption on different surfaces at 298K and pH=6:

A: Effect of contact time,B: Effect of PH,C: Effect of weight ,D: Effect of Temperature onPPC ,E: Effect of Temprature onDPC ,F: the relation ship between 1/T and Ln Keq.

Table.1 Thermodynamic parameters, of oleandrin in aqueous solution by PPC,DPC at 298K

Oleandrin	Thermodynamic parameters	PPC	DPC
	ΔH (KJ/mol^{-1})	29.256	31.19
	ΔG(KJ/mol^{-1})	0.126	0.133
	ΔS(J/mol^{-1})	-7.662	-7.85

5- Kinetics of Adsorption:

The kinetic data of the PPC and DPC were examined in this research employing:

1- Model of pseudo-first order kinetics :

The following was the definition of the pseudo-first-order[29]

$$\ln(qe-qt) = \ln qe - K_1t \text{…….(4)}$$

where K1 is the rate constant for the pseudo-first-order kinetics and qe and qt are the amounts of oleandrin adsorbed per unit weight of the adsorbent (mg/g) at equilibrium time and time t, respectively. Given that the values of log(qe-qt) were linearly connected with t, the values of K1 were selected based on the slope of the log(qe-qt) vs. t plot, which need to show a relationship that is linear. are displayed in Table (2).The pseudo-first-order equation of Lagergen is typically appropriate to the first stage of the adsorption process and does not fit well over the entire range of contact time in many circumstances.as depicted in Figure (4).The fact that the computed qe values don't closely resemble the observed qe values suggests that oleandrin adsorption

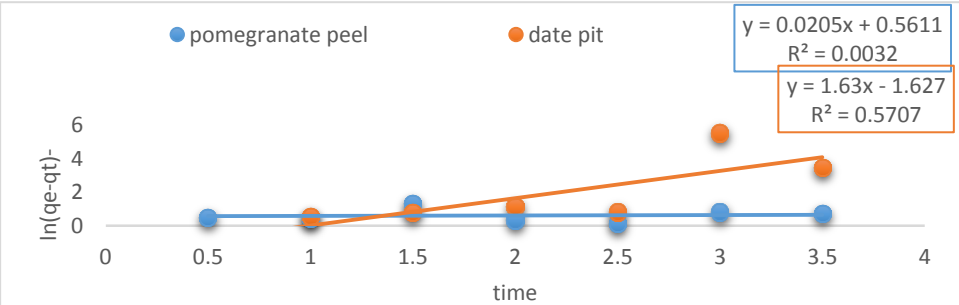

Fig. 4 : First -pseudo order for adsorption oleandrin on different surfaces at 298K and pH=6

2- Model pseudo-second-order :

The differential equation that follows represents the pseudo-second-order model.[30]

$$\frac{t}{qt} = \frac{1}{K2.qe} + \frac{1}{qe}t \ldots\ldots(5)$$

The pseudo-second-order rate constant K2 was determined by calculating the slope and intercept of the plot t/(qt) vs. t.according to Figure (5).Table 3 displays the values of the equilibrium rate constant, K2.All of the data under examination had very strong correlation coefficients, and the estimated qe values are quite close to the experimental qe values.This demonstrates that the model is applicable to the whole adsorption process and verifies that the pseudo-second-order kinetics model describes the oleandrin adsorption on PPC and DPC.

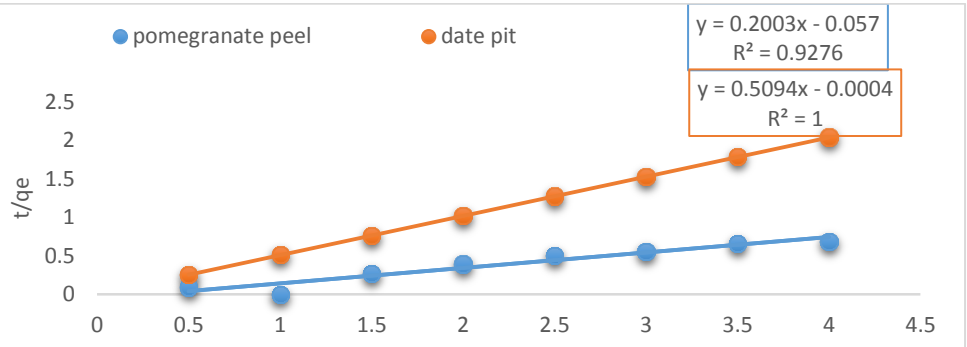

Fig.5: Second -pseudo order for adsorption oleandrin on different surfaces at 298K and pH=6

Table.2 The correlation coefficients, qe, and K1, K2 values at the starting concentration 298K

