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Adsorption Isotherms and Thermodynamic Data for Removal Pesticides from Aqueous Solution on Pomegranate Peel Surface

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Abstract: This work includes the study of the ability of pomegranate peel as adsorbent for two kinds of pesticides (Lambda cyhalothrin and Diazinon) from their aqueous solutions. The equilibrium contact time for the samples was determined. The effect of some factors on the adsorption process which was represented by the effect of acidity function was also studied. It was found that the best adsorption is at pH=2. The effects of the different temperatures within the range (313, 323, and 333K) were studied. The amount of adsorption for the pesticides is decreased with the increase of temperature; this indicates that the adsorption process is exothermic. Finally the study of the adsorption isotherms takes the (S-shape) according to Gile's classification for all the cases from (S2, S4) type which is following the freundlich equation for the adsorption.

Keywords: Adsorption, Pesticides, Freundlich Equation, Gile's Classification

1. Introduction

Industrial wastewaters largely possess organic and lnorganic materials such as pesticides, dyes, phenolic compounds, aromatic compounds and heavy metals [1].

Recently, a number of research works have been performed for the synthesis of conducting composites that contain a natural polymer [24]. Along this, nonocomposites of PANI with starch and chitosan have been studied on the basis of their biocompatility , antioxidant activity, and potential removal of reactive dyes and heavy metal ions.

Water is one of the vital necessities for the survival of human beings, the water demand doubles globally every 21 years due to the rapid increase in rainfall in the previous decade [2]. Most of the currently available technologies are inadequate for the removal of pesticides and color-induced toxic pollutants such as dyes from textile waste water [3]. Most of the conventional methods of wastewater treatment are such as coagulation and flocculation. Sedimentation and floatation, membrane filtration, disinfection is either expensive or not very effective.

Adsorption is a convenient separation process, in which the adsorbent may be of organic, mineral or natural source. (Wan Ngah, Teong & Hanafiah, 2010). Various materials such as zeolites, activated carbon, clays, agricultural wastes, biomass and synthetic polymers were used as an adsorbent (Karami, 2013; Tirtom, Dincer, Becerik, Aydemir& Celik, 2012).

These technologies mostly transform pollutants from one phase to another and do not completely eliminate them [4].

Adsorption has been recognized as a potential technology for the removal of pesticides, dyes and other pollutants from waste water. In comparison to other physical, chemical and biological methods available for the treatment of wastewater, adsorption is the most preferred technique due to simple and flexible design and easy operation. The adsorption process may generate little or no toxic pollutants and involve low initial capital and operating costs [5-7]. Adsorption can be classified as either physical or chemical physical adsorption (physisorption) involves weak for gas and is therefore reversible, it occur at low tem partners. It is very similar to a condensation process and thus it is exothermic with a heat of adsorption similar to that latent heat of condensation [8]. Chemical adsorption (chemisorption) it is important in gas phase catalysis, and it is occur at high temperatures with significant activation energy involves strong bonds and is not reversible different isotherms of adsorption from solution on solid active surface which were classified by Giles [9-11].

The aim of this work was to prepare some novel pomegranate peel adsorbents and to study the adsorption capacity of these adsorbents for two pesticides removal from aqueous solutions. Adsorption isotherms and kinetics were investigated and different adsorption models were used to evaluate the experimental data and to elucidate the possible adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard free energy (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°). These funddamenta data will be useful for further applications in the treatment of practical waste or process effluents.

2. Experimental Part

2.1. Apparatus

1- U.V. – visible T604 spectrophotometer PQ instruments LTd.

2- Laborator oven memmort/w. Germany.

3- Electronic Balance Sartorius, w. Germany.

4- HANNA, pH-meter, Instrument, Portngal.

5- Shaking Indicator. GCA. / Precision scientific Chicago. U.S.A.

6- Distilled- water Apparatus within the type Gel (Gasell schaft fur Labortechnik) Mbh, w. Germany.

2.2. Chemicals

All chemicals used in the present work were used without further purification.

Table (1). *purification values for chemicals were used in this work.*

No.	Chemicals	Company	Purity%
1	Lambda cyhalothrin	B.D.H	90%
2	Dizinon	B.D.H	90%
3	Pomegranate peel	From nature	
4	Sodium hydroxide	B.D.H	98%
5	Hydrochloric Acid	B.D.H	(36.5%)

2.3. Preparation of Solutions

All pesticides solutions are used in this work were prepared by dissolving 0.01gm in 200ml volumetric flask with distilled water to prepare the concentration (500 ppm) as stock solution and prepare a series of different concentrations in the range (2-20 ppm) from the stock solution by dilution law.

