Removal of Chlorpyrifos (Dursban) Pesticide from Aqueous Solutions using Barley Husks

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Abstract

The removal of chlorpyrifos pesticide from aqueous solutions was achieved by adsorption using low cost agricultural residue as adsorbent surface; barley husks. Several variables that affect the adsorption were studied including contact time, adsorbent weight, pH, ionic strength, particle size and temperature. The absorbance of the solution before and after adsorption was measured by using UV-Visible spectrophotometer. The equilibrium data was suitable with Langmuir model of adsorption and the linear regression coefficient R^2 = 0.9785 at 37.5°C was used to knowledge the best fitting isotherm model. The general shape of the adsorption isotherm of chlorpyrifos on barley husks consistent with (H_3-type) on the Giles classification. Several thermodynamic functions such as (Gibb's free energy, enthalpy and entropy) of the on-going adsorption process have also been estimated. ($\Delta H°=0.0080 kJ/mol$) ,($\Delta S° = +16.7778 J/mol.$) and ($\Delta G° = -5.2015 kJ/mol$). The results of the pesticide adsorption process on barley husks indicated that the adsorption process is endothermic. The positive values of $\Delta S°$ propose the increasing randomized. The negative $\Delta G°$ values indicated the spontaneous process of adsorption.

Keywords: adsorption, chlorpyrifos, Langmuir model, Freundlich model, thermodynamic, barley husks adsorbent.

Introduction

Pollution caused by any (biological, physical and chemical side-effects) of people industrial or social activities. It can impact the (rivers, seas, atmosphere or soil). Water pollutants such as chlorinated hydrocarbon pesticides are toxic, non-biodegradable and harmful to people health [1, 2]. Pesticides are introduced into the environment by disposal, application, and a spill [3]. Pesticides freed into environment are present in aquatic systems. They are discovering at low plateau and usually happen in the form of complex mixtures [4]. Filter of pesticides, applied to agricultural ground, is one of the major sources for organic pollution in some water streams [5].

The pesticides can reach water- bearing aquifers below ground from applications onto crop fields of contaminated surface water. Pesticide contamination of ground water is a subject of international importance because ground water is used for drinking aim. Before the mid-1970s, it was thought that ground acted as a defensive filter that stopped the pesticides from reaching ground water [6]. The constant exposure of pesticides to non-target species may lead to induce toxicity once it crosses the threshold limit in the system [7, 8]. The different stages involved in pesticide cycle are illustrated in Figure (1).

Waste water containing pesticides and toxic compounds need very careful treatment before discharge into receiving bodies of water. Several (physical, chemical, physico -chemical and biological methods) have been developed to remove contaminants from wastewater. These methods involved; coupled-column liquid chromatography/electro spray ionization [9], gas chromatography [10], solid-liquid extraction [11], HPLC [12- 14], electrochemical methods [15-17], stripping voltammetry [18], biodegradation and adsorption treatment [19, 20]. Adsorption process has been found one of the most popular physico- chemical treatment methods for take out contaminants [21, 22]. The aim of the present study is to find a low-cost eco-friendly agricultural residue adsorbent surface for the elimination of chlorpyrifos contaminant from waste water.

Experimental

Apparatus

1. A double beam UV-Visible spectrophotometer, Shimadzu 1800 (Japan) with 1 cm matched quartz cells was used for the absorbance measurement.
2. Electronic balance, Radwage AS220/C/1 was used for weighing the samples.
3. Thermostated water bath shaker, LabTech LSB-045S (Korea).
4. Centrifuge, Hettich EBA20 (Germany), 6000 rpm.
5. pH- meter with combined glass electrode.

Materials and Methods

The adsorbate (Chlorpyrifos)

Chlorpyrifos (0,0-diethyl-0-3,5,6-trichoro-2-pyridylphosphorothioate) is a substance used for killing insects, generally famous as Dursban and Lorsban [23]. Chlorpyrifos is highly toxic to all kinds of life such as birds, fresh water fishes, marine organisms and honeybees [24]. The chemical and physical properties of chlorpyrifos are listed in Table (1).

