Adsorption Study for Trifluralin on Iraqi α –Alumina

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Abstract:

Equilibrium adsorption isotherm for the removal of trifluralin from aqueous solutions using α –alumina clay has been studied. The result shows that the isotherms were S_3 according Giels classification. The effects of various experimental parameters such as contact time, adsorbent dosage, effect of pH and temperature of trifluralin on the adsorption capacities have been investigated.

The adsorption isotherms were obtained by obeying freundlich adsorption isotherm with (R^2 = 0.91249-0.8149). The thermodynamic parameters have been calculated by using the adsorption process at five different temperature, the values of ΔH, ΔG and ΔS were (⁻1.0625) kj. mol^{-1}, (7.628 - 7.831) $kj.mol^{-1}$ and (⁻2.7966 - ⁻2.9162) kg. k^{-1}. mol^{-1} respectively.

The kinetic study of adsorption process has been studied depending on three kinetic equations:

1- Allergen equation 2- Morris –weber eguation 3- Reichenberg eguation.

In general, the result shows the isotherm were on α- alumina according to Giels classification.

α –alumina and thermodynamic

Key words: Trifluralin, adsorbent,

Introduction:

Trifluralin [α, α, α –trifluoro-2, 6 dintro-N, N-dipropyl-p-toluidine] used for the control of broadleaf weeds in wide variety of crops including cotton, brassica, soybeans and ornamentals among others [1].

Some studies indicated that herbicides are readily on organic matter and the clay. The effective of the soil applied herbicides is dependent on their relative availability in the soil, the latter being regulated by the extent of adsorption on soil colloids, especially the soil organic matter content [2].

Herbicides are readily adsorbed on organic matter and the clay fraction of the soil [3]. Studies conducted by Parka [2] indicated that trifluralin was strongly adsorbed by organic metter and clay. The effective rate required for weed control increased as the organic matter and clay control increased. Marilia [4] studies of adsorption of trifluralin on chitosan, the adsorption results were well fitted to Langmuir adsorption model. Trifluralin should be incorporated in to the soil by mechanical means with 24 hours of application; granular formulations may be incorporated by overhead irrigation [5]. Trifluralin is available in granular and emulsifiable concentrate formulation [5].

Adsorption is the tendence for accumulation of substance to take place at a surface or at an interface the accummenence of adsorption is due to the atoms in any surface being subject to unbalanced forces of attraction perpendicular to the surface plance and these forces possessing a certain unsaturation [6-7].

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Freundlich Isotherm is one of the most important isotherm that deals with sorption at solid –liquid interface [8]. Freundich equation could be written as follows [9, 10]:

$Q = K f C_e 1 / n$ ----------- (1)

$\text{Log } Q = \text{Log } K_f + 1 / n \text{ Log } C_e$ ----- (2)

Where Q is the adsorbate quantity (mg \L), C_e is the concentration of adsorbate at equilibrium (mg \L), K_f and n is the sorption capacity and an empirical parameter, respectively and also called Freundlichconstants.

The magor objective of this work is to minimize the concentration of trifluralin in aqueous solution to the acceptable levels, by removing it via and an adsorption process is used and the optimum conditions for adsorption process have been found.

Materials and Method:

The α– alumina clay was supplied from the state company for geological survey and mining –Iraq, the α-alumina had the following composition as shown in fig- the clay was ground and sieved to particle size less than75µm.

All spectral and absorbance measurements wave carried out on using UV –Vis shimadzu T60 V Spectrophotometer with 1 cm matched quartz cell.

The prepared ten aqueous solutions of trifluralin in the range (10 -100) ppm and took the absorbance of these solutions at the wave length 273 nm, in order to determine calibration curve. Prepared the aqueous solution of different concentrations of trifluralin and add to it 0.25 of the α – alumina, and then place in the thermostated shaker water bath with speed 100 rpm for 2 hours and then separated by centrifuge with speed 3000 rpm and hardened absorbance of each solution. The experiment were repeated at different temperature (298, 303, 308, 313 and 318) K

The quantity of adsorbate has been calculated by using the following formula:

$Q_e = Vsol. (C_o - C_e) / M$ ----------- (3)

Where Q_e is the Quantity of adsorbate (mg\g), Vsol. is the Total volume of adsorbate solution (L), C_o is the Initial concentration of adsorbate solutions ($mg.L^{-1}$), C_e is the concentration of adsorbate solution at equilibrium ($mg.L^{-1}$), m is the weight of adsorbant (g).

