Adsorption Study for Trifluralin on Iraqi Zeolite

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Abstract

The current work involves the adsorption of trifluralin on the surface of zeolite using UV. spectrophotometer technique to produce quantitative adsorption data at different conditions of contacttime, ionic strength, pH and temperatures. The adsorption phenomenon was examined as a function of temperatures (30, 35, 40, and 45) ˚C, and the results showed that the adsorption of trifluralin on surface zeolite increased with increasing temperatures (endothermic process). The basic thermodynamic functions (ΔH, ΔG, and ΔS) have also been calculated. The effect of ionic strength on adsorption was also studied by using different concentrations of NaCl solution. It was found that increasing the value of ionic strength, leads to decrease the adsorption quantity of trifluralin on the zeolite surfaces at constant temperature. The quantity of trifluralin that was adsorbed on the zeolite was decreased with increasing the pH of the solution at constant temperature. The kinetic study of adsorption process was studied depending on the following kinetic equations: Lagergren, Morris –Weber and Reichenenberg equations.

Keywords: Trifluralin, adsorption, zeolite and kinetic.

Introduction

Trifluralin [α,α,α-trifluoro-2,6-dinitro N, N-dipropy-p-toluidine] has been used commerciality as a preplanting soil-in comported herbicide since 1963 and it is now registered and extensively used on a number of agronomic and horticultural crops [1]. Application, followed by immediate soil in corporation, is made in spring or fall. If stubble ground with a heave trash cover is being treated, two tillage operations are recommended for the incorporation of the chemical. The efficacy of the soil -a pplied 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]. The movement of trifluralin in soil is generally restricted presumably because of its low water solubility and strong adsorption to soil [3].

Goulart [4] studied adsorption of the herbicide trifuralin on chitosan, in the temperatures ranges from 298 up to 313 K. The adsorption results were well fitted to Langmuir adsorption model, and the obtained enthalpic value of -10.2 ± 0.8 $KJ.mol^{-1}$ confirms that the trifuralin chitosan interaction is exothermic. Peter and Weber [5] study the adsorption and efficacy of trifluralin and butralin as influenced by soil properties and they found no differences in the extent of soil adsorption of trifluralin and butralin therefore, difference inefficacy could not be attributed to differences in soil adsorption. McCall [6] investigated the forces involved in the adsorption and desorption of trifluralin using cationic, anionic and nonionic exchange resins, trifluralin was mainly absorbed by physical bonds at sites on the resins where there were no coulombic forces. Hawxby, Basler and santelmann[7] study the temperature effects on adsorption and translocation of trifluralin, the initial rate of absorption of trifluralin was greater in excised lateral root tips than in tap root at 24hr.

In this work the adsorption of trifluralin on the zeolite were studied at different initial concentrations and temperatures.

Experimental

Materials and Methods:

The Zeolite Clay is supplied from the general company for geological survey and mining – Iraq, the molecular formula of zeolite could be written as: [$Na_2AL_2Si_3O_{10}.2H_2O$]. The pesticide trifluralin Molecular Formula [$C_{13}H_{16}F_3N_3O_4$] and Chemical structure:

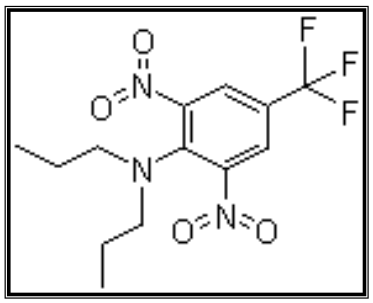

Fig. (a) Chemical structure of trifluralin.

All spectral and absorbance measurements were carried out using UV-Vis. Double beam recording spectrophotometer type (Shimadzu T60 V spectrophotometer with 1 cm matched quartz cell).

The clay was washed with excessive amounts of distilled water, dried at 160 ^{o}C for two hours. The clay was ground and sieved to a particle size less than 75 µm, wave length of maximum absorbency was recorded for trifluralin dissolved in aqueous media and found 273 nm. This value was utilized for estimation of quantity of trifluralin adsorbed. The quantities of adsorbate were calculated using the following equation:

$Q_e = V_{sol}. (C_0 - C_e)/ M$ .....(1)

Where Q_e is the quantity of adsorption (mg / g), V_{sol}.is the total volume of adsorbate solution (L), C_0 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).

The aqueous solutions of different concentrations of trifluralin were added to 0.25 g of the zeolite and then place in the thermo stated shaker **(**Thermo stated shaker water bath, name: JEIO TECH "BS-1"). With speed 100 rpm for 2 hours and then separated by centrifuge with speed 3000 rpm and hardened absorbance of each solution.

