

Chemical Kinetic, and Thermodynamic of Adsorption–Desorption of cypermethrin in the Soil of South Iraq

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Abstract

In the present work change in the adsorption-desorption processes of Cypermethrin (pyrethroid), performed by using batch equilibrium experiments on eight agricultural soil samples. The kinetics study for adsorption-desorption processes investigated that first order rate law. Thermodynamic parameters (ΔG^0 , ΔH^0 and ΔS^0) were also calculated for adsorption process of Cypermethrin at 288.15, 298.15, and 308.15 K. The negative values for each of ΔG^0 , ΔH^0 and ΔS^0 constants confirmed that Cypermethrin adsorption processes more at lower temperature and done via enthalpy effect.

Keywords: Cypermethrin, adsorption, desorption, Thermodynamic parameters

I. INTRODUCTION

The term "pesticide" is a broad non-specific term that covers a large number of substances including insecticides, herbicides and fungicides[1]. Pengman (1996) defined pesticide as any chemical agent used to kill or control undesired insects, weeds, rodents, fungi, bacteria, or other organisms[2, 3].

Pesticides constitute a heterogeneous category of chemicals specifically designed for the control of pests, weeds or plant diseases[4]. There are different groups of pesticide that have been developed depending on the target organism[5].

Cypermethrin [(+/-) α -cyano (3-phenoxyphenyl) methyl (+/-) cis, trans-3-(2,2-dichloroethenyl)-2-,2-dimethylcyclopropanecarboxylate], Its structure is shown in Fig. 1 [6-8].

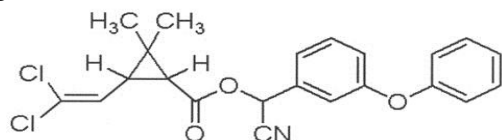


Fig. 1: Structural formula of Cypermethrin.

Cypermethrin has become one of the most important insecticides in wide scale use. It is used to control many pests including lepidopterans pests of cotton, cereals, vegetables, fruit, for food storage, in public health and in

animal husbandry, and is available as an emulsifiable concentrate or wet able powder[9, 10]. Adsorption is the primary process of how the soil retains a pesticide[11, 12]. Adsorption is defined by Koskinen and Harper (1990) as: the attraction and accumulation of molecules at the soil-water or soil-air interface, leading to the formation of molecular layers on the surface of soil particles[13, 14].

Adsorption is due to the attraction or repulsion between a solid surface and, in this case, a vapor or solution. This attraction or repulsion is the resultant of the interaction between the fields of force emanating from the surface of the adsorbent and the molecules or ions of the adsorbate[15]. The adsorbing species, usually an organic compound, is called the adsorbate, and the solid, usually soil, to which the adsorbate is attracted, is known as the adsorbent. This attraction results from some form of bonding between the chemical and adsorption receptor sites on the solid[2].

Depending on attracted or repelled of adsorbate by the surface of the solid there may be classification of adsorption to two different kinds. Positive adsorption occurs when there is an attraction between the adsorbate and adsorbent which results in the concentration of the adsorbate being higher at the interface than in the adjoining phases. Negative adsorption occurs when the adsorbate is repelled from the interface and thus the adsorbate concentration is greater in the bulk solution than at the interface[16].

Adsorption of pesticides to soil components has been extensively studied by the classical batch-equilibration method[17, 18]. This method involves addition of a range of solute concentrations to a known amount of soil at a constant temperature, and agitating the mixture until equilibrium conditions are achieved. Then, the equilibrium concentration in the liquid phase (C_e) is measured, and the equilibrium concentration of the solute in the solid phase (C_s) is usually calculated by mass balance considerations. The plot of C_s versus C_e , the so called adsorption isotherm, is then commonly modeled as a Langmuir, Freundlich, or linear isotherm[18, 19]. But the batch technique has often

been recognized as insufficient to derive the actual field adsorption parameters[20].

II. Material and Methods

All chemicals and solvents used in these experiments were very pure and purchased from Aldrich, Germany. Stock solutions of Cypermethrin were equally mixed and diluted with methanol to make spiking mixture and working standard solutions. Standard solutions were stored at 4°C in the dark. Appropriate volumes of the standard stock solution were diluted by water to obtain the desired concentrations 3, 5, 10, and 15 µg ml⁻¹. Pesticide experiment for calibration and a control in two replicates concentrations were done with methanol: water solution (70:30%). The absorbance's were measured at 246 nm against blank solution. A linear relationship was obtained between the absorbance and the concentration of Cypermethrin within the range (2-15 ppm) [21].

A. Soil Analysis

Eight fresh soil samples were selected from the top layer (0-15cm depth), are which supposed to have the highest organic content. After the removal of stones and debris, the soil was air-dried under shade, ground, sieved through 2 mm mesh screen and stored in closed black glass container. These soils were used for adsorption-desorption studies[22]. Several tests have been conducted in Table 1.

TABLE 1

Soil pH, texture, moisture, Organic carbon and Organic matter for soil before pollution.