The Adsorbent (Barley husks)

Barley husks used as adsorbent throughout this study were obtained from Isaaqi region in Salahuddin province-Iraq. The husks were washed several times with amounts of distilled water to take out (soluble materials or dust), and were dryish in an oven at 40 °C. They were then grinded and sieved by using (75, 150 and 250) μm sieves. Particles of the size (75 μm) was used as adsorbent surface in all experiments of this work. The qualitative analysis for active chemical compounds of barley husks is listed in Table (2).

Chlorpyrifos Stock Solution (100 mg/L)

The stock solution was prepared by dissolving 0.1000g of chlorpyrifos pesticide in 1L of distilled water. The stock solution was protected from light and stored at 25°C.

The Batch Mode of Adsorption Studies

The experiments were done to define the impact of contact time, weight of adsorbent , pH, ionic strength and partical size of adsorbent. Absorbance values of solutions of concentrations range (10- 80) mg/L were measured at selected **λmax** (265 nm) and plotted against the concentration of pesticide, Figure (2) shows the calibration curve of chlorpyrifos.

Percentage removal of pesticide (R%) and (Q_e) was calculated using Eq.1 and 2 respectively [28, 29].

$$R\% = \frac{C_o - C_e}{C_o} * 100 \qquad \text{.............................(1)}$$

$$Q_e = \frac{V(C_o - C_e)}{m} \qquad \text{.............................(2)}$$

Where:

m: The weight of barley husks (g).
C_o : The initial concentration of chlorpyrifos (mg/L).
C_e: The equilibrium concentration of chlorpyrifos (mg/L).
V: The volume of chlorpyrifos solution (L).

Factors Affecting Adsorption Process

Contact Time

In a set of conical flasks 10 ml of a fixed concentration (80 mg/L) and pH (7.3) of chlorpyrifos solution was shaken with 0.2 g of barley husks at 37.5 °C. The solution was withdrawn from the shaker for regular time intervals of (5, 10, 20, 30, 45, 60, 90, 120 and 150 min) , and centrifuged at 3000 rpm for 20 minutes, the concentration of adsorbate solutions were measured spectrophotometrically.

Adsorbent Weight

In a set of conical flasks various weights of barley husks [0.1, 0.2, 0.3, 0.4, 0.5 , 0.6] g were mixed with 10 ml of a fixed concentration of chlorpyrifos solution 80 mg/L and pH= 7.3, the mixture was shaken at a specified temperature 37.5 °C, then centrifuged at 3000 rmp for 20 minutes to separate the adsorbent.

pH Effect

Adsorption experiment were carried out at different pH values (1.5, 3.1, 5.4, 7.3, 9.4 and 11.3). The pH of the solutions were adjusted by adding the required amounts of 0.1 M HCl and NaOH. All other parameters were kept constant while carrying out the experiment.

Effect of Ionic Strength

The effect of the addition (0.1, 0.2, 0.3, 0.4 and 0.5) M of NaCl to solutions containing fixed concentration of adsorbate 80 mg/L and pH= 7.3 equilibrated with (0.2g) of barley husks were exact under the experimental conditions substantive before.

Particle Size Effect

The effect of particle size (surface area) on adsorption was studied by using four different sizes of sieves (75 ,150, 250 and 300 µm). These experiments were performed by using a fixed concentration of adsorbate 80 mg/L and pH= 7.3 with different particle sizes of the same weight of adsorbent 0.2 g under the same experimental conditions described above.

Temperature Effect

The adsorption procedure was purified in the same way at various temperatures (10.0, 25.0 and 37.5 °C) to appreciate the basic thermodynamic parameters.

Result and Discussion

FTIR of the Adsorbent Surface

Fourier Transform Infrared Spectroscopy (FTIR) was performed to give the chemical active groups present in the barley husks. The spectrum of the adsorbent was obtained using (KBr) technique. FTIR of assignment groups of barley husks is shown in Figure (3).

The spectrum shows broad absorption peaks at (3500- 3100) cm^{-1}, corresponding to the overlapping of –OH and –NH peaks. The peaks in the range (1550- 800 cm^{-1}) can be attributed to the stretching of the C-N and C-O, and to the bending of the N-H, C-H and O-H groups [30-32].

Equilibrium Time

The effect of contact time on the chlorpyrifos adsorbed per unit of barley husks was studied at 37.5 °C. Table (3) , Figure (4) show the values of Qe and Ce of 80 mg/L chlorpyrifos solution at 37.5 °C.