Results and Discussion:

The equilibrium of triflurali was studied as a function of concentration. The amount of trifluralin Q_e plotted against the equilibrium concentration C_e for trifluralin, was given in figure (1) and table (1).

Table (1) the values of Q_e and C_e at different time for 50 ppm trifluralin solution at 298K.

C_e / mg. L^{-1}	Q_e / mg. g^{-1}	Time / mint
95.921	0.407	15
86.705	1.329	30
42.392	5.76	60
27.49	7.251	90
22.196	7.78	120

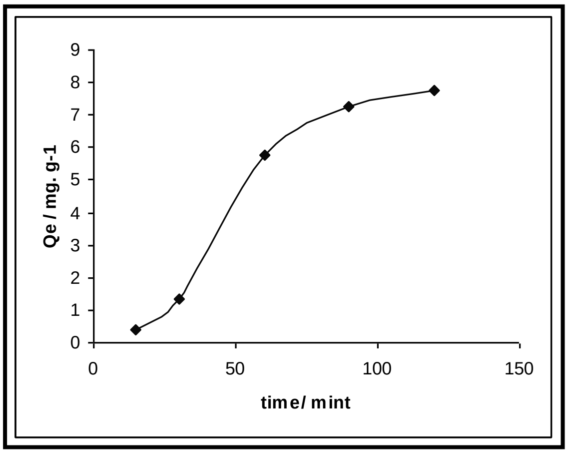

Fig. (1) The variation of Q_e with equilibrium time for 50 ppm trifluralin solution at 298K.

The equilibrium adsorption isotherm of trifluralin increases with the increase of initial of adsorbent concentration.

Freandlich isotherm are the most frequently employed models to describe the equilibrium characteristics of adsorption isotherm. The linearised from of the Freandlich equation[9, 10] is as follows:

Log Q = Log K_f + 1 / n Log C_e ----- (2)

The Freundlich isotherm constants K_f and 1 / n can be calculated from the plot between log Q_e and log C_e fig.(3). K_f (mg / g), 1\n (L / g) and n are the Freundlich constants. Table (2) and figure (2) are shown the Freundlich data which are indicators of adsorption capacity and adsorption intensity, respectively.

Table (2)-The values of C_o, Ce, Q_e, Log C_e and Log Q_e for the adsorption of trifluralin solutions at different temperatures.

298K					303K				
Co/ mg. L $^{-1}$	Ce/ mg.L^{-1}	Qe/ mg. g^{-1}	Log Ce	Log Qe	Co/ mg. L $^{-1}$	Ce/ mg.L^{-1}	Qe/ mg. g^{-1}	Log Ce	Log Qe
60	33.558	2.644	1.525	0.422	60	46.029	1.397	1.663	0.145
80	61.088	1.891	1.785	0.276	80	62.147	1.785	1.793	0.251
100	74.558	2.544	1.872	0.405	100	70.441	2.955	1.847	0.47
120	81.558	3.844	1.911	0.584	120	70.97	4.903	1.851	0.69
140	94.911	4.508	1.977	0.653	140	85.97	5.403	1.934	0.732
160	128.205	3.179	2.107	0.502	160	95.5	6.45	1.98	0.809
180	124.5	5.55	2.095	0.744	180	97.558	8.244	1.989	0.916
200	136.97	6.303	2.136	0.799	200	105.382	9.461	2.022	0.975