Soil Properties	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈
pH value	7.67	8.34	7.84	8.19	8.21	7.82	8.03	7.83
Clay (%)	43.01	43.01	51.87	53.56	25.25	22.45	22.79	49.41
Silt (%)	52.49	52.49	52.49	45.30	22.10	25.67	74.31	34.08
Moisture content	1.95	2.10	1.49	5.90	3.66	1.43	1.49	5.90
Organic Carbon %	0.13	0.38	0.19	1.02	0.32	1.98	0.19	1.02
Organic matter %	6.697	9.321	4.863	2.373	0.434	4.525	4.863	2.373
CEC (meq 100g ⁻¹)	43.13	8.94	1.98	5.40	0.118	10.87	7.02	10.83

B- Adsorption study

1-Kinetic Study

The adsorption kinetic study was carried out in batch mode using 10 ml centrifuge tubes with Teflon screw caps with (1 g) of solid: solution mass ratio of (1:10) and 1 ml of 3, 5, 10, and 15 µg ml⁻¹ of technical Cypermethrin solution. The studies were first conducted in duplicate for all soils, without any herbicide, on an orbital shaker for a period of 24 h at room temperature (25 ± 21°C). Then to each test tube the appropriate concentration of herbicide was added. After equilibration for 0.5, 1, 2, 3, 6, 24, 48, and 72 h, the suspension was then centrifuged for 30 minutes at 3500 rpm, and 1 ml aliquot of each clear supernatant solution was removed and analyzed on UV-Visible spectrophotometer[23].

2- Desorption

After completion of the adsorption study process, the entire reaction mixture was centrifuged and the supernatant in the conical flask was decanted carefully and analyzed for the residual Cypermethrin sodium concentration. The same amount of decanted supernatant was replaced with different eluents De-ionized water and methanol. The flasks were then kept in an orbital shaker at 3500 rpm for a period of 24 h at 25°C. Soils were left for 0.5, 1, 2, 3, 6, 24, 48, and 72 h to attain the desorption equilibria. After 24 h, 5 mL of sample was withdrawn from each flask and analyzed for Cypermethrin concentration using UV-visible spectrophotometer[24].

III. Results and Discussion

1-The effect of time on concentration of Cypermethrin

Fig. 2 represents the concentration of control solution during the course of the batch experiments for Cypermethrin. It is evident that there was no significant losses of pesticide from the solution during the experiment by the equipment that used[25].

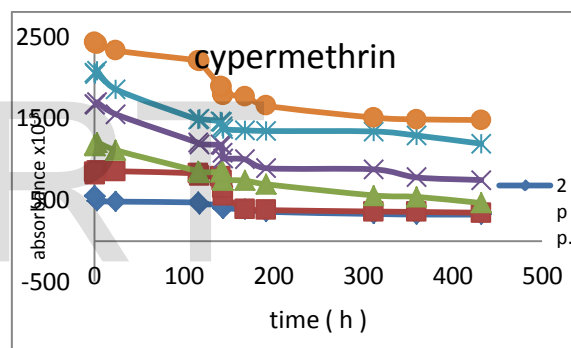


Fig.2: Variation of absorbance with time for Cypermethrin.

2-The effect of concentration of Cypermethrin on adsorption of soils

The mention Figures 3(a-h) showed an extremely rapid rate of the pesticide being removed from solution within the first few hours of the 24 h sorption experiments. Whilst, a second phase of slow sorption appeared to occur over the remaining 48h of the experiment, the duration of which presides any definite conclusions on long term sorption phenomena[25].

The rapid phase is most likely the result of adsorption on surface sites of organic matter, clay colloids, and soil organic matter colloid complexes. The rapid phase of sorption was regarded to be reversible, resulting in sorption and desorption partitioning coefficients that are practically equal. The more gradual phase of sorption probably results in diffusion of pesticides into three-dimensional soil structures[26]. So suggests that the 24h "equilibrium" distribution coefficients may be adequate to characterize the sorption of these chemicals in the field. So sorption coefficients

which were derived by using batch techniques that gave the reproducible results are unaffected by losses arising from the sorption to the experimental apparatus[27].

