A study of adsorption isotherms for the removal of herbicide Atlantis WG from aqueous solutions by using Bentonite clay

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Abstract:

The subject of this research involves studying adsorption to removal herbicide Atlantis WG from aqueous solutions by bentonite clay. The equilibrium concentration have been determined spectra photometry by using UV-Vis spectrophotometer. The experimental equilibrium sorption data were analyzed by two widely, Langmuir and Freundlish isotherm models. The Langmuir model gave a better fit than Freundlich model The adsorption amount of (Atlantis WG) increased when the temperature and pH decreased. The thermodynamic parameters like ΔG, ΔH, and ΔS have been calculated from the effect of temperature on adsorption process, is exothermic. The kinetic of adsorption process was studied depending on Lagergren ,Morris − Weber and Rauschenberg equations.

Key words: Adsorption isotherms, kinetic,Atlantis WG [Mesosulfuron-methyl (3% W/W), lodosulfuron-methyl sodium (0.6% W/W), Mefenpyr-diethyl (9% W/W)]. Bentonite.

Introduction:

The adsorption – desorption process was very important to understand the behavior of pesticide in the environment. Mobility, leaching, movement and volatilization of pesticides in soil are great factors which effect the pollution of the surfaces and ground water. Therefore the removal of pesticide residue from water by adsorption onto different types of minerals and clays has been reported in literature [1-2].The some studies herbicides in dictated that 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[3]. Adsorption is the tendency for accumulation of a substance to take places 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 plane and these forces possessing ascertain UN saturation [4-6]. However, adsorption is considered more effective and less expensive them other technologies[7-9]. Clays have been used as promising low-cost adsorbents. There are several types of clays such as smectites, mica (1 lilt) , kaolinite, serpentine, pylophylite, vermiculite and sepiolite [10-12] .The moleculer formula of bentonite could be written as (Mg_2 Al_{10} Si_{24} O_{60} $(0H)_{12}$[Na,Ca])[13].These materials are classified based on differences in their layered structures. Clay material have high porosities, Also, they have anent negative charge, and hence, they have the capacity to

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adsorb positively charged materials [14-15].In the present work, we have studied the adsorption of herbicide Atlantis from aqueous solutions by Iraqi bentonite in different pH solutions and different temperatures.

Materials and Methods:

2.1 Adsorbent.

Bentonite supplied from (the state company for geological survey and mining - Iraq) was used during this experiment. The chemical composition of bentonite shown in table (1).

Table (1): the chemical composition of Iraqi Bentonite.

compound	% Wt
Na_2O	0.65
MgO	6
Al_2O_3	14.65
SiO_2	54.66
CaO	4.77
Fe_2O_3	4.88
K_2O	0.6
L.O.I	13.06

The clay was thoroughly rinsed with distill water, and then it was allowed to dry at room temperature. The dried clay was grounded to a fine powder in grinding mill and sieved to size fraction less75 µm, and then dried in oven at 160 C for 24 h.

2.2 Materials.

All the chemicals used were of analytical reagent (AR) grade. Stock solutions of 1000 mg/L of Atlantis WG were prepared which were purchased from(State Board of Agricultural Researches. Purity 97%) using double distilled water. Desired test solutions of Herbicide were prepared using appropriate subsequent dilutions of stock solution. The range of concentration of herbicide prepared from standards solutions various between 20-200 mg/L. Before mixing the adsorbent, the pH of each test solution was adjusted to the required value with 0.1M NaOH or 0.1M HCl. A sample of (50 ppm) Atlantis solution was taken and spectrum scan was measured by using UV-Vis spectrophotometer and showed λ_{max} at 302 nm.

2.3 Analysis.

The herbicide concentrations in solutions and after equilibrium were determined by using UV-Vis spectraphotometer (shimadzu, Japan, T60 V). The pH of the solution was measured with a WTW pH meter using a combined glass electrode.