An acute change in adsorption is notice at beginning and thereafter a slow increase was notice in adsorption with increasing time up to 90 minutes, after which a maximum value of adsorption is attained. The time of 90 minutes is treat as the optimum contact time.

Adsorbent Weight

The effect of adsorbent dosaget on the R% of chlorpyrifos adsorbed was calculated with 10ml of 80 mg/L initial concentration of chlorpyrifos the results are shown inTable (4) and Figure (5). It is obvious that R% of chlorpyrifos increased with increasing the adsorbent weight. This may be due to the increase in availability of surface active sites resulting from increased dose.

Effect of PH

The effect of pH on the amount of chlorpyrifos adsorbed was studied by varying the initial pH under constant process parameters at equilibrium conditions. Table (5) and Figure (6).

The extent of adsorption may(increase, decrease, or remain unchanged) as a result of changing the pH [33].

The results in Table (5) indicate that the adsorption capacity in acidic medium increase with increasing pH up to 7.3, the maximum adsorption from the original solution takes place at pH value of 7.3. Beyond this value the increase in pH was accompanied by a decrease in adsorption capacity.

Ionic Strength

The effect of ionic strength on adsorption uptake of chlorpyrifos on barley husks has been studied by adding variable concentrations of sodium chloride (0.1, 0.2, 0.3, 0.4 and 0.5) M.

In a previous study for our group at this department [34], the following empirical equation was suggested for the relationship between the ionic strength (I) and the amount of adsorption (Qe).

$$Qe = Qe° - AI \quad \text{-------------------(3)}$$

Where:

Qe°: the amount of adsorption at (I=zero]

A: Empirical constant for the system.

I: Ionic strength.

It was found that the effect of the ionic strength (I) on the adsorption quantity (Qe) at equilibrium is a linear relationship as indicated in Table (6) and Figure (7).

Generally, the rise in the salt concentration resulted in a lowering of chlorpyrifos removal by barley husks. This result show that the adsorption activity decreases when NaCl concentration increases in the chlorpyrifos solution, which could be assign to the competitive effect between pesticide ions and the salt ions for the locations ready for the adsorption process [35].

Particle Size

The effect of particle size on adsorption process was studied by using a fixed concentration (80 mg/L) of chlorpyrifos solution as an adsorbate and four samples of a same weight of barley husks (0.2 g) of different particle sizes (75, 150, 250 and 300 μm). Table (7) and Figure (8) illustrate the influence of particle size of the adsorbent on the amount of chlorpyrifos adsorbed by barley husks at (37.5 °C).

The results indicate that the maximum quantity of chlorpyrifos which was adsorbed on the barley husks followed the order: 75 μm > 150 μm > 250 μm > 300 μm.

Hence the increase of the surface area (decrease in the particle size) leads to an increase in the adsorption uptake of chlorpyrifos on the barley husks, such an increase can be attributed to the increase in the active sites exposed to the adsorbate [37, 38].

Adsorption Isotherms

Adsorption isotherm can be realized as the relation between Qe and Ce at fixed temperature. The study of the adsorption isotherm give great and advantageous information to depict the nature of adsorption process and its condition and knowing about the amount of pesticides adsorbed with its concentration in the adsorption process.

Adsorption of chlorpyrifos from aqueous solution on barley husks was studied at three temperatures (10.0, 25.0, and 37.5 °C) keeping the other parameters of adsorption unchanged.

The resulst of this study represented by the initial concentration of adsorbate (Co), the equilibrium concentration (Ce) and the quantity adsorbed (Qe) are indicated in Table (8) .The values of (Qe) were plotted versus (Ce) to take out the adsorption isotherms as shown in Figure (9).

The results showed an increase in adsorptive capacities of barley husks as the concentration of pesticide increases until reaching a limited value. The general shape of the adsorption isotherm of chlorpyrifos on barley husks consistent with (H_3-type) on the Giles classification which indicates high affinity between the adsorbate and adsorbent even in very dilute solution [38].