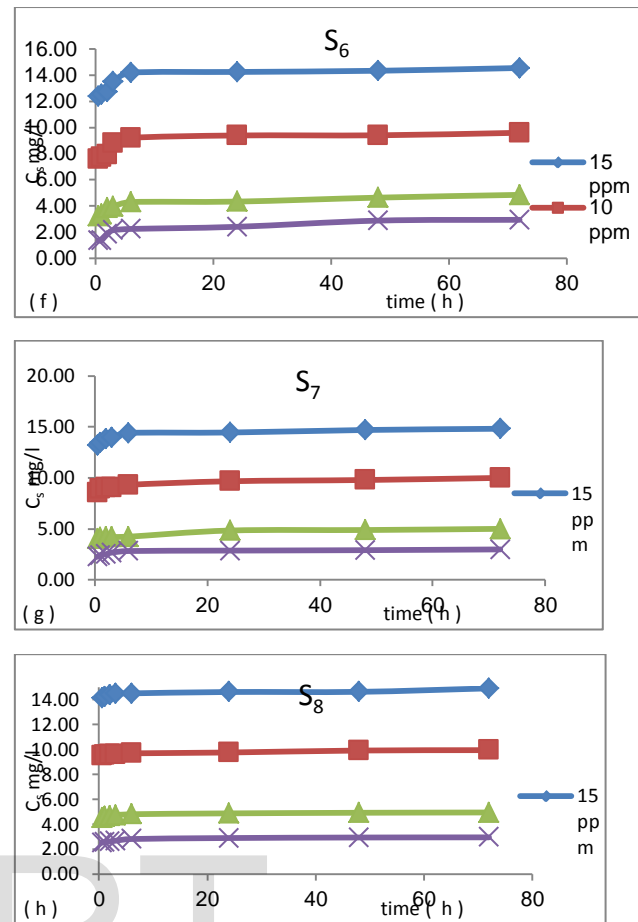
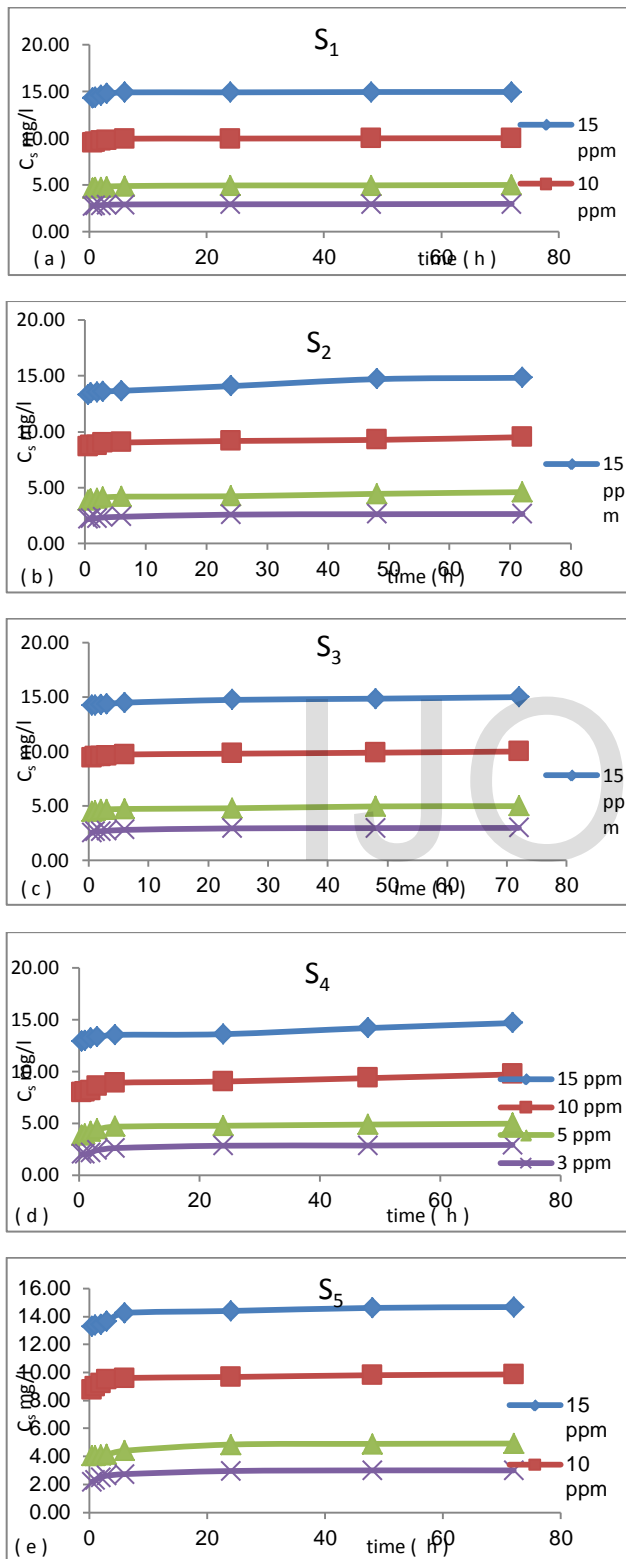


Fig. 3: Variation of concentration with time for adsorption of Cypermethrin on selected soil samples (a) S₁, (b) S₂, (c) S₃, (d) S₄, (e) S₅, (f) S₆, (g) S₇, (h) S₈.