Results and Discussion

Effect of Contact Time:

Adsorption study was carried out by adding a known amount of zeolite into (0.25 g) trifluralin solutions (100 ppm), the solutions were centrifuged at a desired time intervals and the residual trifluralin concentration was determined.

Most of the maximum quantity adsorption of trifluralin was attained after about 180 min of skaking time at different initial concentration. The increasing contact time increased the trifluralin adsorption and it remains constant after equilibrium reached for different initial concentrations.

Fig.(1) show the variation of Q_e with the contact time for ppm trifluralin solution at constant temperature to be in attachment with (0.25g) of zeolite clay.

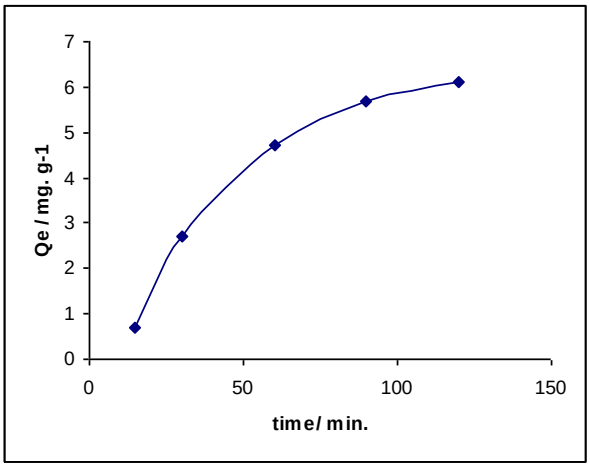

Fig. (1) The values of Q_e with equilibrium time for 100 ppm trifluralin at temperature constant.

Effect of PH:

The mechanism of the adsorption at zeolite surface reflects the nature of physicochemical interaction of the metal ions in the solution and the active sites of the zeolite[8] .The pH is varied (2,4,6,8 and10) during study. The effect of pH to the removal of trifluralin by zeolite is found to be significant as shown in Fig. (2). It's clear that (pH=2) has the maximum Q_e value, and this pH was chosen to all experiments of adsorption done subsequently. 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. The structure of zeolites, Particularly with low Si/Al ratio may collapse in the presence of acids with pH lower than 4 [9].

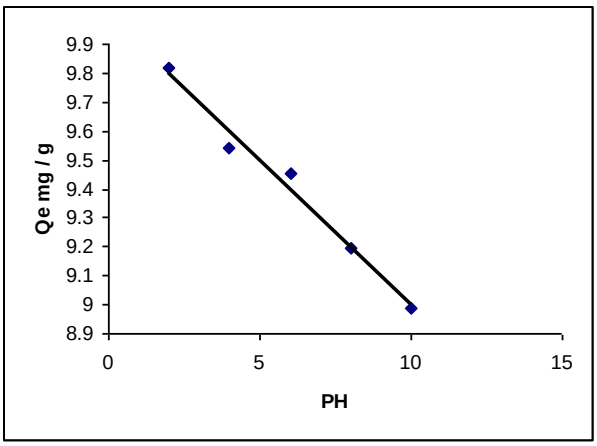

Fig. (2) The quantity of adsorption at different pH valiues zeolite at temperature constant for 100 ppm trifluralin solution.

Effect of Ionic strength:

The effect of ionic strength adsorption was studied using different concentrations of NaCl solution with solutions containing different concentrations of trifluralin added to flasks containing (0.25) g of zeolite. It was found that the extent of adsorption of trifluralin on zeolite surface decreases with increasing ionic strength at constant temperature. This is believed to be due to the increase in competition process between trifluralin and electrolyte ion on the adsorption sites on the zeolite surface [10].

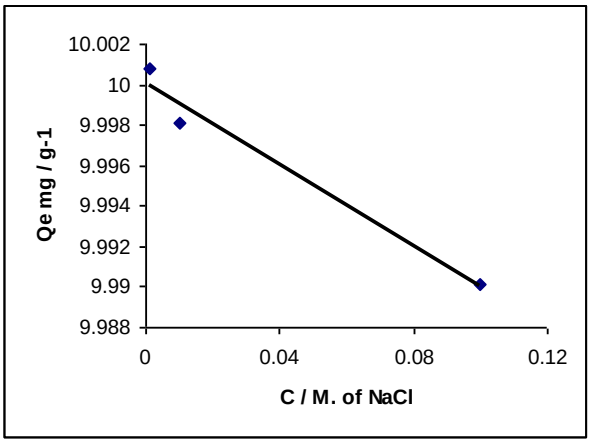

Fig. (3) The plot of Q_e against concentrations of NaCl for the adsorption of 100 ppm trifluralin solution at temperature constant.