The experimental adsorption data were applied to the empirical Langmuir isotherm (Eq. 4) [39]. and Freundlich isotherm (Eq. 5) [40] equations

$$\frac{C_e}{Qe} = \frac{1}{a.b} + (\frac{1}{a}).C_e \quad \text{----------------(4)}$$

$$\log Q_e = \log K_f + \frac{1}{n}\log C_e \quad \text{----------------(5)}$$

These results indicated the applicability of Langmuir and Freundlich isotherms according to the values of linearity (R^2) as shown by the linear relationship of (Ce/Qe) versus (Ce) and (log Qe) versus (log Ce) at different temperatures in Tables (9), (10) and Figures (10), (11).

The Langmuir and Freundlich constant empirical values were obtained from the linear equation at different temperatures. The values are summarized in Tables (11), (12).

Thermodynamic of Adsorption Process

The Thermodynamic functions related to the adsorption of pesticide, like, Gibbs free energy change ΔG° , enthalpy change ΔH° and entropy change ΔS° .

The change in free energy (ΔG) could be determined from the following equations [41].

$$\Delta G = -RT \ln K_{ads} \quad \text{----------------} (6)$$

$$\ln K_{ads} = (-\Delta H / RT) + (\Delta S / R) \quad \text{----------------} (7)$$

$$\Delta G = \Delta H - T\Delta S \quad \text{----------------} (8)$$

Where R is the gas constant (8.314 J/mol.deg), K_{ads} is adsorption equilibrium constant which was calculated at each temperature (T) from the following equation [42].

$$K_{ads} = \frac{Q_e.0.2(g)}{C_e.0.01(L)} \quad \text{--------------} (9)$$

Where Qe is the amount adsorbed (mg/g), Ce is the equilibrium concentration of the adsorbate expressed in mg/L. The values of ΔH and ΔS were determined from the slope and intercept of the linear plot of (ln K_{ads}) vs. (1000/T). The results obtained are given in Table (13) and Figure (12). ΔG, ΔH and ΔS values were listed in Table (14).

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Table (1): Physical and chemical characteristics of chlorpyrifos [25, 26]

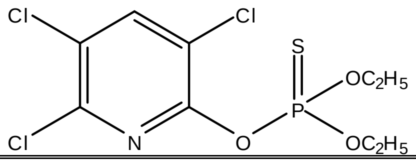
IUPAC name	0,0-diethyl-0-3,5,6-trichoro-2-pyridyl phosphorothioate
Trade name	Dursban or Lorsban
Chemical structure	
Chemical formula	$C_9H_{11}Cl_3NO_3PS$
Molecular weight	350.59 g/mol
Solubility	In water 2 mg/ L (25°)
Poling point	100 °C
Colour	White

Table (2) The active chemical compounds of barley husks [27]

Active organic compound	Barley husks
Saponins	+
Alkaloids	+
Resins	+
Coumarins	-
Flavones	+
Tannins	+
Terpenes	-

Table (3): The variation of Qe and Ce values with time in the adsorption process

Time (min)	Ce (mg/L)	Qe (mg/g)
5	7.2439	3.6378
20	7.7317	3.6134
30	7.8537	3.6073
60	8.0976	3.5951
90	8.2195	3.5890
120	8.2195	3.5890
150	8.2195	3.5890

Table (4): The quantity of adsorbent and R% values for (80 mg/L) chlorpyrifos pesticide

Weight of adsorbent (g)	Ce	R%
0.1	31.6341	60.4573
0.2	26.7561	66.5549
0.3	20.7805	74.0244
0.4	18.0976	77.3780
0.5	15.1707	81.0366
0.6	11.8780	85.1524

Table (5): The values of R% and Ce for (80 mg/L) chlorpyrifos pesticide at different pH

pH	Ce	R%
1.5	30.6585	61.6768
3.1	21.7561	72.8049
5.4	14.1951	82.2561
7.3	9.4390	88.2012
9.4	32.0000	60.0000
11.3	47.9756	40.0305

Table (6): The effect of addition of different concentrations of NaCl on the adsorption quantity of (80 mg/L) chlorpyrifos pesticide at 37.5 C°.