3-Kinetics study of adsorption on soils

The array of kinetics equations used to describe kinetics of soil-pesticide interactions include zero-, first-, and second order[28]. Sorption rate constants were estimated by using the first order rate expression for the pesticide[29]. Which can be formulated as:-

$$C_t = C_0 e^{-K_0 t} \dots\dots\dots (1.1)$$

$$K_0 = \left(\frac{2.303}{t} \right) \log \left[\frac{C_0}{C_0 - C_t} \right] \dots\dots\dots (1.2)$$

Where k_0 is the rate constant (h^{-1}), t the time (h), C_0 the concentration of pesticide added ($\mu g ml^{-1}$) and C_t the amount adsorbed ($\mu g ml^{-1}$) at time t . In all cases, first order equation provided satisfactory fit for the data by linear plots of $\log(C_0 - C_t)$ against[30].

The calculated values of k_0 were summarized in Table 2 for Cypermethrin. Values of k_0 were determined also graphically from the slope of a linear plot of $\log(C_0 - C_t)$ against t . Fig. 4 illustrates the final results which support that the adsorption of the studied pesticides followed first order kinetics; such results are in accordance with those obtained for other system. The calculated K_0 values were oscillated from 0.39 to 1.98, for Cypermethrin. This can be attributed to the value of octanol water

partition coefficient $\log K_{ow}$ 3.98×10^6 for Cypermethrin.
 The Standard error (S.E) values were from 0.001 to 0.079 for Cypermethrin.

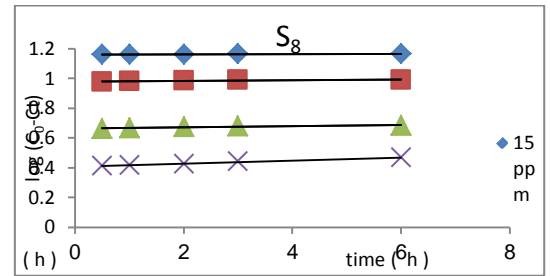
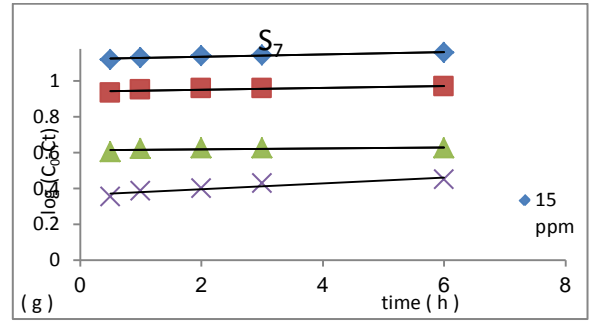
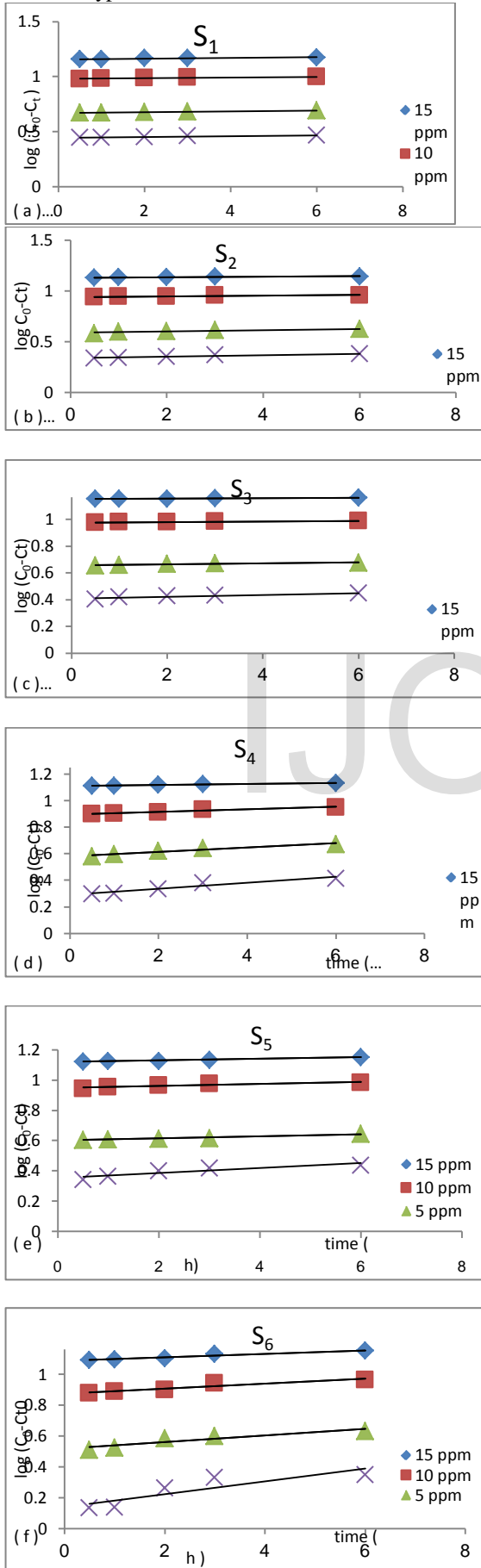


Fig.4: Application of 1st order rate law for Cypermethrin on the selected soil samples (a) S₁, (b) S₂, (c) S₃, (d) S₄, (e) S₅, (f) S₆, (g) S₇, and (h) S₈

TABLE 2

Adsorption rate constants calculated for Cypermethrin on the selected soil samples.

