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Equilibrium, Kinetic and Thermodynamic of Adsorption of (2 , 4 - Dichlorophenoxy Acetic Acid) Herbicide from Aqueous Solutions onto Zeolite Clay

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Abstract: ***Adsorption of the herbicide 2, 4- dichlorophenoxy acetic acid from aqueous solutions onto zeolite mud minerals, was examining. Variables impacting adsorption, for example, pH of the arrangement, adsorbent measurements, molecule estimate, herbicide fixation and temperature have been examined. The adsorption procedure was moderately quick and harmony was accomplished after 120 min. Adsorption harmony information could likewise be depicted by Freundlich models at the centralization of (2, 4-D) who going of (40-200) mg L-1. Thermodynamic fromework, for example, ΔH, Δ G and ΔS were calculate. The kinetic of adsorption process was studied depending on Lagergen, morris- weber and rauschenberg equations.***

Keywords: Adsorption, Herbicide, (2, 4- D), Zeolite and Thermodynamic

1. Introduction

The specific and regularity herbicide 2, 4-dichlorophenoxy acidic acid is utilized to dominance wideband grass after rise, althoug 2, 4-D is one of the most seasoned compound herbicidal on the planet it is still generally utilized as a part of agrarian fields due to its astounding selectively between the windeband grass and graminaceous products and its sensible price [1].The in number auxinic activity of 2, 4-D is accepted to hold on in plant without critical biodegradation and to exasperate hor nonal adjust bringing about vegetation death.Kavanagh et.al [2] announced that geethite (press oxy hydoxide)adsorbed 2, 4-D essentially by a particle trade response, despite the fact that the measure of 2, 4-D adsorption was impressively more noteworthy than would be normal absolutely on the premise of straightforward electrostatic reaction. koskinen and Harper [3] scrutinized the overwhelming part of particle trade responses on 2,4-D adsorption on ground since strata silicate muds and ground natural material (SOM) are for the most part either notcharged or contrarily charged .Bhaskar and Bhamidimarr [4] examines removal energy of 2, 4-D on to initiated carbon is introduced and the balance adsorption of 2, 4-D is depicted by a freundlich sort isotherm and the bunch active trials are broke down utilizing a surface dissemination display. The herbicide 2, 4-D(5) synthetically secured on a silica gel has been utilized for Coppre (bivolent), Nickel (bivolent), Zinc (bivolent) and Cadmium (bivolent) removal from watery and ethanolic arrangement at room temperature. This search includes,we have examined the likelihood of the removal distinctive centralization of 2, 4-D from water on to zeolite in various pH solution and temperature .

2. Experimental

Materials

The zeolite mud was provide for geological survey and minig-Iraq, chemical analysis of alumina is listed in table the mud was soil and strain to particle extent less than 75 µm. The(2, 4- D) was utilized as a part of this review. Sample of (100 ppm) 2, 4-D arrangement was possessed and a range sweep was metrical by utilizing uv.vis demonstrated a λmax at 284nm. The herbicide chemical structure is appeared in figure (1) [1]:-

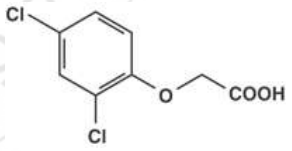


Figure 1: Chemical form of (2, 4- D)

Method

The adsorption isotherms have been controlled by 2, 4-D arrangement of know, introductory focus to be blended with precisely measured measure of zeolite in a firmly shut vial at certain temperature and measured of pH. The measure of zeolite in the mud has been 0.25 gm / 25 ml arrangement. A consistent blending at a steady temperature and pH was accomplished utilizing a shaker water bath . The zeolite arrangement have been then equilibrated for 2 hours, dirt comment have been then sparted by rotator with speed 3000 rpm and the supernatant arrangement was exposure to examination utilizing bright noticeable strategy λ_{max} = 284 nm , a similar trial was rehashed at various introductory fixation, temperature and pH.

3. Impact of Contact time

Adsorption study was done by including a known measure of zeolite (0.25 g) 100 ppm of 2, 4-D arrangement. The measure of 2, 4-D (Qe), is given in figure (2).