Conc. Of NaCl (M)	Ce	Qe
0.1	13.0976	3.3451
0.2	16.1463	3.1927
0.3	18.9512	3.0524
0.4	21.0244	2.9488
0.5	22.8537	2.8573

Table (7): Adsorption quatities for (80 mg/L), chlorpyrifos pesticide adsorbed by different particle sizes of barley husks at 37.5 C°

Particle size (μm)	Ce	Qe
75	8.9512	3.5524
150	11.7561	3.4122
250	14.5610	3.2720
300	17.8537	3.1073

Table (8): Data of pesticide uptake by barley husks at different temperature and pH 7.3

Co (mg/L)	10.0 °C		25.0 °C		37.5 °C	
	Ce	Qe	Ce	Qe	Ce	Qe
10	0	0.5	0	0.5	0	0.5
20	0	1	0	1	0	1
30	0	1.5	0	1.5	0	1.5
40	0	2	0	2	0	2
50	6.8780	2.1561	6.0244	2.1988	0	2.5
60	9.5610	2.5220	8.8293	2.5585	6.7561	2.6622
70	10.6585	2.9671	9.5610	3.0220	7.8537	3.1073
80	11.3902	3.4305	10.2927	3.4854	8.9512	3.5524

Table (9): Adsorption quantities of chlorpyrifos on barley husks at various temperatures and pH 7.3 according to the application of Langmuir equation

Co (mg/L)	10.0 °C			25.0 °C			37.5 °C		
	Ce (mg/L)	Qe (mg/g)	Ce/Qe (g/L)	Ce (mg/L)	Qe (mg/g)	Ce/Qe (g/L)	Ce (mg/L)	Qe (mg/g)	Ce/Qe (g/L)
10	0	0.5	0	0	0.5	0	0	0.5	0
20	0	1	0	0	1	0	0	1	0
30	0	1.5	0	0	1.5	0	0	1.5	0
40	0	2	0	0	2	0	0	2	0
50	6.8780	2.1561	3.1900	6.0244	2.1988	2.7399	0	2.5	0
60	9.5610	2.5220	3.7910	8.8293	2.5585	3.4510	6.7561	2.6622	2.5378
70	10.6585	2.9671	3.5922	9.5610	3.0220	3.1638	7.8537	3.1073	2.5275
80	11.3902	3.4305	3.3203	10.2927	3.4854	2.9531	8.9512	3.5524	2.5198

Table (10): Adsorption quantities of chlorpyrifos on barley husks at various temperatures according to the application of Freundlich equation

Co (mg/L)	10.0 °C		25.0 °C		37.5 °C	
	logCe	logQe	logCe	logQe	logCe	logQe
10	……..	-0.3010	……..	-0.3010	……..	-0.3010
20	……..	0	……..	0	……..	0
30	……..	0.1761	……..	0.1761	……..	0.1761
40	……..	0.3010	……..	0.3010	……..	0.3010
50	0.8375	0.3337	0.7799	0.3422	……..	0.3979
60	0.9805	0.4017	0.9459	0.4080	0.8297	0.4252
70	1.0277	0.4723	0.9804	0.4803	0.8951	0.4924
80	1.0565	0.5354	1.0125	0.5423	0.9519	0.5505

Table (11): The Langmuir constants empirical values and the correlation coefficients for the removal of chlorpyrifos by barley husks at various temperatures

Temperature (°C)	a (mg/g)	b (L/g)	R^2
10.0	2.9189	3.8670	0.9491
25.0	2.9700	4.3384	0.9504
37.5	3.1726	15.9236	0.9785

Table (12): The Freundlich constants empirical values and the correlation coefficients for the removal of chlorpyrifos by barley husks at various temperatures

Temperature (°C)	n	Kf	R^2
10.0	2.4510	1.0988	0.6020
25.0	2.2962	1.0995	0.6120
37.5	2.3652	1.2996	0.4660

Table (13): The effect of temperature on the thermodynamic equilibrium constant (k) for the removal of chlorpyrifos by barley husks

Temperature (°C)	Temperature	1000/T	Ce	Qe	k	ln *k*
10.0	283	3.5335	8.0	2.20	5.50	1.7047
25.0	298	3.3557		2.40	6.00	1.7918
37.5	310.5	3.2206		3.00	7.50	2.0149

Table (14): Values of thermodynamic functions for the adsorption of chlorpyrifos on barley husks at different temperatures