Soil	Conc ppm	Cypermethrin		
		K(calc h ⁻¹)	S.E	R ²
S ₁	3	1.407	0.023	0.984
	5	1.486	0.004	0.669
	10	1.695	0.004	0.880
	15	1.987	0.003	0.819
S ₂	3	0.692	0.030	0.910
	5	0.792	0.006	0.860
	10	1.075	0.004	0.762
S ₃	15	1.163	0.002	0.729
	3	1.052	0.039	0.900
	5	1.248	0.004	0.801
S ₄	10	1.547	0.002	0.944
	15	1.559	0.001	0.995
	3	0.628	0.079	0.649
S ₅	5	0.842	0.016	0.923
	10	0.857	0.010	0.780
	15	1.040	0.004	0.971
S ₆	3	0.821	0.025	0.943
	5	0.882	0.007	0.907
	10	1.201	0.007	0.823
S ₇	15	1.161	0.005	0.971
	3	0.394	0.009	0.968
	5	0.625	0.023	0.823
S ₈	10	0.809	0.016	0.911
	15	0.967	0.011	0.986
	3	0.855	0.033	0.879
S ₈	5	0.898	0.004	0.900
	10	1.098	0.006	0.770
	15	1.187	0.007	0.912
	3	1.027	0.007	0.986
S ₈	5	1.315	0.004	0.905
	10	1.571	0.002	0.888
	15	1.532	0.001	0.722

4. Adsorption isotherm

The most simple and widely used model of the equilibrium adsorption isotherms is that given by a linear relationship, by which it is assumed that the amount of the solute adsorbed by the soil matrix and the concentration C_s of the solute in the soil solution is given by the relationship:-

$$K_d = C_s/C_e \dots\dots\dots (1.3)$$

Where the distribution coefficient " K_d ", is a measure of the retention of the solute by the soil matrix, C_s is the concentration of adsorbed pesticide and C_e the pesticide concentration, in the supernatant solution at equilibrium. The K_d values for Cypermethrin were ranged from 7.298-20.254 $ml\ g^{-1}$.

The adsorption isotherms are well fitted to the Freundlich model: it can be expressed as:-

$$C_s = K_f C_e^n \dots\dots\dots (1.4)$$

Where: C_s is the amount of adsorbed pesticide per unit mass of soil, C_e is the equilibrium pesticide concentration in solution, K_f is Freundlich sorption coefficient, n is empirical constant[31]. Adsorption isotherm parameters were calculated by using the linearized form of Freundlich equation "(1.5)" :-

$$\log C_s = \log K_f + n \log C_e \dots\dots\dots (1.5)$$

Values of K_f calculated from the linearized form of equation "(1.5)" by plotting of $\log C_s$ versus $\log C_e$, were also summarized in Table 3. Which oscillated between 9.204-46.374 $ml\ g^{-1}$. Values of K_f were in the following order $S_7 > S_8 > S_1 > S_5 > S_2 > S_6 > S_3 > S_4$.

Data from the batch adsorption on the selected soil samples will conform to Langmuir equation[32].

$$C_s = C_m \frac{K_1 C_e}{1 + K_1 C_e} \dots\dots\dots (1.6)$$

Where C_s and C_e are defined before, C_m is the maximum amount of pesticide adsorbed (adsorption maxima $\mu g\ g^{-1}$), and it reflects the adsorption capacity and K_1 is Langmuir adsorption coefficient,(binding energy coefficient) (mlg^{-1}). The linear form of Langmuir equation is:-

$$\frac{C_e}{C_s} = \frac{1}{(C_m K_1)} + \frac{C_e}{C_m} \dots\dots\dots (1.7)$$

Values of K_1 were obtained by plotting C_e/C_s versus C_e , and data are tabled in table 3 such values of adsorption capacity K_1 ranged from 0.203-2.163 mlg^{-1} because they can vary among soils due to the quantities and composition of soil components[32]. Values of K_1 for adsorption of Cypermethrin were in the order $S_6 > S_1 > S_3 > S_5 > S_4 > S_2 > S_7 > S_8$. The maximum amount of pesticides adsorption ($C_m\ \mu g\ g^{-1}$) ranged from 6.285-53.19.

TABLE 3

Adsorption isotherm parameters for the linear, Freundlich and Langmuir models for Cypermethrin.