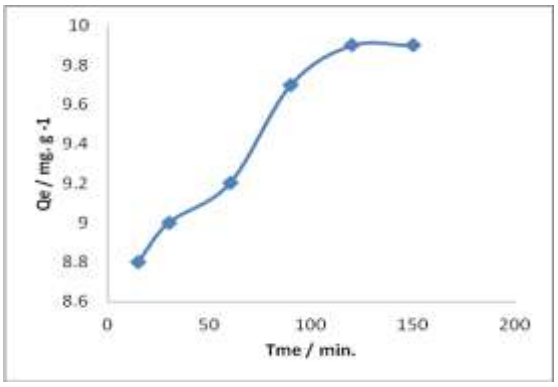


Figure 2: The relationship of Q_e with equilibrium time for 2, 4- D solution at 298K

Plurality the most magnitude adsorption of (2, 4- D) was achieved after around 180 mint of shaking time in various starting fixation. The expanding contact time expanded the (2, 4 -D adsorption and it stays consistent next balance went after various beginning focuses.

4. Adsorption Isotherms

Freandlich isotherm is the plurality much of the time utilized models to depict the harmony attributes of adsorption isotherm. The linearised from of the freandlich condition [6, 7] the following:

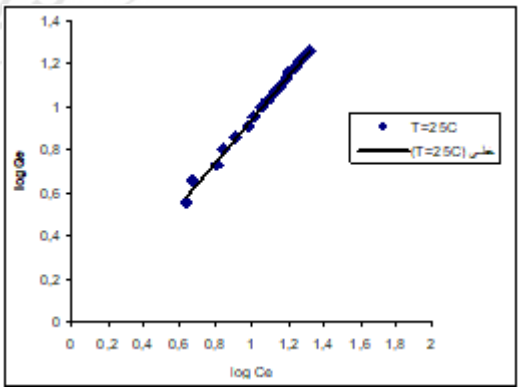
$\log Q_e = \log K_f + 1 / n \log C_e$ ---------- (1)

The Freandlich isotherm unchanging factors Kf and 1 / n can be ascertained from the plot between log Qe and Ce fig.(4) , Kf , 1/n and n are the Freundlich steady. Chart (1) and figure (3) are shown the Freandlich datum.

Chart 1: The values of C_o, Log C_e and Log Q_e for the adsorption of 2, 4-D solution at different temperature

298K 303					308K 313K			
Co/ mg. L $^{-1}$	Log Ce	Log Qe	Log Ce	Log Qe	Log Ce	Log Qe	Log Ce	Log Qe
40	0.6321	0.5528	0.6579	0.5496	0.6778	0.5487	0.6822	0.5464
50	0.6733	0.6559	0.7325	0.6493	0.7715	0.6443	0.7568	0.6462
60	0.8029	0.7295	0.8161	0.7279	0.8332	0.7258	0.8321	0.7259
70	0.8456	0.7992	0.8576	0.7979	0.8673	0.7967	0.889	0.7941
80	0.914	0.856	0.9175	0.8556	0.9192	0.8554	0.9418	0.8528
90	0.9829	0.9051	0.9844	0.9049	0.9902	0.9042	0.9917	0.9041
100	1.0136	0.9526	1.0205	0.9519	1.0074	0.9534	1.0265	0.9511
110	1.0532	0.9943	1.0631	0.9931	1.0668	0.9927	1.0588	0.9936
120	1.094	1.0373	1.0865	1.0325	1,0957	1.0315	1.1048	1.0304
130	1.1234	1.0671	1.1287	1.0665	1.134	1.0658	1.1355	1.0657
140	1.1589	1.0989	1.1633	1.0984	1.1589	1.0989	1.1628	1.0984
150	1.1875	1.129	1.1768	1.1302	1.1939	1.1282	1.1907	1.1286
160	1.21	1.1576	1.2153	1.157	1.2174	1.1568	1.2196	1.1566
170	1.2418	1.1834	1.2373	1.1839	1.243	1.1832	1.2422	1.18336
180	1.257	1.2093	1.259	1.209	1.2546	1.2095	1.2933	1.205
190	1.2896	1.2317	1.2885	1.2318	1.2819	1.2326	1.2969	1.2309
200	1.3148	1.2537	1.311	1.2541	1.3026	1.255	1.3058	1.2547

318K		
Co/mg. L $^{-1}$	Log Ce	Log Qe
40	0.6672	0.5484
50	0.7739	0.644
60	0.8279	0.7264
70	0.8945	0.7934
80	0.945	0.8524
90	0.9902	0.9042
100	1.0285	0.9509
110	1.0643	0.993
120	1.0974	1.0313
130	1.1355	1.0657
140	1.1623	1.0985
150	1.1898	1.1287
160	1.2192	1.1566
170	1.2294	1.1848
180	1.2679	1.208
190	1.2826	1.2325
200	1.2845	1.257