Surfaces	Pseudo 1st order			Pseudo 2nd order		
	qe mgg^{-1}	K_1 min^{-1}	R^2	qe mgg^{-1}	K_2 gmg^{-1} min^{-1}	R^2
PPC	1.752	-0.02	0.003	5	-0.701	0.927
DPC	5.088	-1.630	0.570	1.964	-1.1	1

6- Isotherms of adsorption

To describe how adsorbates and adsorbents interact and to make the most use of adsorbents, adsorption isotherms are crucial. [31]. The correlation of equilibrium data using a theoretical or empirical equation, thus, is necessary for the interpretation and prediction of adsorption data. To explain experimental data on adsorption isotherms, numerous mathematical models can be employed.In Figure

(6), as displayed.This work applies the five well-known isotherms equations: the Freundlich, Langmuir, Tempkin, Hartkins-Jura, Elovich, and Dubinin-Radushkevich isotherms.

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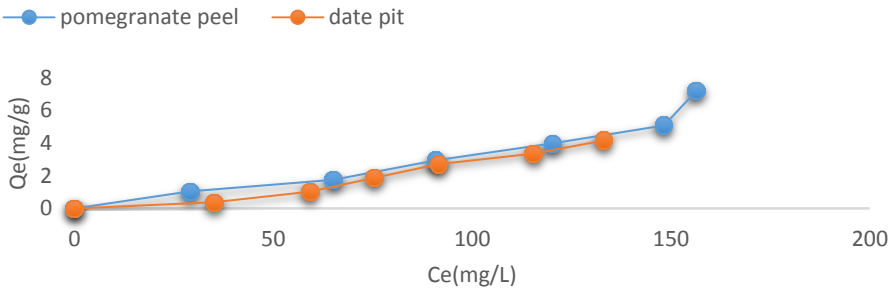

Fig.6: Adsorption isotherm for adsorption oleandrin on different surfaces at 298K and pH=6

The Langmuir isotherm is computed under the assumption that an oleandrin molecule occupies a site and that the adsorption process takes place at specific homogenous sites within the adsorbent surface. The fact that there is no longer any room for adsorption suggests that the adsorption process is monolayer in nature.The linear form of the Langmuir equation, which is valid for monolayer adsorption onto a fully homogeneous surface with a finite number of identical sites and minimal interaction between adsorbed molecules, is as follows [32].

$$\frac{Ce}{qe} = \frac{1}{K1_{qm}} + \frac{1}{qm}\text{Ce}\ldots\ldots\ldots(6)$$

where qm is the theoretical maximal adsorption capacity (mg/g) and Kl is the Langmuir adsorption constant (L/mg). The Langmuir Ce/qe vs. Ce plots for oleandrin adsorption at 298K are displayed in Figure (7).Table 3 displays the correlation coefficients and the values of the Qm and Kl constants for the Langmuir isotherm..

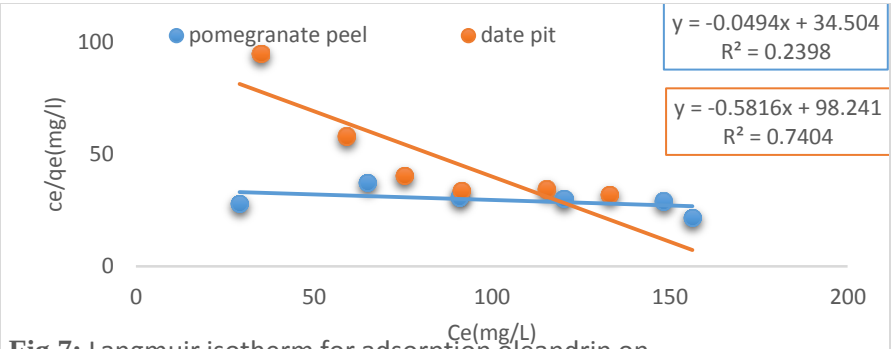

Fig.7: Langmuir isotherm for adsorption oleandrin on different surfaces at 298K and pH=6

The isotherm Freundlich:
is produced by assuming that the surface is heterogeneous and that the heat from adsorption is distributed unevenly over the surface. It was demonstrated in the following linear form[33] :

$$\log qe = logKf + \frac{1}{n}\, logCe \ldots\ldots (7)$$

where the isotherm constants Kf(L/mg) and n denote the adsorption's capacity and intensity, respectively.Heterogeneous factor is also indicated by the 1/n factor.The Freundlich log qe vs. log Ce graphs for the adsorption of oleandrin at 298 K are displayed in Figure (8). The Freundlich adsorption isotherm constant and its corresponding correlation coefficients are shown in Table 3.