Adsorption Isotherms:

Adsorption isotherms, which are presentation of the amount of solute adsorbed per unit of adsorbent [11], as a function of equilibrium concentration in bulk solution at constant temperature, were studied, in order to optimize the design of a sorption system to remove trifluralin from aqueous solutions, it is important to establish the most appropriate correlation for the equilibrium curve. The Freundlich isotherm equation for representing equilibrium data is given by [12, 13]:

$$Q = K_f C_e^{1/n} \quad \text{.....(2)}$$

$$\text{Log } Q = \text{Log } K_f + 1/n \text{ Log } C_e \quad \text{.....(3)}$$

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 freundlich constants. Table (1) and Fig.(4) and (5) show the Freundlich data.

Table (1)
The values of C_o, C_e, Q_e, Log C_e and Log Q_e for the adsorption of trifluralin solution at different temperatures.

303K				
C_o/ mg. L^{-1}	C_e/ mg.L^{-1}	Q_e/ mg. g^{-1}	Log C_e	Log Q_e
60	17.558	4.244	1.244	0.627
80	24.205	5.579	1.383	0.746
100	25.911	7.408	1.413	0.869
120	28.794	9.12	1.459	0.959
140	43.382	9.661	1.637	0.985
160	49.382	11.061	1.693	1.043
180	53.088	12.691	1.724	1.103
200	61.5	13.85	1.788	1.141

308K					313K				
C_o/ mg.L^{-1}	C_e/ mg.L^{-1}	Q_e/ mg. g^{-1}	Log Ce	Log Qe	C_o/ mg. L^{-1}	C_e/ mg.L^{-1}	Q_e/ mg. g^{-1}	Log C_e	Log Q_e
60	19.205	4.079	1.283	0.61	60	18.441	4.155	1.265	0.618
80	20.735	5.926	1.316	0.772	80	18.558	6.144	1.268	0.788
100	24.029	7.597	1.38	0.88	100	19.735	8.026	1.295	0.904
120	22.794	9.72	1.357	0.987	120	19.676	10.032	1.293	1.001
140	28.029	11.197	1.447	1.049	140	26.558	11.344	1.424	1.054
160	35.794	12.42	1.553	1.094	160	36.558	12.344	1.562	1.091
180	40.97	13.903	1.612	1.143	180	38.382	14.161	1.584	1.151
200	50.911	14.908	1.706	1.173	200	48.558	15.144	1.686	1.18

318K				
C_o/ mg. L^{-1}	C_e/ mg.L^{-1}	Q_e/ mg. g^{-1}	Log C_e	Log Q_e
60	18.088	4.191	1.257	0.622
80	20.617	5.938	1.314	0.773
100	16.852	8.314	1.226	0.919
120	18.029	10.197	1.255	1.008
140	19.205	12.079	1.283	1.082
160	18.5	14.15	1.267	1.15
180	19.264	16.073	1.284	1.206
200	22.147	17.785	1.345	1.25

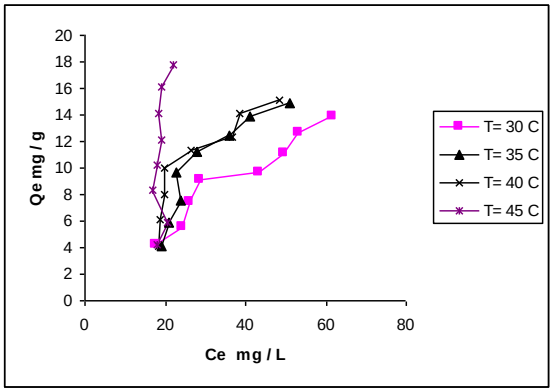

Fig. (4) The plot of Q_e against C_e for the adsorption of trifluralin solutions at different temperature.

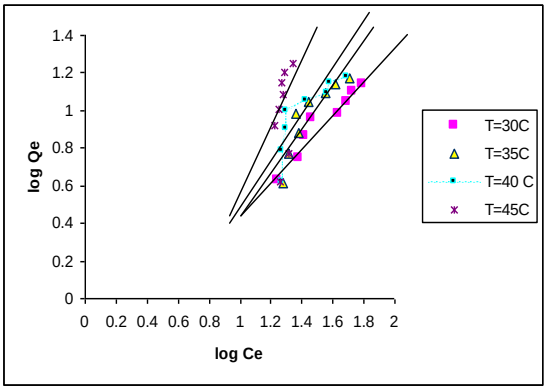

Fig. (5) Freundlich linear relationship between Log Qe and Log Ce for trifluralin solutions at different temperature.