2.4 Adsorption experiments:

Batch sorption experiments were conducted by mixing sorbent with herbicide solutions with desired concentration in 250 mL glass flask. The glass flasks were stoppered during the equilibration period and placed on a temperature controlled shaker at speed 100 rmp for 2 hours and then separated by centrifuge with speed 3000 rpm. The effect of pH on the equilibrium. Prepared the aqueous solution of different concentrations of atlantis and add to it 0.1 gm of the Bentonite , and then place in the thermo stated shaker water bath with speed 100 rmp for 2 hours and then separated by centrifuge with speed 3000 sorption of herbicide was investigated by mixing. . The experiments were repeated at different temperature (298, 308 and 318)K. The quantity of adsorbate was calculated based on the different between the initial and final concentration in every flask , as follow:-

$$Qe = \frac{V\,(C_o - C_e)}{m} \qquad \ldots\ldots(1)$$

where q_e is the Quantity of adsorbate (mg/g) , V 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 adsorbent (g).

Results and Discussion:

3.1 The Effect of contact time.

The rate of adsorption is important for designing batch sorption experiments. Therefore, the effect of contact time on the sorption of herbicide was studied. The sorption yield increased of herbicide increased considerably until the contact time reached 120 min. further increase in contact time did not enhance the sorption, so, the optimum contact time was selected as 120 min for further experiments. Table (2) and figure (1) show that variation of Q_e with the contact time for 100 ppm of Atlantis WG solution at 298 K to be in attachment with 0.1 gm of bentonite clay.

Table (2): The values of Q_e and C_e at different time for 100 ppm of Atlantis WG solution at 298 K temperature.

C_e / mg. l^{-1}	Q_e/ mg. g^{-1}	Time / min
91.147	2.214	15
87.809	3.047	30
87.333	3.166	45
86.380	3.405	60
85.904	3.524	75
84.952	3.762	90
83.523	4.119	105
83.523	4.119	120

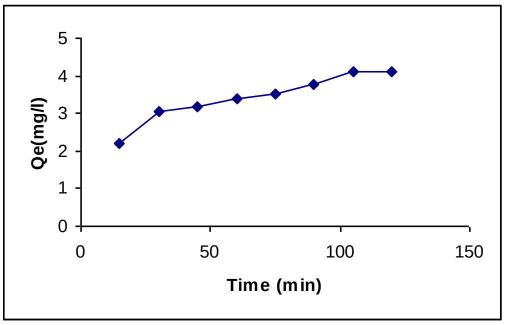

Fig. (1) The variation of Q_e with the contact time for 100 ppm of Atlantis WG solution at 298 K temperature.

3.2 The Effect of pH.

The pH has been identified as one of the most important parameter that is effective on herbicide sorption. It is directly related with competition ability of hydrogen ions with herbicide to active sites on the adsorbent surface. The effect of initial pH on bentonite was examined over arrange of pH values from 2 to 12. The maximum adsorption was observed at pH 8 for herbicide. Therefore, the remaining all sorption experiments were carried out at this pH values. The sorption mechanisms on the bentonite surface reflect the nature of the physicochemical interaction of the solution. At highly acidic pH became positive and herbicide and protons complete sites on cell wall charge, which results in lower uptake of herbicide molecules. Increasing adsorption yield at higher pH (pH>8) is related to the ionized for nature of the cell wall under the studied pH.

3.3 The Effect of Ionic Strength.

Table (3) shows the effect of ionic strength on the uptake of herbicide by bentonite. The result show that increasing the ionic strength of the solution decreased the uptake of herbicide, because the added concentration of NaCl solutions cause an increase in competition between ions of the Atlantis WG and electrolyte ions on the adsorption sites on the surface [16]. The reduction in uptake is probably due to the excess of ions which inhibit the approach of herbicide to active sites of the sorbent.

Table(3): The adsorption isotherms of 100 ppm Atlantic WG solution at 298K temperature of different concentrations NaCl.

C / M of Na Cl	Ce / mg. l^{-1}	Qe / mg. g^{-1}
0.001	90.19	2.45
0.01	95.90	1.023
0.1	99.71	0.714

3.4 The Effect of adsorbent dose on adsorption.

The adsorbent dosage is an important parameter because this determines the capacity of adsorbent for given initial concentration. The adsorption efficiency for herbicide as a function of adsorbent dosage was investigated. The percentage of the herbicide steeply increase with adsorbent loading up to 0.1 g/100 ml. These results can be explained by the fact that the adsorption sites available for adsorption site increase by increase the adsorbent dose. The maximum adsorption 90% for herbicide was attained at adsorbent dosage. 0.1 g/l. Therefor, the optimum adsorbent dosage was taken as 0.1 gm forfurther experiments[17].