Temperature (K)	ΔG(kJ/mol)	ΔH(kJ/mol)	ΔS(J/mol.k)
283	-4.0110	+0.0080	+14.2014
298	-4.4392		+14.9235
310.5	-5.2015		+16.7778

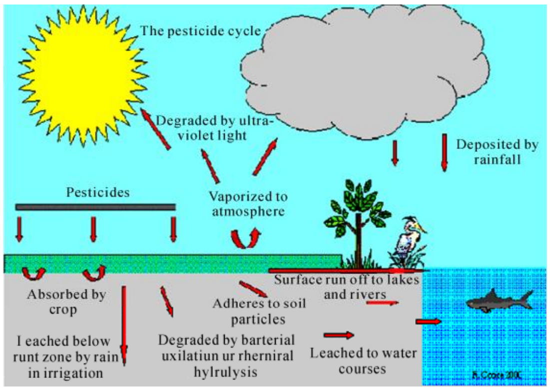


Figure (1): The different stages involved in pesticide cycle

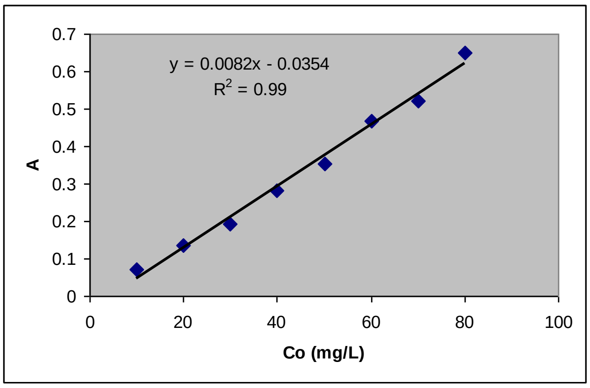


Figure (2): Calibration curve of chlorpyrifos

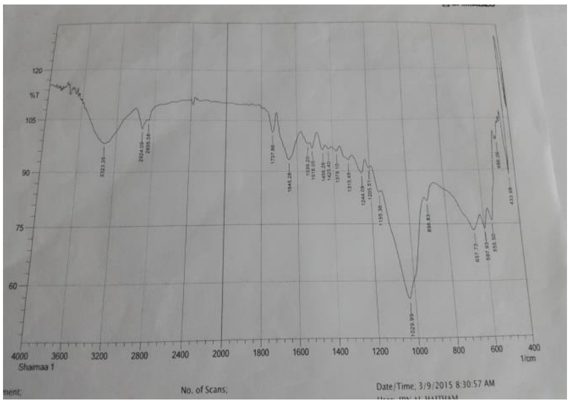


Figure (3): FTIR spectrum of barley husks

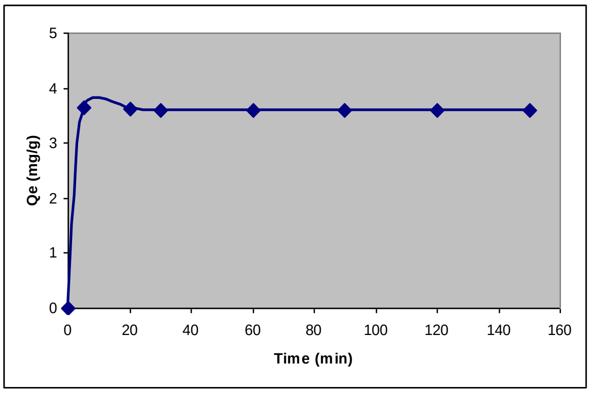


Figure (4): Effect of contact time on the adsorption of chlorpyrifos by the adsorbent

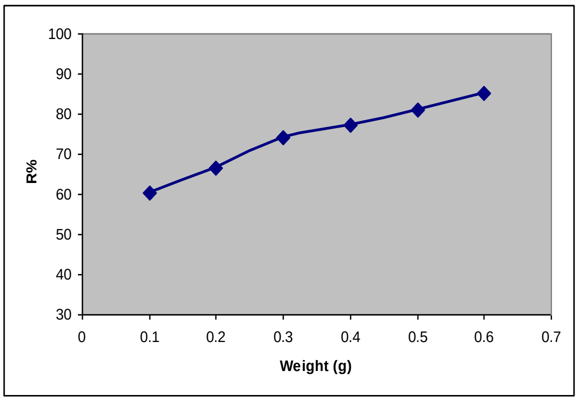


Figure (5): Effect of adsorbent weight on adsorption of chlorpyrifos by the adsorbent