Adsorption Model	Parameter	Soils							
		S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	S ₈
Distr.	K_d (calc.)	20.122	12.825	12.974	20.254	17.002	7.298	7.89	14.484
	S.E	2.672	2.576	2.664	2.534	2.616	2.552	2.642	2.624
coffi.	R^2	0.93	0.97	0.98	0.96	0.97	0.89	1.00	0.99
	K_f ($ml\ g^{-1}$)	21.979	16.557	13.803	9.204	21.071	15.132	46.374	45.656
Freundlich	S.E	0.156	0.163	0.156	0.154	0.166	0.154	0.156	0.156
	N	1.17	1.96	1.17	0.87	2.55	0.57	1.33	1.13
Langmuir	R^2	0.94	0.98	0.96	0.98	0.96	0.95	0.98	0.97
	K_1 (mlg^{-1})	1.980	0.777	1.5460	0.873	1.427	2.163	0.737	0.203
Langmuir	S.E	0.005	0.019	0.001	0.293	0.002	0.007	0.003	0.002
	C_m	16.835	6.285	49.751	26.385	53.905	16.806	53.191	20.408
Langmuir	R^2	0.79	0.95	0.87	0.94	0.81	0.87	0.92	0.77

5. Desorption Kinetics

Desorption of pesticides was studied in the eight selected soil samples initially treated with different concentrations (3, 5, 10, 15) $\mu g\ ml^{-1}$. The amount of pesticides that remained on soils at each desorption stage was calculated as the difference between the initial amount adsorbed (the amount of pesticides sorbed at equilibrium concentration corresponding to the initial concentration) and the amount desorbed (after each removing), all determinations were carried out in duplicate.

The percentage of adsorption is calculated for each test tube at each time, according to the equation "(1.8)":-

$$\% \text{ Sorption} = \frac{C_i - C_e}{C_i} \times 100 \dots\dots\dots (1.8)$$

where C_i = the concentration before adsorption, C_e = the concentration after adsorption[33].

While the percentage of desorption is calculated from equation"(1.9)"[34]:-

$$\% \text{ Desorption} = \frac{\text{amount of eluted pesticide}}{\text{total amount of adsorbed pesticide}} \times 100 \dots\dots\dots (1.9)$$

Values of % Desorption for adsorption of the three pesticides on the eight selected soil samples are shown in Fig. 5 and the results are summarized in Table 4, In general, it is obvious that Adsorption % is increase in concentration of pesticides, while desorption decreases apart from some exceptional cases in both processes. This trend is the previous studies[35, 36].

Table 4: Percentage of cypermethrin adsorbed (ads%) and desorped (% Des) on the selected soil samples.

Soils	Conc. ppm	% ads	% des
S ₁	3	99.18	25.96
	5	99.15	14.89
	10	99.45	10.65
	15	99.31	10.67
S ₂	3	87.46	31.09
	5	88.96	25.66
	10	92.78	12.96
	15	93.93	9.35
S ₃	3	98.58	21.66

S ₁	5	99.02	16.08
	10	98.91	8.89
	15	99.03	6.20
S ₄	3	95.14	30.50
	5	95.26	26.07
	10	93.63	15.54
S ₅	15	94.66	12.66
	3	98.58	13.14
	5	97.93	14.01
S ₆	10	98.06	7.32
	15	97.45	7.10
	3	96.15	16.84
S ₇	5	97.08	11.68
	10	94.05	6.19
	15	95.59	7.68
S ₈	3	96.96	27.41
	5	97.69	16.44
	10	97.94	9.54
S ₈	15	98.02	12.42
	3	96.76	21.10
	5	97.57	15.96
S ₈	10	97.57	8.34
	15	97.45	7.06