3.5 The Adsorption isotherms.

An adsorption isotherm describes the fraction of sorbent molecules that are partitioned between liquid and solid phases at equilibrium. The equilibrium adsorption isotherms on fundamental importance in the design of adsorption systems [18].

3.5.1 The Freundlish isotherm.

The Freundlich isotherm model is the well known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [19].

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \ldots\ldots (2)$$

where K_f is the Freundlich constant related to the bonding energy. $1/n$ is the heterogeneity factor and n(g/L) is a measure of the deviation from linearity of adsorption. Freundlich equilibrium constants were determined from the plot of $\log q_e$ versus $\log C_e$, are listed in table (4) and preseuted in figure (2) on the basis of the linear of Freundlich equation (2). The n value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n = 1$, then adsorption is linear; if $n < 1$, then adsorption is a chemical process; if $n > 1$, then adsorption is a physical process. The $1/n$ value in Freundlich equation was found to be 1.2-2.4 for bentonite. Table (5). Since n lie between 1 and 10, this indicates the physical biosorption herbicide onto bentonite The values of regression coefficients R^2 are regarded as a measure of goodness of fit of the experimental data to the isotherm models.

Table (4): Shows the effect of the temperatures on the data of equilibrium concentration and quantity adsorption.

298K			308K			318K		
Co/mg.l-1	Log Ce	Log Qe	Co/mg.l-1	Log Ce	Log Qe	Co/mg.l-1	Log Ce	Log Qe
20	0.499	0.624	20	0.988	0.409	20	1.078	0.302
40	0.716	0.939	40	1.015	0.869	40	1.053	0.855
60	0.994	1.097	60	1.072	1.08	60	1.095	1.075
80	1.081	1.23	80	1.235	1.195	80	1.242	1.193
100	1.084	1.341	100	1.244	1.314	100	1.272	1.307
120	1.104	1.428	120	1.314	1.395	120	1.316	1.394
140	1.155	1.497	140	1.316	1.474	140	1.328	1.472
160	1.183	1.558	160	1.375	1.532	160	1.377	1.531
180	1.227	1.61	180	1.385	1.59	180	1.435	1.581
200	1.317	1.651	200	1.429	1.636	200	1.436	1.635

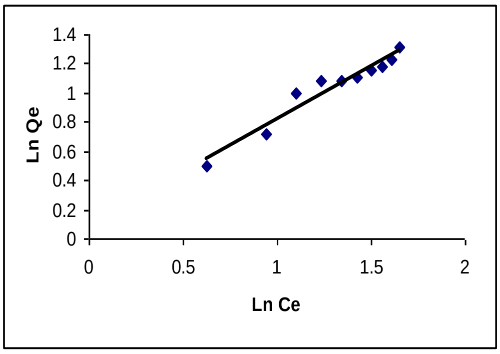

Fig.(2) Shows the linear relationship of freundlich isotherm between log Q_e and log C_e at 298k temperature.

Table (5) : The values of parameters (K_f, 1/ n, R^2).

K_f (mg/g)	1/n (g/l)	R^2	T (K)
0.9087	1.2921	0.944	298
0.0291	2.2508	0.889	308
0.01208	2.4949	0.781	318

3.5.2 The Langmuir isotherm:

The Langmuir isotherm assumes monolayer aseorption on auniform surface with a finite number of adsorption sites [20] Once asite is filled , no further sorption can take place at that site.. AS such the surface will eventually reach saturation point where the maximum adsorption of the surface will be achieved . The linear form of the Langmuir isotherm model is described as :

$$Ce/qe=1/K_Lq_{max}+Ce/q_{max.}$$

Where K_L is the Langmuir constant related to the energy of adsorption and qmax is the maximum adsorption capacity (mg/g). Values of Langmuir parameres q_{max} and K_L were calculated from the slop and intercept of the linear plot Ce/qe versus Ce as shown in Fig(3). Values of q_{max}, K_L and regression coefficient R^2 are listed in Table (6).