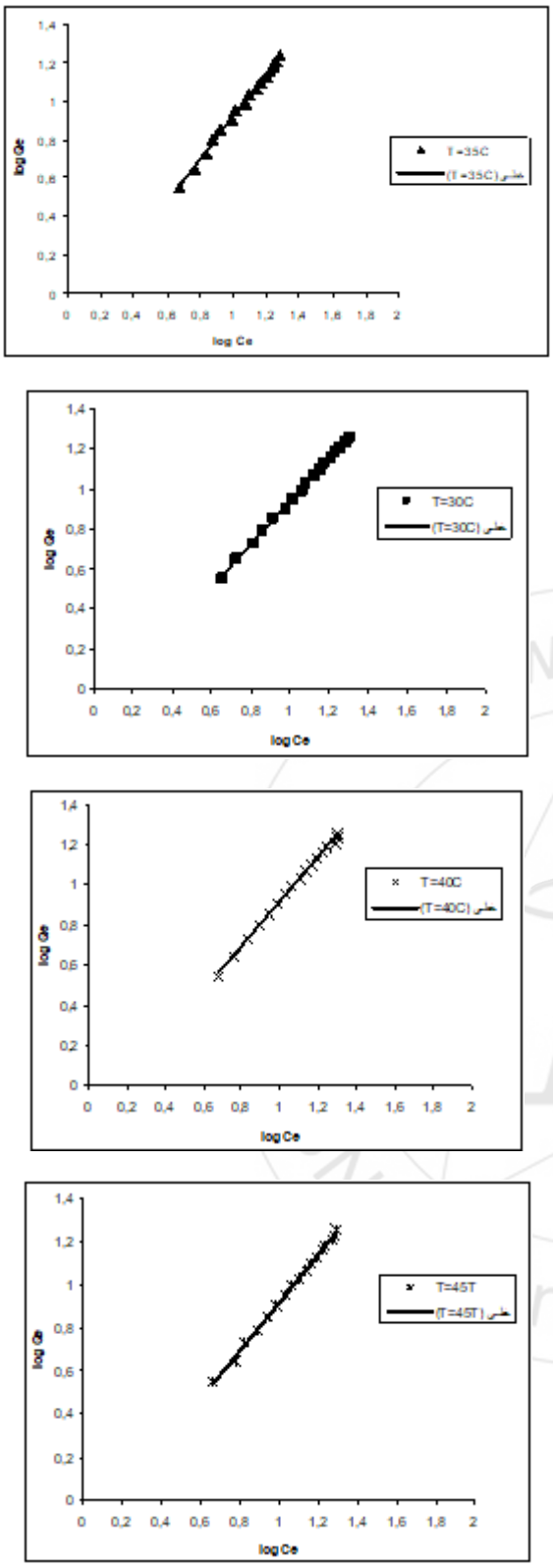


Figure 3: Freundilch linear ship between log Q_e and log C_e for(2, 4-D) at different temperature

Chart 2 shows the Freundilch constants at different temperature.

T	R^2	n	K_f
25	0.9958	1.0020	1.1365
30	0.9981	0.9390	1.3626
35	0.9957	0.8956	1.5696
40	0.9975	0.9085	1.5395
45	0.9985	1.0015	1.6538

Note from Freundilch isotherms adsorption on the surface of zeolite the amount of removal was expanded of 2.4- D by soft temperature to be specific that the sort of removal operation exothermic as not as much as the amount of adsorbent high temperature in light of the fact that the intensity of removal strata layer will be diminished with expanding temperature, this because of increment the arrangement temperature that prompts to increment in Kinetic vitality of the particles adsorbed at first glance adsorbentive which prompts to isolate from the surface of adsorptive and come back to the arrangement [8].

5. Impact of PH

The impact of beginning pH on zeolite was analyzed obove organize of pH qualities of 2 to 10 and the outcome are available in fig. (4) and chart (3), the removal measures of (2, 4 -D) were graet at soft pH It is acomon perception that anions are positively adsorbed on the surface of adsorptive at low pH in light of the fact that the nearness of hydrogen particle activate the surface dynamic for the removal of cations at high pH values [9] .

Chart 3: The quantity of removal at pH value, utilized zeolite for (2, 4-D) solution.

pH	Qe/ mg. g^{-1}	Ce/ mg. L^{-1}
2	9.9647	0.3524
4	9.4590	5.4099
6	9.2846	7.1532
8	9.1938	8.0613
10	9.0969	9.0306

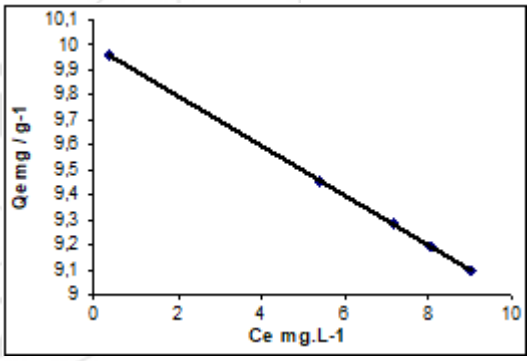


Figure 4: The magnitude of removal at pH amount, utilize zeolite for 2, 4-D solution