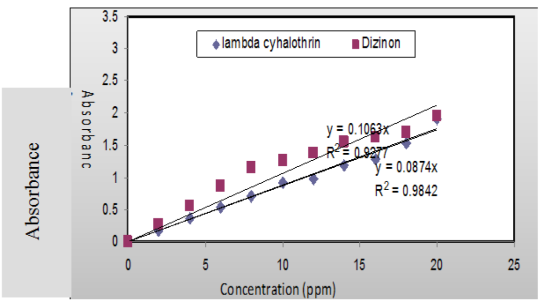

Figure (1). *Calibration curve for adsorption the compounds on pomegranate peel at 313K.*

Determination of λ max and calibration curves for the pesticides (lambda cyhalothrin and Diazinon).

The maximum wavelength of each pesticide was specified by using spectrophotometer in the range of (200-800nm) and recording the spectra of absorption as shown in figure 1 and table 2.

Table (2). *values of λ max for the pesticides were used in this work.*

Pesticides	λ Max /nm	
	Literature	Observed
Lambda cyhalothrin	217	222
Diazinon	218	220

2.4. Adsorption Studies

The adsorption experiments were studied in aqueous solution, using a constant weight adsorbent surface (0.2gm) immersed in (15) ml aqueous solutions (20mgL-1) of pesticides. The mixtures were agitated at 5000rprm at room temperature for different contact times then the adsorbent surface was separated by filtration and the filtrate was analzed uv-visible spectrop-hotometer at wavelength corrws -ponding to the λ max of each pesticide. The PH values of the initial solutions were fixed using IM NaOH or (1m) HCL solutions and PH meter (HANNA, PH, meter , Instrument, Portnyal was employed for PH measurements. The equilibrium time for adsorption of lambdacyha lothrin pesticide was much longer (120 min) than that for Diazinon (30 min) the results wew demonstrated that the tendency adsorbent surface for removed of lambdacyhalothrin much more than that for diazinon pesticide in fact due to diffuse in composite matrix easier than diazinon that is accessible coordinating sites become excluded after equilibrium state [12].

2.4.1. Preparation of Pomegrante Peel (pp)

Raw pomegrant peel was selected and washed with water several times to remove ash and other contaminants. Then it was washed with double distilled water and was dried at 70ºc indside convection over for 24h. The dried Pomegrante peel was crushed and sieved to be a smaller particle by a 50 meshsieve. The obtained product was named pp for further adsorption study.

2.4.2. Adsorption Isotherms

Batch adsorption experiments were conducted using 50 ml stoppered conicalflasks at room temperature (25ºc) twenty mg of adsorbent was added to each flask which consisted of 10ml pesticides solution of various initial concentrations from [two pestieides]. All flasks were shaken at 5000rpm in a thermostated shaker for (120min). After decantation and filtration, the pesticides concentration in the filtration solution was analyzed by using UV-visible spectrophotometer the amount of pesticides adsorbed was calculated from the following equation.

$$Qe = \frac{V_{sol}(C_0 - C_e)}{m} = \frac{x}{m} \quad (1)$$

Where Qe=x/m the quantity of adrobed material (mg) /g adsorbent

V= volume of pesticide solution (L) that was used

C0= Initial concentration (mg/L)

Ce= Equilibrium concentration (mg/L)

m= weight of adsorbent (g)

The amount of adsorption is expressed by the ratio x/m which is defined as the quantity of adsorbate in (mg) held by weight of adsorbent (g).

$$Removal\% = [(C0 - Ce)/C0] \times 100 \quad (2)$$

[13].

2.5. Factors influencing Adsorption Process

(A) * Effect of Adsorbent weight

The effect of adsorbent weight on the adsorption was studied by using 15 ml of 20 ppm from each pesticide with different weigh of adsorption (0.05, 0.1, 0.2. 0.3. 0.4. 0.5 gm) at 313K for suitable time. The maximum adsorption weight for lambda cyhalothrim was (0.2gm) while 0.05 gm for Diazinon. With a molecule size of 212 nm by suitable sieving.