308K					313K				
Co/ mg. L $^{-1}$	Ce/ mg.L^{-1}	Qe/ mg. g^{-1}	Log Ce	Log Qe	Co/ mg. L $^{-1}$	Ce/ mg.L^{-1}	Qe/ mg. g^{-1}	Log Ce	Log Qe
60	41.264	1.873	1.615	0.272	60	45.029	1.497	1.653	0.175
80	52.029	2.797	1.716	0.446	80	57.147	2.285	1.756	0.358
100	61.617	3.838	1.789	0.584	100	70.679	2.932	1.849	0.467
120	73.735	4.626	1.867	0.665	120	88.852	3.114	1.948	0.493
140	83.264	5.673	1.92	0.753	140	95.088	4.491	1.978	0.652
160	86.558	7.344	1.937	0.865	160	112.617	4.738	2.051	0.675
180	105.558	7.444	2.023	0.871	180	118.088	6.191	2.072	0.791
200	124.147	7.585	2.093	0.879	200	125.029	7.497	2.097	0.874

318K				
Co/ mg. L $^{-1}$	Ce/ mg.L^{-1}	Qe/ mg. g^{-1}	Log Ce	Log Qe
60	49.441	1.055	1.694	0.023
80	67.441	1.255	1.828	0.098
100	86.97	1.303	1.939	0.114
120	96.088	2.391	1.982	0.378
140	111.147	2.885	2.045	0.46
160	116.5	4.35	2.066	0.638
180	121.617	5.838	2.084	0.766
200	131.794	6.82	2.119	0.833

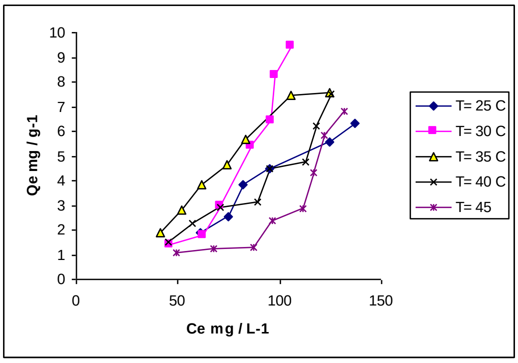

Fig. (2)-The plot of Q_e against C_e for the adsorption trifluralin solutions at different temperatures.

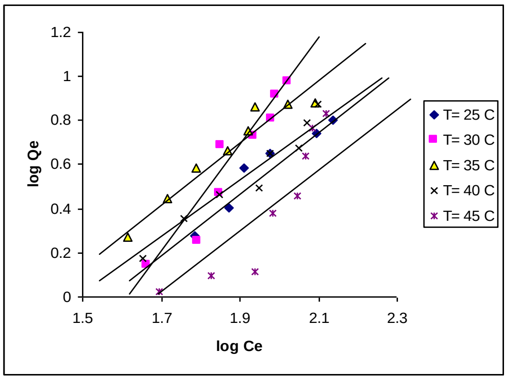

Fig. (3)- Freundilch linear relationship between Log Q_e and Log C_e for trifluralin solutions at different temperature.

Table (3) shows the Freundlich constants at different temperatures.

T	R^2	n	K_f
25	0.924	0.5659	0.758
30	0.914	0.2989	0.478
35	0.933	0.7173	1.445
40	0.9433	0.7344	0.794
45	0.814	0.4278	0.301

Effect of PH:

The effect of initial pH on α-Alumina was examined over arrange of pH values from 2 to 10 and the result are presented in fig. (4) and table (4), the adsorption amounts of trifluralin were higher at lower pH. The increase of trifluralin sorption at acidic PH should be due to the electro static attraction between positively charged groups of biomaterial surface and the metal- anion, which is the dominant species at low PH. Also, at low PH, there is presence of a larger number of H^+ ions, which in turn neutralize the negatively charged adsorbent surface thereby reducing hindrance to the diffusion of trifluralin.

Table (4) The quantity of adsorption at different pH value, using α-Alumina at 298K for 100 ppm trifluralin solution.

pH	Qe/ mg. g^{-1}	Ce/ mg. L^{-1}
2	9.7967	2.0327
4	9.5344	4.6557
6	9.518	4.8196
8	9.1737	8.2622
10	8.977	10.2295

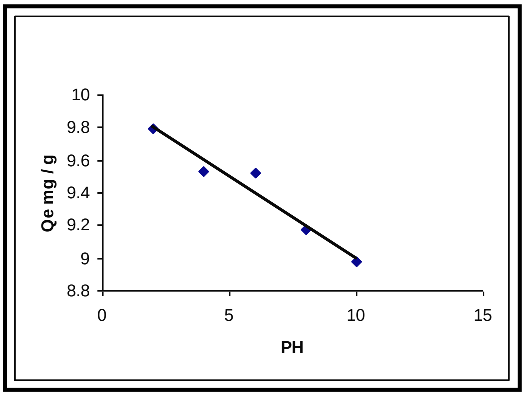

Fig. (4)The quantity of adsorption at different pH value, using α-Alumina at 298K for 100 ppm trifluralin solution.