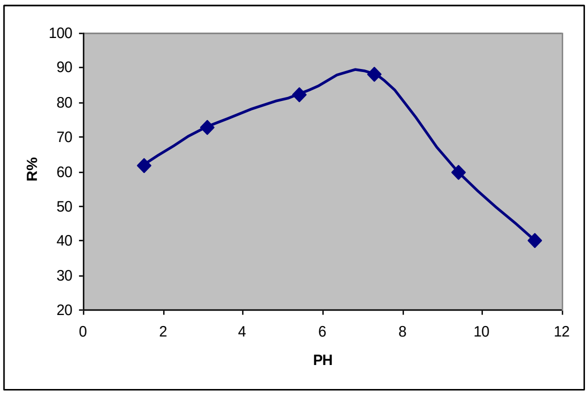


Figure (6): Effect of pH on adsorption of chlorpyrifos by the adsorbent

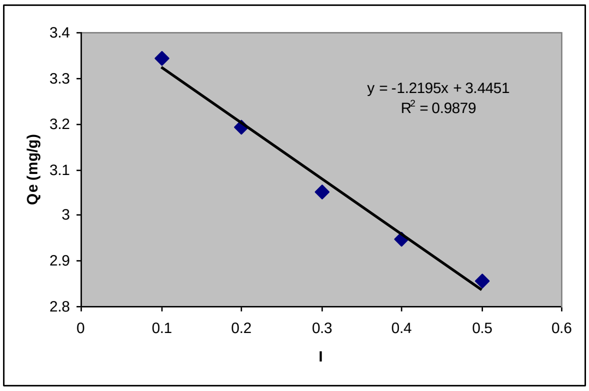


Figure (7): Effect of ionic strength on the adsorption of chlorpyrifos on the adsorbent

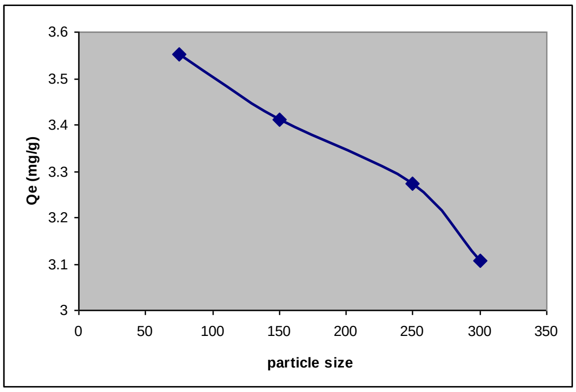


Figure (8): Effect of adsorbent particle size on the adsorption

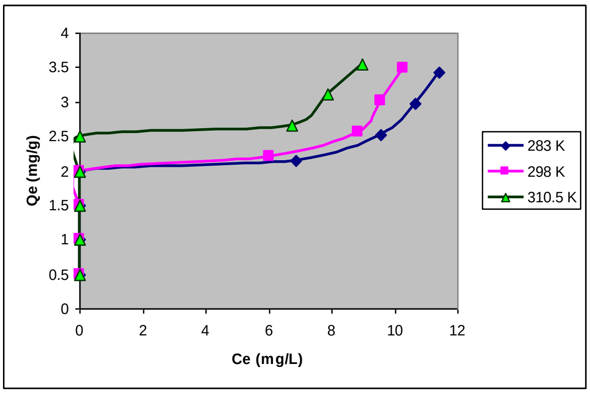


Figure (9): Adsorption isotherm of chlorpyrifos on the adsorbent at different temperatures