(B) Effect of pH

Adsorption experiments were carried out as a function of pH by using 15 ml of 20 ppm solution from each pesticide in different pH- media. NaOH (0.1N) and (0.1 N) HCL were used to adjust the pH in the range (2-12) and at 313K. the concentration of the adsorbent was measured by UV-visible spectrophotometer.

(c) Effect of Temperature

Adsorption process were performed in the same manner as mentioned in the above paragraph at temperature (313, 323, 333K) to estimate the thermodynamic behavior of adsorption process, this depends if the adsorption decreases with increasing temperature then the process is exothermic and vice versa.

3. Results and Discussion

* Adsorption ability on surface of pomegranate peel Figure (2) represents the adsorption Isotherms for the two Pesticides

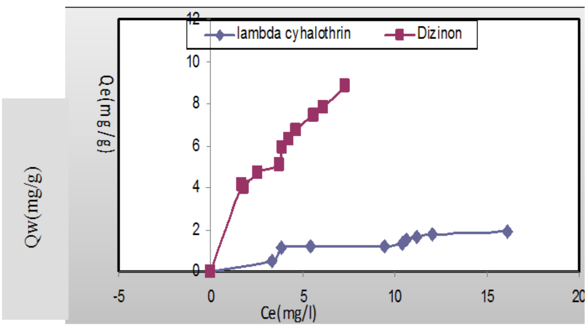

Figure (2). *Shows the Isotherms adsorption on pomegrante surface for the two pesticides.*

The equilibrium adsorption data were analyzed using Langmuir and freundlich adsorption isotherm models [14,15],as in figures3 and4 respectively.

The pesticides are organic compounds in nature with functional groups either drawing or pumping electrons which are very effected on the adsorption processes, so the pesticiedes with electrons pumping groups will be increase the adsorption process while groups with drawing electrons will be decrease the adsorption isaotherm [16].

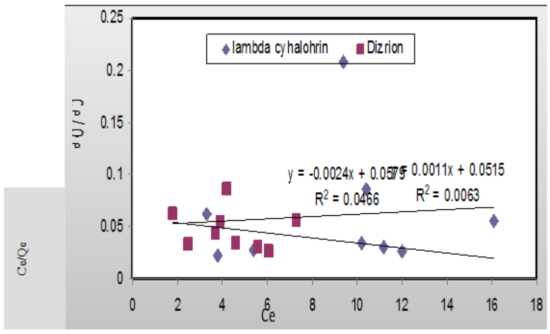

Figure (3). *The Langmuir isotherms for the two pesticides on the pomegrante peel surface.*

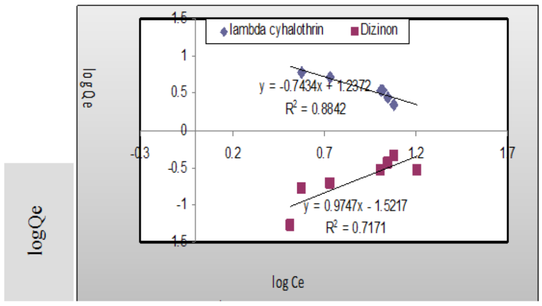

Figure (4). *Freundlinch isotherms for adsorption on the pomegrante peel surface.*

According to Gile's classification the data obtained in this research are followed the type (S2, S4). Also the maximum adsorption time was 30 minute for diazinon and120 minute for lambda cyhatothrin as shown in figure (5) at 313K and the maximum weight for the adsorption was 0.2g diazinon and 0.05g cyhatothrin as in figure (6) and were studied the freundhich and Langmuir constants for adsorption process as well as in table 2 [20-21].

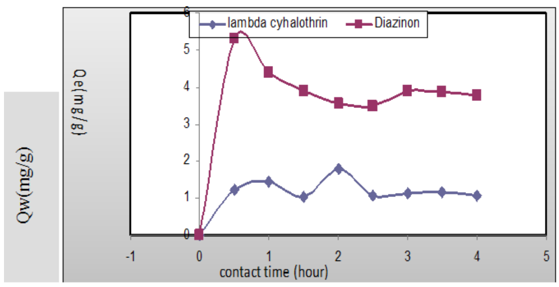

Figure (5). *The effect of contact time on the surface for adsorption isotherms of the two pesticides.*