6. Impact of Ionic Strength

Investigation of the impacts of quality particle by including distinctive fixations sodiuml chloride, and found that the measure of sabstance on whole surfaces diminishes with builds centralization of sodiuml chloride arrangement , in order to the fact

that the additional grouping of sodiuml chloride arrangements reason an expansion in rivalry between particles of the 2,4-D and electrolyte particles on the removal destinations at first glance [10].

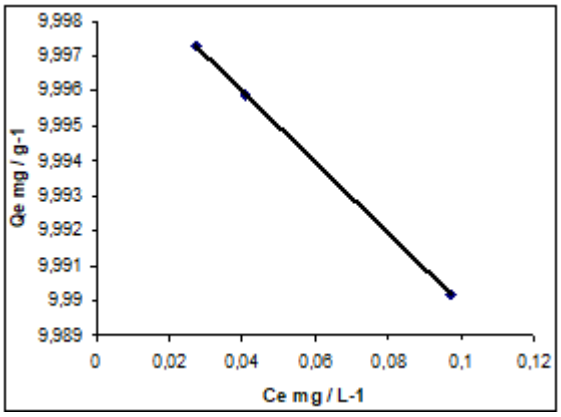


Figure 5: The plot of Q_e against concentricity of sodium chloride

7. Thermodynamic Parameters

The adsorption of 2, 4- D adsorption different temperatures has been carried out. 2, 4-D adsorption diminishes with expanding temperature, demonstrating the exothermic way of the procedure. The thermodynamic capacities enthalpy change, free energy change and entropy change were ascertained utilizing the accompanying equations [11-13]:

$$\log X_m = \frac{-\Delta H}{2.303\ RT} + \text{constant} \text{ ------ (2)}$$

$$\Delta G = \Delta H - T\Delta S \text{ ---------- (3)}$$

$$\Delta G = -RT \ln (Q_e / C_e) \text{ ---------- (4)}$$

Where Xm is the greatest adsorption amount for different 2, 4-D arrangement at various temperature The condition (2) was utilized to ascertain the ΔH, by plotting against 1/T. In the condition (4).

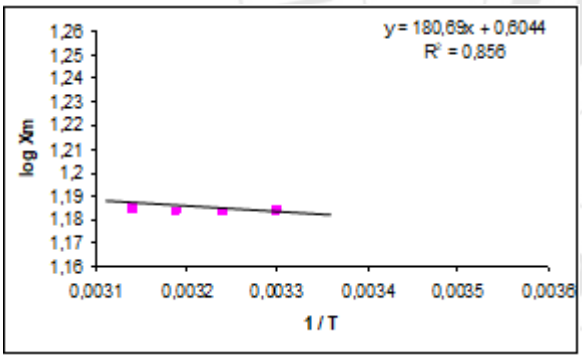


Figure 6: The plot of Log X_m against 1/T

Chart 4: Shows the thermodynamic functions for the (2,4-D) solution procedure.

T (K)	ΔH (KJ. mol^{-1})	ΔG	ΔS ($J.mol^{-1}.K$)
298	-1.5022	349.9139	-1.1792
303		759.5571	-2.5117
308		775.9334	-2.5241
313		787.9838	-2.5223
318		791.7635	-2.4945

From the chart (4), unmistakably enthalpy chang has the negative qualities, which pointer the perfect and greatest estimation of material science sorption handle. All estimations of free energy change were positive, these esteem demonstrate that the adsorption procedure went with the procedure of retention.

As the pervasion atoms adsorbed inside the pores of the zeolite and builds speed of sending with expanding temperature and this conduct is owing to expansion al ingestion .Entropy chang was had the negative esteem, this demonstrates the adsorbed particles are masterminded at first glance as an aftereffects of its relationship with zeolite . This is the typical outcome of the physical adsorption wonder, which takes stage through electrostatic connections.

8. Kinetic type

To explore the component of adsorption, dynamic type has been utilized to test information. The motor type in this review incorporates the spurious -first order condition. The spurious-first request condition of lagergreen is for the most part communicated as takes after [14]:

$$\text{Ln}\ (q_e - q_t) = \text{Ln}\ q_e - K_{ads}.\ t \text{ ---------- (5)}$$

Where qt and qe are the measure of 2, 4-D adsorbed at time (min.), and at balance time separately, and Kads. /min.- 1 is the rate steady. The straight relation was gotten by means of plotting Ln qe –qt values t/min. as appeared in figure (7), qt and qe qualities are given in chart (5).