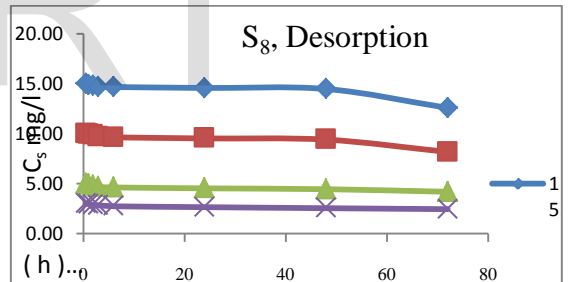
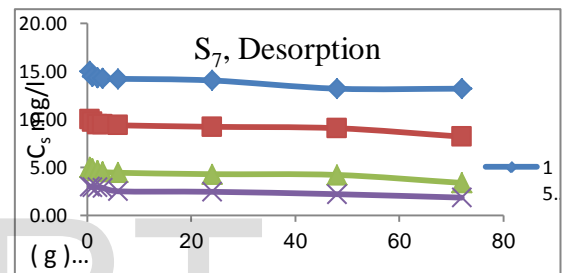
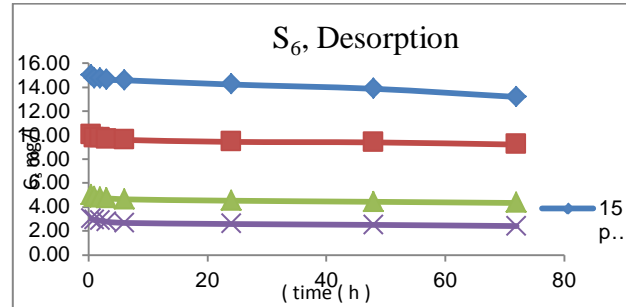
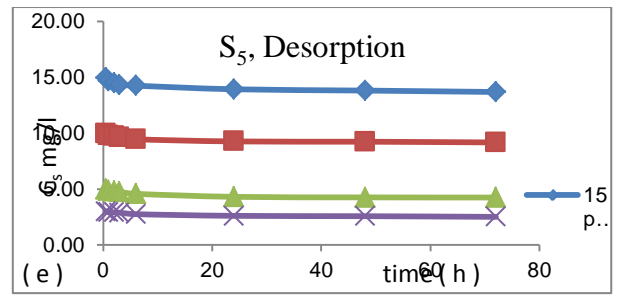
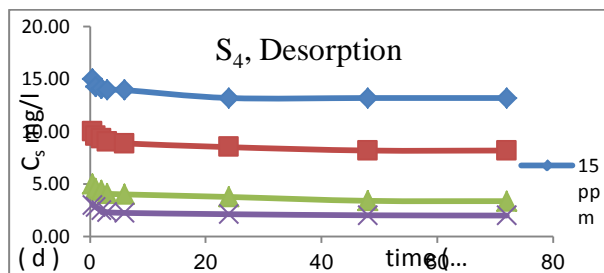
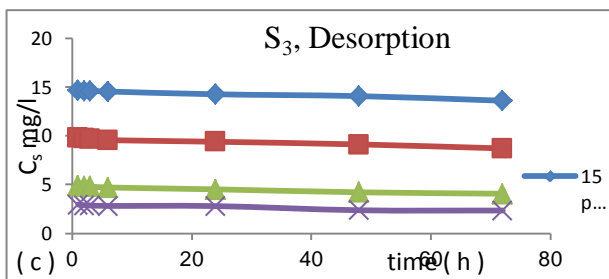
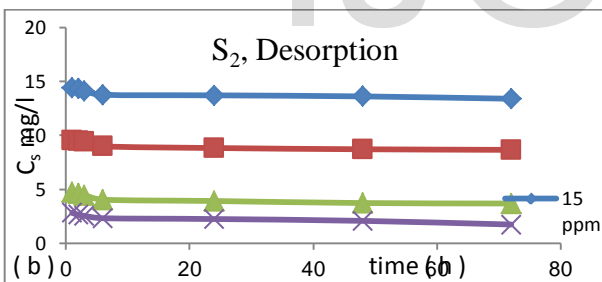
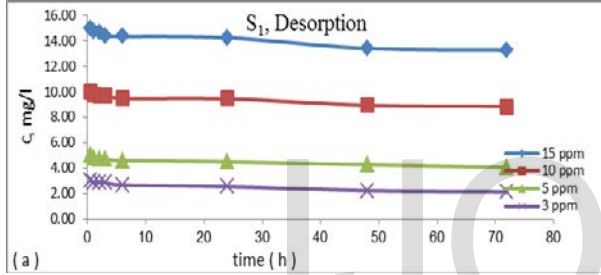


Fig.5 (a-h): amount of cypermethrin desorption kinetically with time on selected soil samples

6. Thermodynamic studies of adsorption

6.1. Standard thermodynamic functions of adsorption

The knowledge of kinetic and thermodynamic is essential to understand the basic reactions in soils, but unfortunately such investigations of clay and soils are limited. This is particularly true for soils that contain complex mixtures of clay minerals, non-crystalline components, oxides, hydroxides and organic matter[37, 38]. So adsorption experiments were conducted at 288.15, 298.15, and 308.15 K to study the thermodynamic (equilibrium) parameter, associated with the adsorption of the studied pesticides on the selected soil samples.

6.2. Equilibrium constant

The values of K_0 were obtained by plotting $\ln(C_s/C_e)$ vs. C_s and then extrapolating C_s to zero from equation "(10)" [39,40].

$$\ln K_0 = \ln \frac{C_s}{C_e} \dots\dots\dots(1.10)$$

The results of equilibrium constants obtained at 288.15, 298.15, and 308.15 K for soils are summarized in Table 5. It is obvious that the trend of thermodynamic equilibrium constant K_0 is decreasing with increase in temperature for all soil pesticides interaction[41]. However, for cypermethrin the trend was $S_3 > S_8 > S_7 > S_1 = S_5 > S_4 > S_6 > S_2$ soils.

6.3. Standard free energy change

The standard free energy for the transfer of pesticide molecules between the solid and aqueous phases was estimated using

$$\Delta G^0 = - RT \ln K_0 \dots\dots\dots(1.11)$$

Where R is the universal gas constant ($J. mol^{-1}.K^{-1}$) and T (K) is temperature[42]. The values of ΔG^0 for adsorption of the studied pesticides on the selected soil samples at 288.15, 298.15, and 309.15 K were summarized in Tables 5 . The ΔG^0 values were in the range -10.296 to -0.179 ($kJ mol^{-1}$). Values of adsorption at the three temperature 288.15, 298.15, and 309.15 K of pesticide on soil samples were in the order: $S_3 > S_8 > S_7 > S_1 = S_5 > S_4 > S_6 > S_2$, $S_3 > S_8 > S_1 > S_7 > S_5 > S_4 > S_2 > S_6$, and $S_3 > S_1 > S_8 > S_4 = S_7 > S_5 > S_2 > S_6$ respectively.