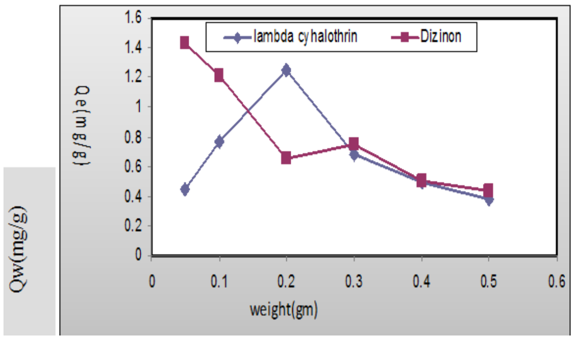

Figure (6). *The effect of weight of adsorbent on the isotherm of the two pesticides Gap not given.*

Table (3). *Frendlinch and Langmuir constants for adsorption the two pesticides at 313k.*

Pesticides	Kf	n	R2	a	k	R2
Iambda cyhalothrin	17.26	-1.344	0.884	0.001	19.61	0.006
Diazinon	0.030	1.027	0.717	0.002	17.54	0.001

Two isotherms equations have been tested in the present study to analyze the equilibrium data of (PP) and (PP) namely, Langmuir, Freundich. The results are shown in table 2 and the modeled isotherms are plotted Fig (3-4).

Based on the assumption that all adsorption sites are equivalent and adsorption in active sites is indepent of whether the adjacent is occupied, the Langmuir adsorption model can be expressed as :

$$\frac{C_e}{q_e} = \frac{1}{q_1 K_1} + \frac{1}{q_L} Ce \qquad (3)$$

Where q_e is the mono-layer adsorption capacity adsorbent (mg/g), K_1 is the Langmuir adsorption constant (L/mg) and q_L is the mono-layer adsorption capacity of adsorbent (mg/g). Therefore, a plot of Ce/q_e versus Ce gives a straight line of slope 1/q_L and intercepts1/ (q_L K_L).

From table 2 the correlation coefficients of broth (PP) and KOP are very high, indicating a good fit of the mono – layer langmuir to the adsorption of (PP).the mono- layer adsorption capacity .

The Freundlich model can be expressed as [25] :

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \qquad (4)$$

Wher KF and n are the Freundlich adsorption constants, which can be determined by the linear plot of log qe versus log Ce.

As it can be seen in table 2. the value of the correlation coefficients, R2 is 0.006 for Lambda cyhalothrin and 0.001 for Diazinon . Thus it comes to the conclusion that the Freudlichmodel does not fit the data of two pesticides as well as the langmuir model does.

Comparison of pesticides adsorption on surface were found in the order diazinon > lambda-cyhalothrin because diazinon due to the electron pumping groups in diazinon which increase the adsorption process thus the stability of diazinon on the surface is higher than other decrease pesticides .

3.1. Effect of Temperature

The effect of temperature is shown in figures 7 and 8.The experimental data indicates that the pesticides adsorption decrease with increasing temperature and that agree with thermodynamics properties. The heat of adsorption (ΔH°) may be obtained from van't Hoff's equation [17, 18].

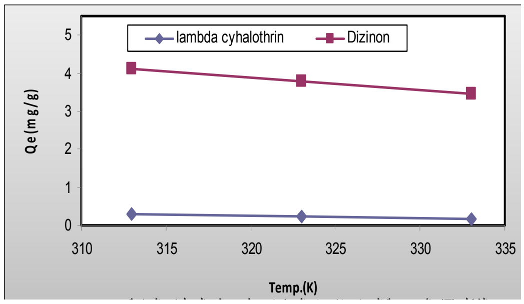

Figure (7). *Effect of temperature on the adsorption processes.*

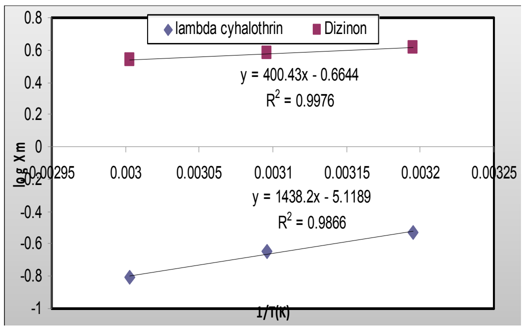

Figure (8). *The relationship between the adsorbate quantity and temperature.*

Thermddynamic studies

The standard free energy (ΔG°), enthalpy change (ΔH^{o}) and entropy change (ΔS^{o}) thermodynamic parameters were estimatedto evaluate the feasibility of the adsorption process [28,32-35]. The Gibb's free energy change of the process is related to the Kc by the folloeing equation:

$$\Delta G^{\circ} = -RT \ In \ K_c \qquad (5)$$

Where T is temperature in K, the ideal gas constant (8.314J/ mol K) and Kc is the thermodynamic equilibrium constant, which is defined as:

$$K_c = \frac{C\delta}{Ce} \qquad (6)$$

Where $C\delta$ is mg of adsorbate adsorbed per liter and Ce is the equilibrium concentration of solution , mg/L. According to thermodynamics, the Gibb;s free energy is also related to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the van't Hoff equation:

In

$$k_c = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \qquad (7)$$

In order to determine the thermodynamic parameters. Experiments were carried out at different temperature in the range of (40,50,60)ºC (fig.7) .the values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of the plot In Kc versus 1/T. the calculated values of thermodynamic parameters are listed in (table 3).

Table (4). *Thermodynamic parameters for the adsorption two pesticides on (pp) surface.*

Pesticides	-ΔH° (kJ/ mol)	-ΔG° (kJ/ mol)	-ΔS° (J/mol K)
Diazinon	7.666	3.137	34.51
Lambda cyhulothrin	27.533	5.544	70.09

For both pesticiedes the valuses of (ΔH°) are negative, indicating the exothermic nature of the process, which further explain the fact that the adsorption efficiency decreased with the increase of temperature. Negative values of (ΔS°) indicate a decrease in randomness at the solid/ solution interface during the adsorption process while low value of (ΔS°) indicates that no remarkable change on entropy occurs. All engative values of (ΔG°) in the range of 40,50, 60ºC indicat the spontaneous nature of the adsorption processes. It was also noted that the change of free energy decreases with increase of temperature. This could be possinle because fewer active sites are available on the surface of adsorbents.

The mangnitude of ΔH may give an idea about the type of sorption. Two main types of adsorption are physical and chemical. Basically, the heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1-209kJ/mol, while the heats of chemisorption generally falls into a range of 80-200KJ/mol [22].

3.2. Effect of Ph

The pH is an important factor which controls the adsorption process [19]. The adsorption of both pesticides on the pomegranate peel in different media (pH= 2-14) was studied by using a fixed concentration of the two pesticides at 313k as shown. in figure e (9). The results indicate at low pH the pesticides become protonated.

It can be explaind by the following facts. At lower pH values, H+ in the solution will compete strongly with pesticises for the active sites.therefore , it reduces pesticises binding on the adsorbent surface. When pH increases, the electrostatic requlsion between pesticises and surface sites and the competing effect of H+ decrease and consequently the pesticises adsorption increases [25]. However at higher pH values pesticises will be precipitated so the experimental pH values should be controlled at 2-3.

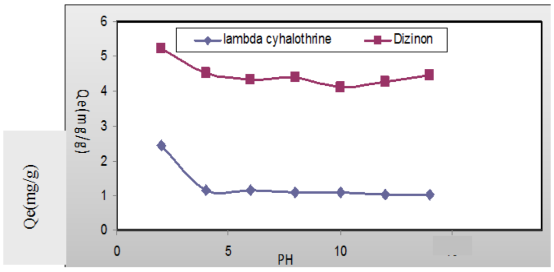

Figure (9). *Effect the pH on the adsorption of two pesticides.*

According to Gile's classification the data obtained in this research are followed the type (S2, S4). Also the maximum adsorption time was 30 minute for diazinon and120 minute for lambda cyhatothrin as shown in figure (5) at 313K and the maximum weight for the adsorption was 0.2g diazinon and 0.05g cyhatothrin as in figure (6) and were studied the freundhich and langmuire constants for adsorption process as well as in table 2 [20-21].

4. Conclusions

The main object of the present work is to explore the possibility of using pomegranate peel as adsorbents for the cationic pesticides water pollutants.

The experimented data at different temperatures for the pesticides pollutants were fitted to the Langmuir and freundlich isotherms models, and the shape of isotherms was (S-type) on Gile's classification from the thermodynamic values of ΔG, ΔH and ΔS are negative indicating that the process is spontaneous and exothermic the effect of various operating parameters, such as contact time, pH, adsorbent dosage and temperature was estimated.

The thermodynamic functions are very useful if the present results are to be utilized on large scale in dustrail processes.

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