Chart 5: The given q_t and q_e of(2, 4- D .)

time	q_t	q_e	$q_e - q_t$	Ln $q_e - q_t$
15	87.9616	99.0385	11.0769	2.4048
30	91.4231		7.6154	2.0301
60	91.9616		7.07769	1.9568
90	97.2693		1.7692	0.5705
120	99.0385		0.0000	--------

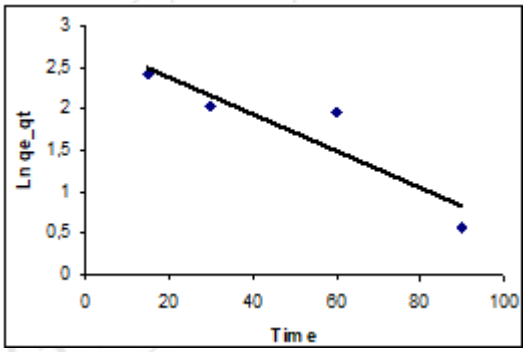


Figure 7: The Legergren model for a 2, 4- D at 289K

The estimation of average consistent for the spurious first order response is ascertained tentatively by plotting Ln qe - qt versus time of the adsorption of 2,4-D on to zeolite clay as per condition (5),K_{ads}.= - 0.02221.

9. Morris –Weber type

The kinetic type was applied to estimation the averange limiting step of any adsorption process, the equation of this type could be expressed as follows [15]:

$$q_t = K_d \sqrt{t} \text{ ---------- (6)}$$

Where qt is the amount of adsorbed sabstance at any tim\mg.g-1, Kd is the dissemination consistent, antt is season of dispersion \mint, the plotting of qt against √t was expert at 298K.

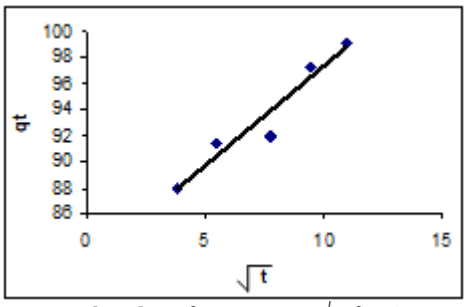


Figure 8: The plot of q_t Against √ t for (2 , 4 – D)

10. Reichenberg type

This active model has been suggested to examine the conduct of numerous adsorption procedure in arrangement and Reichenberg had presented taking after equation [16]:

$$F= (1 – 6 / \pi^2) e^{-Bt} \quad \ldots\ldots\ldots\ldots\ldots (7)$$

$$Bt=- o.4977-Ln (1-F) \quad \ldots\ldots\ldots\ldots\ldots .. (8)$$

$$F=q_t/q_e \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

Plotting of time (mint) against Bt uncovered a straight association with moderately adequate R2 values .

As per this type, it portrayed the average deciding components which was dissemination handle for 2, 4-D particles from the mass answer for the spongy surface and ingestion happened.

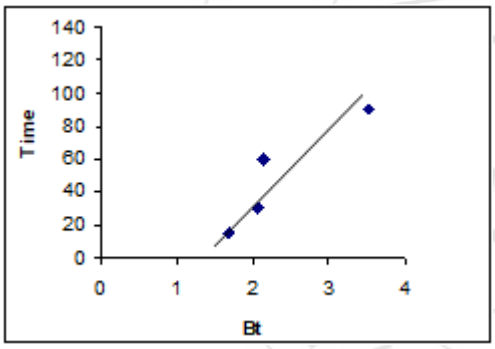


Figure 9: The relationship of Bt among time for(2 , 4 - D)of at 298 K

11. Conclusions

1) From Freundilch isotherms adsorption on the surface of zeolite the amount of removal was expanded of 2.4- D by soft temperature to be specific that the sort of removal operation exothermic.
2) The removal measures of (2, 4 -D) were graet at soft pH It is acomon perception that anions are positively adsorbed on the surface of adsorptive at low pH.
3) The measure of sabstance on whole surfaces diminishes with builds centralization of sodiuml chloride arrangement , in order to the fact that the additional grouping of sodiuml chloride arrangements.
4) Enthalpy chang ha negative qualities, free energe chang were positive and entropy chang was had the negative esteem. 5- The estimation of average consistent for the spurious first order response is ascertained tentatively by plotting Ln qe - qt versus time of the adsorption of 2,4-D on to zeolite clay as per condition (5),K_{ads}.= - 0.02221

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