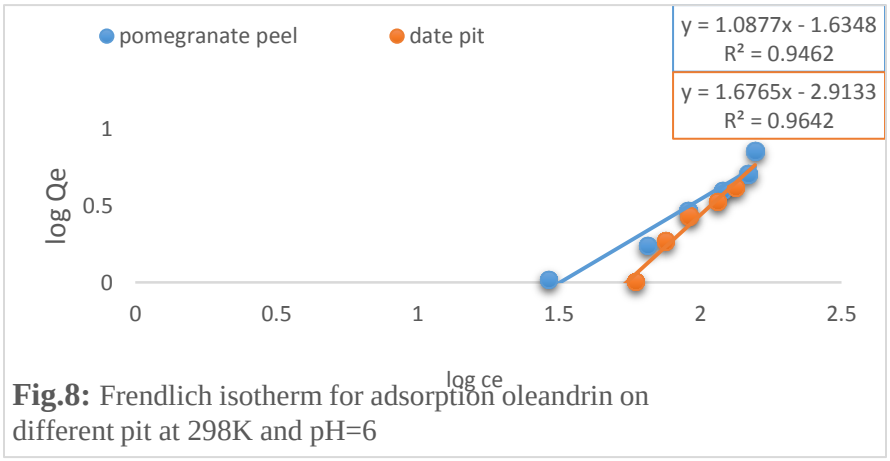

Fig.8: Frendlich isotherm for adsorption oleandrin on different pit at 298K and pH=6

Tempkin analyzed the heat of adsorption and the effect of the adsorbent-adsorbate interaction on adsorption isotherms; its equation is as follows: [34].

$$qe = Bt \ln Kt + Bt\ lnCe \ldots\ldots (8)$$

T is the absolute temperature in kelvin, Kt is the equilibrium binding constant (L/mg), and Bt is the heat of adsorption. In this equation, Bt=RT/bT.The tempkin

qe vs. ln Ce graphs for the adsorption of oleandrin at 298 K are shown in Figure (9).Table 3 displays the constants found for the Tempkin isotherm.

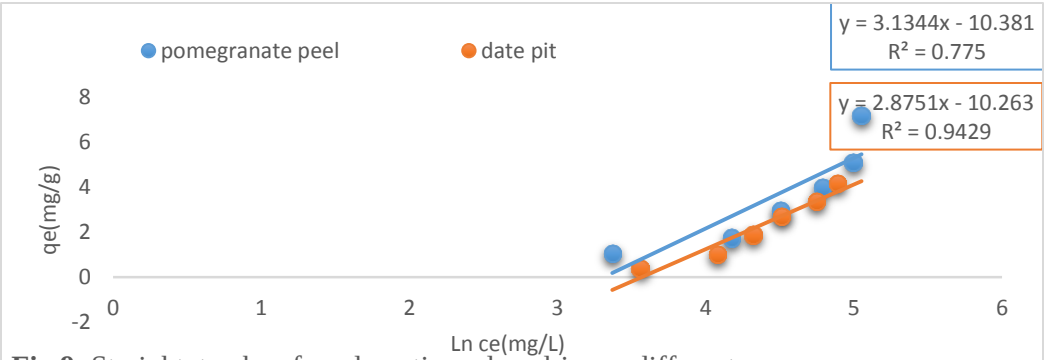

Fig.9: Straight temken for adsorption oleandrin on different surfaces at 298K and pH=6

The Dubinin-Radushkevich isotherm equation can be represented in its linear formas[35]:

$$\ln qe = \ln qm - K \epsilon^2 \ldots\ldots(9)$$

In this case, Qm is the theoretical monolayer saturation capacity (mg/g), K is the Dubinin-Radushkevich model constant (mol2.Kj-2), and Σ is the Polanyi potential, which is equivalent to:

$$\epsilon = RT \ln\left(1 + \frac{1}{Ce}\right) \ldots\ldots 10$$

Plotting ln qe against −2 at various temperatures for oleandrin.as illustrated in Figure (10).Table 3 presents the constant derived for the D-R isotherm.

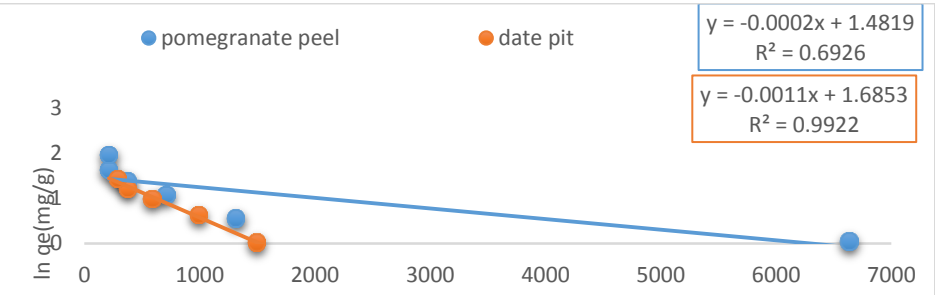

Fig. 10: Dubinin adsorption oleandrin on different surfaces at 298K and pH=6

The Harkins –Jura adsorption can be expressed [36]

$$\frac{1}{qe^2} = \frac{B_2}{A} - \frac{1}{A} \log Ce \ldots\ldots(11)$$

where A and B_2 are the isotherm constants.Plotting 1/qe^2 vs. log Ce indicates the presence of a heterogeneous pore distribution, which is indicative of multilayer adsorption in the Harkins-Jura adsorption.as depicted in Figure (11).Table 3 displays isotherm constants and correlation coefficients.