TABLE 5

Equilibrium constants and standard free energy change at three different temperatures for adsorption of cypermethrin on the selected soil samples.

cypermethrin	parameter	Soil							
		S1	S2	S3	S4	S5	S6	S7	S8
T:k	lnK ₀	3.5	1.5	4.3	3.4	3.5	2.5	3.7	3.8
	ΔG ⁰ (kJ.mol ⁻¹)	-8.38	-3.59	-10.29	-8.26	-8.38	-5.98	-8.85	-9.09
T:K	lnK ₀	3.2	1.2	4.0	2.4	2.8	1.1	3.2	3.6
	ΔG ⁰ (kJ.mol ⁻¹)	-8.17	-2.97	-9.91	-5.94	-6.93	-2.72	-7.92	-8.91
T:K	lnK ₀	3.1	1	3.9	2.2	1.7	0.07	2.2	3
	ΔG ⁰ (kJ.mol ⁻¹)	-7.93	-2.56	-9.98	-5.63	-4.35	-0.17	-5.63	-7.68

6.4. Standard enthalpy change

The standard enthalpy change of adsorption (ΔH^0) represents the difference in binding energies between the solvent and the soil with the pesticides. The ΔH^0 values explained the binding strength of pesticides to the soil[25]. By non-calorimetric method for the measurement of reaction enthalpies, values of ΔH^0 also determined graphically from the following equation "(12)"[43].

$$\ln K_0 = - \frac{\Delta H^0}{RT} + \text{const} \dots\dots\dots(1.12)$$

The enthalpy of adsorption in the range 288.15-308.15 K was calculated from the slope of the plot of $\ln K_0$ against $1/T$ Fig. 6. It is evident that a straight line is expected with slope equal to $-\Delta H^0/R$. the results were

summarized in Table 6. Values of ΔH^0 oscillated in the -55.31 to -14.75 $kJ mol^{-1}$.

The values of R^2 were in the range 0.88-1.00 cypermethrin which supported the linear nature of the plot. The amount of energy released during adsorption is changed because the supply of thermal energy is different. The negative values pointing to the formation of an activate complex by coordination or association of the both pesticides and exchangeable cation with results loss in the degree of freedom of the pesticide. The different values of ΔH^0 for adsorption of the same pesticide ON the selected soils may be correlated to differences in soil constituents[25].

6.5. Standard entropy change

The values of standard entropy change ΔS^0 of adsorption were determined by using the "equation below"

$$\ln K_0 = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \dots\dots\dots(1.13)$$

The values of ΔS^0 were determined from the plot of $\ln K_0$ against $1/T$ Fig. 6 from which a straight lines were obtained with a slope of $-\Delta H^0/R$ and intercept equals $\Delta S^0/R$. The results were summarized in Table 6. The values of ΔS^0 followed the range -159.77 to -15.98 $Jmol^{-1}K^{-1}$.

TABLE 6

Standard enthalpy change and standard entropy change (determined graphically) for adsorption of cypermethrin.

parameters	Soils							
	S1	S2	S3	S4	S5	S6	S7	S8
ΔH ⁰ (kJ.mol ⁻¹)	-14.75	-18.44	-14.75	-46.09	-40.56	-37.98	-55.31	-29.50
ΔS ⁰ (J.mol ⁻¹ .K ⁻¹)	-22.63	-51.71	-15.98	-133.60	-117.56	-122.73	-159.77	-69.65
R ²	0.93	0.99	0.93	0.88	0.98	1.00	0.96	0.91

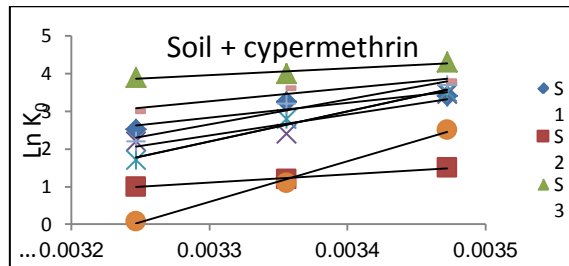


Fig. 6: Variation of $\ln K_0$ with $1/T$ for adsorption of cypermethrin.

Conclusions

The batch kinetics experiments were used to investigate the behavior of Cypermethrin in eight agricultural soil samples. Generally, adsorption

increased with concentration, the initial step was characterized as rapid and low energy while the second step was slow and high energy accompanied by slow diffusion to sites within the soil matrix. The magnitude of all K_d , K_f and K_1 values were indicated as moderate to low adsorption for all pesticides. Freundlich model more accurately predicted the behavior of pesticides desorption. The values of ΔG^0 increased with rise in temperature.

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