Effect of Ionic strength:

We study of the effects of strength ion by adding different concentrations NaCl, and found that the amount of material adsorbed on all surfaces decreases with increases concentration of NaCl solution,because the added concentration of NaCl solutions cause an increase in competition between ions of the trifluralin and electrolyte ions on the adsorption sites on the surface [11].

Table (5) the adsorption isotherms of 100 ppm trifluralin solution at 298 K of different concentrations NaCl.

C / M of Na Cl	Ce / mg. L^{-1}	Qe / mg. g^{-1}
0.001	0.095	9.9904
0.01	0.053	9.9946
0.1	0.022	9.9978

Effect of Temperature and Thermodynamic parameters:

The adsorption of trifluralin at five different temperatures has been carried out. Trifluralin adsorption decreases with increasing temperature, showing the exothermic nature of the process.

The thermodynamic functions Δ H, ΔG, and ΔS have been calculated by using the following formulas [12-15]:

$\Delta G =- RT \, Ln \, K$ --------------- (4)

$L \, n \, K = -\Delta H /RT + constant$ -------- (5)

$\Delta G = \Delta H - T\Delta S$ ----------------- (6)

In the equation (4), where ΔG is the change in the value of free energy (KJ .mol $^{-1}$), R was the gas constant [8.314 (J.mol $^{-1}$.deg^{-1})], K is the thermodynamic equilibrium constant of adsorption process. The plotting of Log xm against 1000/T we get linear relationship and slope represents-ΔH/R.

Table (6) show the thermodynamic functions of the adsorption process

T (K)	ΔH (KJ. mol^{-1})	ΔG	ΔS (J.mol^{-1}.K)
298	-1.0625	7.628	-2.9162
303		6.074	-2.3552
308		7.162	-2.6702
313		7.325	-2.6797
318		7.831	-2.7966

From the table (6), It's clear that Δ H has the negative values, which indicator the ideal and the maximum value of physics-sorption process. All values of ΔG were positive, these values indicate that the adsorption process accompanied the process of absorption. As the spreading molecules adsorbed inside the pores of the α-alumina and increases speed of deployment with increasing temperature and this behavior is attributable to additional absorption. ΔS was had the negative values, this indicates that the adsorbed molecules are arranged on the surface as a results of its association with α-alumina. This is the normal consequence of the physical adsorption phenomenon, which takes phase through electrostatic interactions.

Kinetic analyses:

The kinetic of the adsorption process has been studied via introducing three models:

1- Lagergren model:

The equation of this model could be expressed as follows [16] :

$Ln \, q_e - q_t = Ln \, q_e - K_{ads.}t$ --------- (7)

Where q_t and q_e are the amount of trifluralin $K_{ads.}$/ mint^{-1} is the rate constant .Q_t and q_e values are given in table (7) at 298 K.

Table (7) the values q_t and q_e of trifluralin of 100 ppm at 298K.

Time	q_t	q_e	q_e - q_t	Ln q_e - q_t
15	4.079	77.804	73.725	4.3003
30	13.295		64.509	4.1668
60	57.608		20.196	3.0054
90	72.51		5.294	1.6665
120	77.804		0.000	0.000

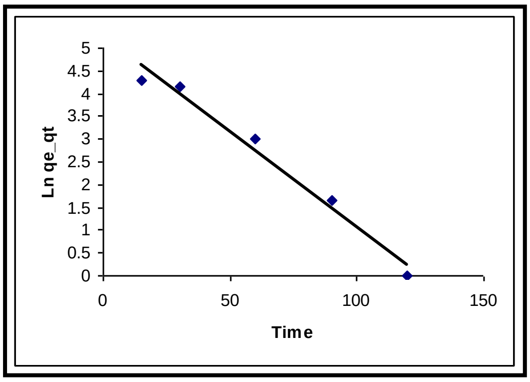

Fig (5) The Lagergren model for atrifluealin of 100 ppm at 298K

2- Morris –Weber model:

The kinetic model was used to estimate the rate limiting step of any adsorption process, the equation of this model could be expressed as follows [17]:

$q_t = K_d \sqrt{t}$ ------------------ (8)

Where q_t is the quantity of adsorbed material at any tim\mg.g^{-1}, K_d is the diffusion constant, antt is time of diffusion \mint, the plotting of q_t

against √t was accomplished at 298K. Figure (6) shows the plot of q_t Against √t for trifjuralin of 100 ppm at 298K.

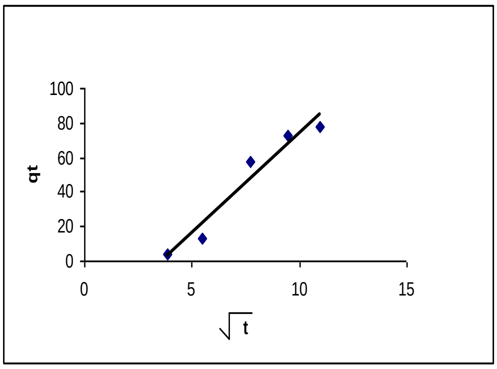

Fig (6) The plot of q_t against √t for trifluralin of 100 ppm at 298K.

3- Reichenberg model:

This kinetic model has been proposed to discuss the behavior of many adsorption process in solution and Reichenberg had introduced following formula [18]:

$F= (1-6/\pi^{2})\, e^{-Bt}$ ----- (9)

$Bt=- o.4977\text{-}Ln\,(1\text{-}F)$ ---- (10)

$F=q_t/q_e$ ----- (11)

Plotting of time (mint) against B_t revealed a linear relationship with relatively acceptable R^2 values.

Figure (7) shows the variation of Bt with time for trifluralin of 100 ppm at 298 K.

According to this model, it characterized the rate determining mechanisms which was diffusion process for trifluralin ions from the bulk solution to the absorbent surface and absorption occurred.

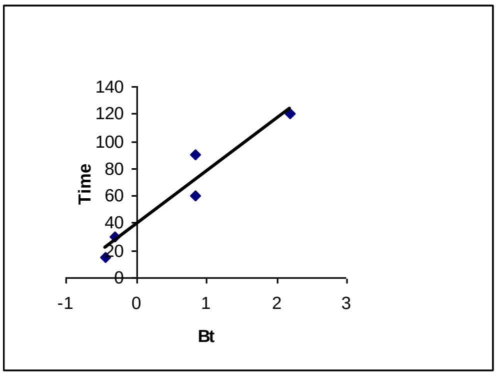

Fig. (7) The variation of Bt with time for trifluralin of 100 ppm at 298 K.

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دراسة امتزاز مبيد الترفلان على طين الفا- الومينا العراقي

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الخلاصة:

يتضمن موضوع البحث دراسة امتزاز الترفلان لأزالته من المحاليل المائية باستخدام الفا- الومينا. تم الحصول على ايزوثرمات الامتزاز بتطبيق معادلة فرندلش بنسبة خطية (0.91249-0.8149) واوضحت النتائج ان الأيزوثيرم من نوع (S_3) وفق لتصنيف كيلز. درس من خلال تجارب مختلفة تأثير زمن الأتزان والدالة الحامضية وكمية المادة الممتزة ودرجة الحرارة لترفلان على سعة الامتزاز.

تم حساب القيم الثرموديناميكية بخمس درجات حرارية وكانت انثالبي التفاعل (1.0625−) كيلوجول. مول$^{-1}$ وقيم الطاقة الحرة لكبس محصورة بين (7.831 - 7.628) كيلوجول. مول$^{-1}$ وقيم الانتروبي بين (2.7966- − 2.9162−) جول.مول$^{-1}$ على التوالي.

تمت دراسة حركيات الامتزاز اعتمادا على ثلاث معادلات حركية هي:

1- معادلة لنكماير 2- معادلة موريس/ ويبر 3- معادلة ريجمبرج .