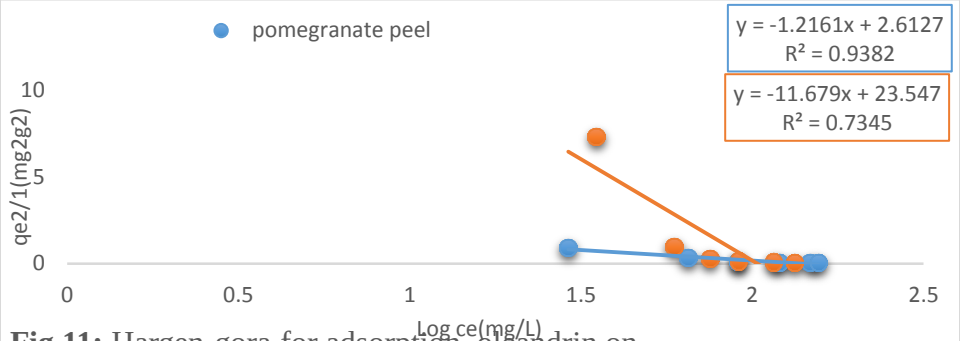

Fig.11: Hargen-gora for adsorption oleandrin on different surfaces at 298K and pH=6

The Elovich isotherm[37] **is:**

$$ln\ \frac{qe}{Ce} = \ln K.qm - qe/qm \ldots\ldots (13)$$

The Elovich constant and maximum adsorption capacity can be computed using the slope and intercept of the ln $qe/$ce against qe plot. On heterogeneous surfaces, the adsorption rate based on absorption capacity can be investigated using the Elovich kinetic model. The results of the isotherm adsorption modeling plot of oleandrin on (PPC)and (DPC) displayed in Figure(12) .The constant obtained for Elovich isotherm are shown in Table 3.

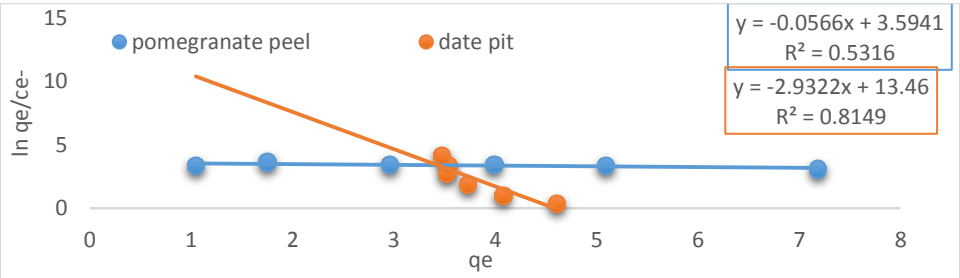

Fig.12: Elovich for adsorption oleandrin 0n different surfaces at 298K and pH=6

Table.3 The Langmuir ,Temkin Freundlich, D-R and Harkins -jura constants for the adsorption of oleandrin solutions on PPC and DPC at 298K

surface	Langmuir		Freundlich		Temkin		D-R		Elovich		Harkins-jura	
	K_L Lmg^{-1}	$-q_m$ mgg^{-1}	K_f $mg^{1-(1-n)}g^{-1}L^{1/n}$	n	Ln kt $Jmol^{-1}$	Bt Lmg^{-1}	lnQm mol^2J^{-2}	k mgg^{-1}	k	qm	B_2	A
PPC	-1.69	-20.40	0.023	0.919	-3.312	3.134	1.481	0.002	-0.817	-17.857	2.147	0.822
DPC	-0.09	-1.721	0.001	0.596	-3.356	2.875	1.685	0.001	1.385	-0.341	2.001	0.085

Conclusions:

In this research, the adsorption of the compound oleandrin extracted in water was studied on two surfaces: activated pomegranate peel charcoal and activated date pit charcoal. It was found that its adsorption on both surfaces decreases with increasing temperatures and follows the Freundlich isotherm, indicating that it is a physical adsorption process that is endothermic and spontaneous, exhibiting a second-order reaction.

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