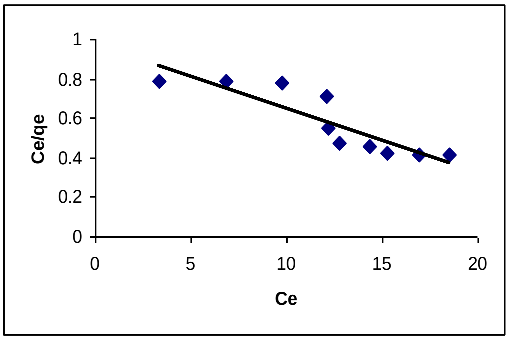

Fig .(3) Langmuir isotherm for Atlantis WG at 298K temperature.

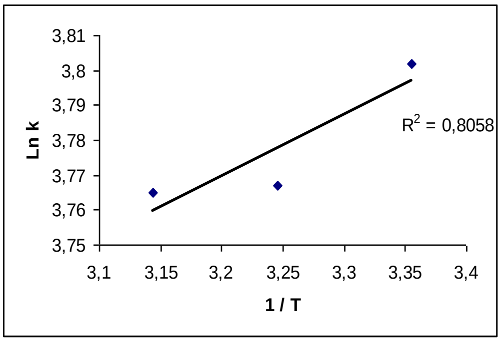

Fig. (4) the plot of Ln K with(1 / T) the reciprocal of temperature

Table(6): Langmuir constants for Atlantis adsorption by bentonite clay.

k_l (mg/l)	Q_{max} (mg/g)	R^2	T (K)
1.925	0.027	0.789	298
0.457	0.029	0.905	308
0.399	0.029	0.892	318

The Effect of Temperature and Thermodynamic parameters:

The adsorption of Atlantis WG at three different temperatures has been carried out. Atlantis WG adsorption decreases with increasing temperature, showing the exothermic nature of the process. The thermodynamic functions ΔH, ΔG, and ΔS have been calculated by using the following equations [21-23]:

$\Delta G = - RT \ln K$ ------------------- (3)

$\ln K = - A \ \Delta H / RT$ ------------ (4)

$\Delta G = \Delta H - T\Delta S$ -------------- (5)

Where K is the maximum adsorption quantity for various Atlantis WG solution at deferent temperature. The equation (4) was used to calculate the ΔH, by potting against 1 / T. Fig. (7) show a linear relationship and the slope represent -ΔH/R where R is the gas constant [8.314 ($J.mol^{-1}.K^{-1}$)].

The ΔG and ΔS values at different temperature (298, 308 and 318) K given in table (7).From the table (7), It's clear that ΔH has the negative values, which indicates 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 bentonite and increases speed of deployment with increasing temperature and this behavior is attributable to additional absorption[19]. ΔS 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 Atlantis WG ions in the bentonite pores[23].

Table (7): Shows the thermodynamic functions of the adsorption process

T (K)	ΔH (KJ. mol^{-1})	ΔG ($J.mol^{-1}.K$)	ΔS ($J.mol^{-1}.K$)
298	- 0.163	9.419	0.032
308		9.646	0.031
318		8.312	0.026

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 [24]:-

$Ln\ q_e - q_t = Ln\ q_{e} - K_{ads}.t$ ------- (6)

Where q_t and q_e are the amount of Atlantis adsorbed at time (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 figure (5), q_t and q_e values are given in table (8).

Table (8): The values q_t and q_e of Atlantis WG of 100 ppm at 298 K temperature.

Time (min)	q_t	q_e	q_e - q_t	Ln q_e - q_t
15	2.145		1.974	0.680
30	3.047		1.072	0.069
45	3.166		0.953	-0.048
60	3.405		0.714	-0.336
75	3.524	4.119	0.595	-0.519
90	3.762		0.357	-1.03
105	3.999		0.12	-2.21
120	4.119		0	

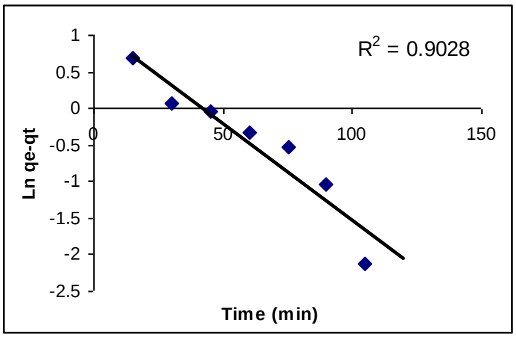

Fig. (5) The Legergren model for a Atlantis WG of 100 ppm at 298 K temperature.