Effect of Temperature and Thermodynamic parameter:

The adsorption of trifluralin on zeolite at four temperatures has been carried out the results showed that the adsorption of trifluralin on zeolite increased with increasing temperature (endothermic process).

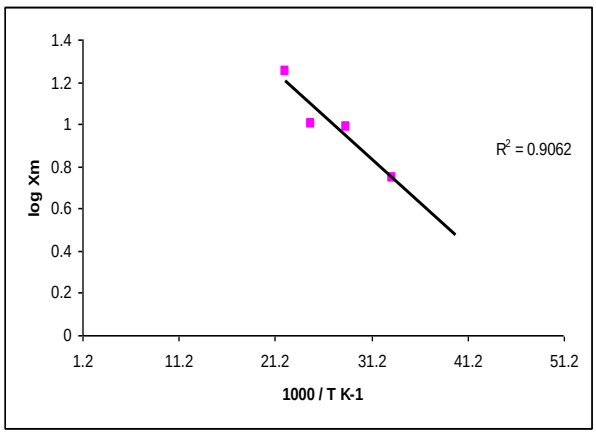

Fig. (6) The effect of temperature on the adsorption.

The thermodynamic functions ΔH, ΔG and ΔS were calculated using the following formulas [14-17]:

$\Delta G = -RT \ln$ .....(4)

$\ln k = -\Delta H/RT + \text{constant}$ .....(5)

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

In the equation (4), were ΔG is the change in the value of free energe ($KJ.mol^{-1}$), R is 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 liner relationship and slope reprepresent -ΔH/R.

Table (2)
Shows the thermodynamic functions of the adsorption process.

T (K)	*ΔH ($KJ.mol^{-1}$)*	*ΔG ($KJ. mol^{-1}$)*	*ΔS ($J.mol^{-1}.K^{-1}$)*
303	3.766	3.757	2.9702
308		3.145	2.0162
313		3.032	2.345
318		1.867	5.9716

From the Table (2), it's clear that ΔH value is positive, which indicate the ideal and the maximum value of a physic-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 zeolite and increases speed of deployment with increasing temperature this behavior is attributable to additional absorption. ΔS was had positive values, and it was increased with the temperature increase, the disorder of the system increase. The system becomes more disordered, which due to the absorption process and diffusion of trifluralin ions in the zeolite pores.

The kinetic of the adsorption:

The kinetic of the adsorption process was studied via introducing three models.

1- Lagergren Modle

The equation of this model could be expressed as follows:-

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

Where q_t and q_e are the amount of trifluralin adsorbed at time t/mint, and at equilibrium time respectively,K_{ads}. /min.$^{-1}$ is the rate constant.

The linear relationship was obtained via plotting $\ln q_e - q_t$ values t/min. as shown in Fig.(7), q_t and q_e values are given in Table (3).

Table (3)
The values q_t and q_e of trifluralin of 100 ppm at temperature constant.

Time	*q_t*	*q_e*	*$q_e - q_t$*	*$\ln q_e - q_t$*
15	7	87	80	4.382
30	27		60	4.0943
60	47		40	3.6888
90	57		30	3.4011
120	87			

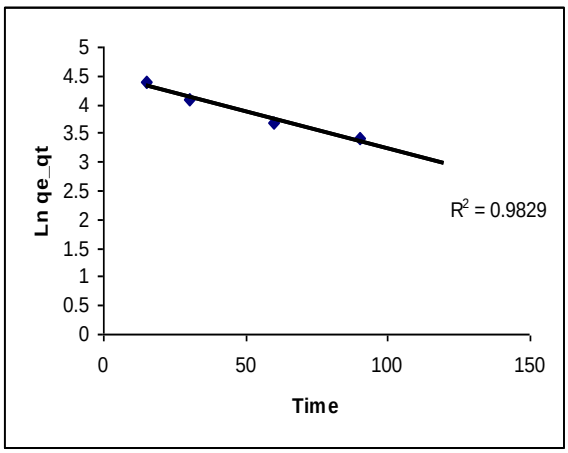

Fig. (7) The Legergren model for a trifluralin of 100 ppm at temperature constant.