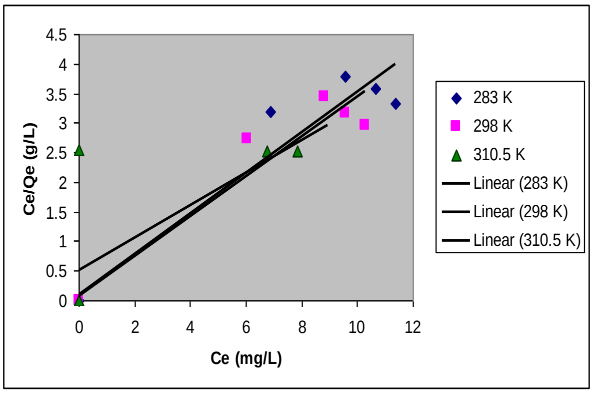


Figure (10): Linear form of Langmuir isotherm of chlorpyrifos on the adsorbent at different temperatures

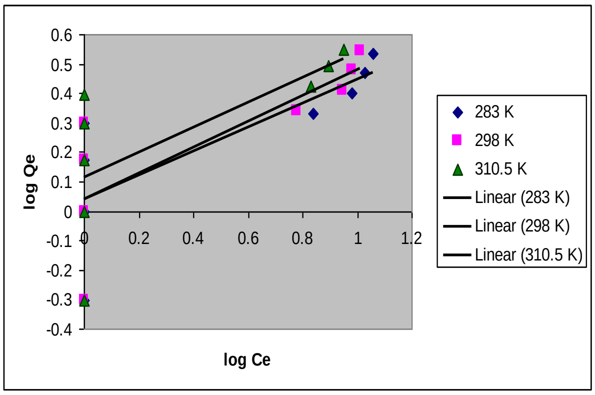


Figure (11): Linear form of Freundlich isotherm of chlorpyrifos on the adsorbent at different temperatures

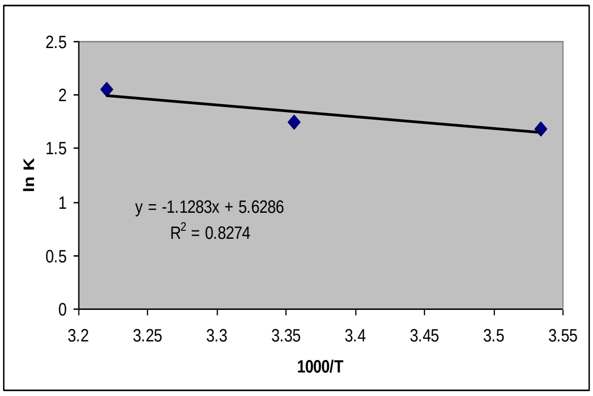


Figure (12): Plot of lnk against reciprocal absolute temperature for adsorption of chlorpyrifos on the adsorbent

ازالة مبيد الكلوربايريفوس (الدورسبان) من المحاليل المائية باستعمال قشور الشعير

شيماء خلف غاطي
انتظار داود سلمان
نجوى اسحق عبد الله
قسم الكيمياء/ كلية التربية للعلوم الصرفة (ابن الهيثم)/ جامعة بغداد

استلم في:27/كانون الثاني/2016، قبل في:6/اذار/2016

الخلاصة

تم ازالة مبيد الكلوربايريفوس (الدورسبان) من المحاليل المائية باستخدام قشور الشعير سطح ماز من بقايا نباتية واطئ الكلفة. درست العديد من المتغيرات المؤثرة في عملية الامتزاز والمتضمنة زمن الاتزان، وزن المادة المازة، الدالة الحامضية، الشدة الايونية، المساحة السطحية للمادة المازة، وتأثير درجة الحرارة في عملية الامتزاز. تم قياس قيم الامتصاص للمحلول قبل وبعد الامتزاز باستخدام مطيافية الاشعة المرئية- فوق البنفسجية. ان ايزوثيرمات الامتزاز تخضع الى معادلة لانكماير وان الشكل العام للايزوثيرم يتوافق مع الصنف (H_3) من تصنيف Giles. تم حساب الدوال الثرموداينامكية الاساسية لعملية الامتزاز والمتضمنة الانثالبي ، الانتروبي ، وطاقة جيبس الحرة. اظهرت النتائج ان عملية امتزاز مبيد الدورسبان على سطح قشور الشعير من النوع الماص للحرارة وان العملية من النوع العشوائي غير المنتظم.

الكلمات المفتاحية: الامتزاز، مبيد الدورسبان، نموذج لانكماير، نموذج فريندلش، الدوال الثرموديناميكية، قشور الشعير.