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 Atlantis WG on to bentonite clay according to equation (6), K_{ads} ($min.^{-1}$) equal - 0.0261.

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 [23]:-

$q_t = K_d \sqrt{t}$ ---------- (7)

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 Figure (6) shows the plot of q_t values and $\sqrt{t}$ for Atlantis WG of 100 ppm at 298 K temperature.

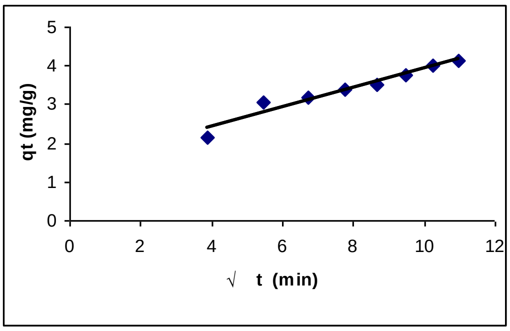

Fig (6). The plot of q_t against $\sqrt{t}$ for Atlantis WG of 100 ppm at 298 K temperature

3- Rauschenberg Model.

This kinetic model was proposed to discuss the behavior of much adsorption process in solution and Rauschenberg had introduced following formula [22]:-

$F = [1-6/\pi^2]\ e^{-Bt}$ ------------ (8)

$B_t = -0.4977 - Ln\ (1-f)$ ---------- (9)

$F = q_t / q_e$ ----------------- (10)

Figure (7) shows the variation of B_t with time for 100 ppm of Atlantis WG at 298 K temperature. According to this model, it characterized the rate determining mechanisms which was diffusion process for Atlantis WG ions from the bulk solution to the absorbent surface and absorption occurred.

Table (9) :The values of Bt with time for 100 ppm of Atlantis WG solution at 298 K temperature.

Time (min)	Bt
0	0.154
15	0.272
30	0.845
45	0.963
60	1.250
75	1.433
90	1.944
105	3.008
120	0

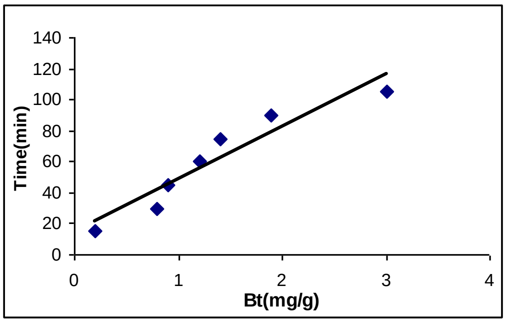

Fig. (7) The variation of B_t with time for Atlantis WG of 100 ppm at 298 K temperature.

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دراسة امتزاز ايزوثيرمات لازالة لمبيد اعشاب الاتلانتس من المحاليل المائية باستخدام طين البنتونايت

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الخلاصة:

يتضمن موضوع البحث دراسة امتزاز مبيد الاتلانتس لازالته من المحاليل المائية باستخدام طين البنتونايت، حددت تراكيز الاتزان طيفيا باستخدام تقنية الاشعة المرئية فوق البنفسجية وحللت نتائج الاتزان مع معادلتي لنكماير وفرندلج، وجد ان ايزوثيرم فرندلج افضل تطابقا من ايزثيرم لنكماير، ووجد ان سعة الامتزاز تزداد مع نقصان درجة الحرارة والدالة الحامضية.

تم حساب الدوال الثرموديناميكية (ΔH وΔG وΔS) بوساطة تأثير درجة الحرارة على عملية الامتزاز. وجد من خلالها ان عملية الامتزاز هي باعثة للحرارة ، وتم كذلك دراسة حركية الامتزاز اعتماداً على معادلات لاجرجرينزومورس-ويبروراشينبرك.