The kinetic model in this study includes the pseudo - first order equation. The value of rate constant for the pseudo first order reaction is calculated experimentally by plotting Ln q_e-q_t against time of the adsorption of trifluralin on to zeolite clay according to equation (7), K_{ads}. (min.$^{-1}$) = 0.01155.

2- Morris- Weber Model

This kinetic model was used to estimate the rate limiting step of any adsorption process, the equation of this model could be expressed as follows [19]:-

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

Where q_t is the quantity of adsorbed material at any time/mg.g-^{1},K_d is the diffusion constant, and t is the time of diffusion/min., the plotting of q_t values and $\sqrt{t}$ was accomplished at temperature constant. Fig.(8) shows the plot of q_t values and $\sqrt{t}$ for trifluralin of 100 ppm at temperature constant.

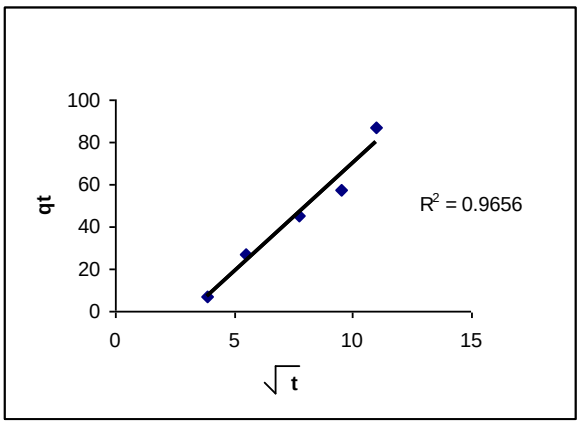

Fig. (8) The plot of q_t against $\sqrt{t}$ for trifluralin of 100 ppm at temperature constant.

3- Rauschenberg Model

This kinetic model was proposed to discuss the behavior of much adsorption process in solution and Rauschenberg had introduced following formula [20]:-

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

$B_t = -0.4977 - \mathrm{Ln}\,(1-f)$ ..... (10)

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

Plotting of time values, B_t revealed a linear relationship with relatively acceptable R^2 values. Fig.(9) shows the variation of B_t with time for 100 ppm of trifluralin at temperature constant. 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.

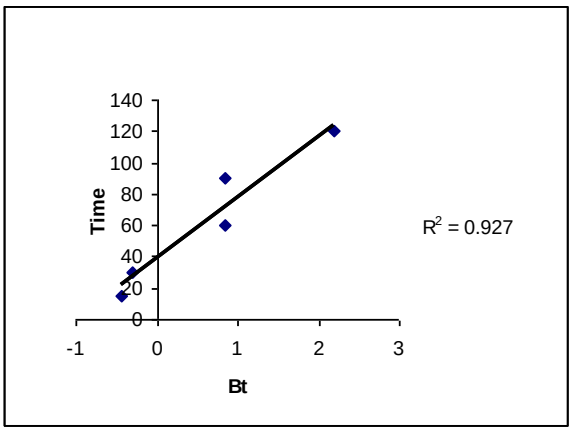

Fig. (9) The variation of B_t with time for trifluralin of 100 ppm at temperature constant.

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الخلاصة

تناولت هذه الدراسة امتزاز الترفلان على سطح الزيولايت عند تراكيز مختلفه وقد تم استخدام تقنية مطيافية الاشعة فوق البنفسجية لمعرفة كميات الامتزاز عند ظروف متباينة من الاس الهيدروجيني ودرجة الحرارة والقوة الايونية لمحلول الامتزاز. بينت الدراسة ان امتزاز الترفلان على سطح الزيولايت عند درجات حرارية مختلفة (٤٥,٤٠,٣٥,٣٠)^{o}C يزداد مع زيادة درجة الحرارة اي ان العملية ماصة للحرارة. كما حسبت القيم الثرموديناميكية الاساسية لعملية الامتزاز. ودرس تأ ثير الشده الايونيه في عملية الامتزاز وذلك بأ ستخدام تراكيز مختلفه من ملح كلوريد الصوديوم، ووجد ان كمية الامتزاز تقل بزيادة الشده الايونيه عند ثبوت درجة الحرارة. كما ودرس تأ ثير الداله الحامضيه (pH) في عملية الامتزاز عند ثبوت درجة الحرارة، واظهرت النتائج ان كمية الامتزاز تقل بزيادة الداله الحامضية للمحلول. تمت دراسة حركيات الامتزاز اعتمادا على ثلاث معادلات حركيه هي: معادلات لنكماير و موريس – ويبر و ريجمبرغ.