Kinetic & Thermodynamic Study for Adsorption– Desorption of Diazinon with Copper in The Presence of Surfactant

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Abstract - In the present work change in the adsorption-desorption processes of Diazinon[O,O-diethylo-(2-isopropyl-6-methyl4pyrimidinyl) phosphorothioate] which is nonionic-organophosphorous pesticide, preformed by using batch equilibrium experiments on six agricultural soil samples. The kinetics study for adsorption processes investigated that first order rate law and power function equation model provided the best correlation with experiment results. The isothermal models Linear, Freundlich, and Langmuir were applied to describe the adsorption-desorption affinities to the soils. Thermodynamic parameters (ΔG, ΔH and ΔS) were also calculated according to the values of binding Langmuir constant K_L at 10, 25, 40 $\pm$1ºC. Linear coefficient K_d values for adsorption process of diazinon varied between 3.261 - 6.413 mlg-1. Freundlich coefficient KF values for adsorption process varied between 1.194 - 1.506 mlg^{-1}. Langmuir coefficient KL for adsorption process varied between 0.017 - 0.020 mlg^{-1}. The negative values for each of ΔG, ΔH and ΔS constants confirmed that diazinon adsorption processes more at lower temperature and done via enthalpy effect.

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KINETIC THERMODYNAMIC STUDY FOR ADSORPTION DESORPTION OF DIAZINON WITH COPPER IN THE PRESENCE OF SURFACTANT

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Abstract - In the present work change in the adsorption-desorption processes of Diazinon[O,O-diethylo-(2-isopropyl-6-methyl ₄ pyrimidinyl) phosphorothioate] which is nonionic-organophosphorous pesticide, preformed by using batch equilibrium experiments on six agricultural soil samples. The kinetics study for adsorption processes investigated that first order rate law and power function equation model provided the best correlation with experiment results. The isothermal models Linear, Freundlich, and Langmuir were applied to describe the adsorption-desorption affinities to the soils. Thermodynamic parameters (ΔG, ΔH and ΔS) were also calculated according to the values of binding Langmuir constant K_L at 10, 25, 40 $\pm$1°C. Linear coefficient K_d values for adsorption process of diazinon varied between 3.261 - 6.413 mlg^{-1}. Freundlich coefficient KF values for adsorption process varied between 1.194 - 1.506 mlg^{-1}. Langmuir coefficient K_L for adsorption process varied between 0.017 - 0.020 mlg^{-1}. The negative values for each of ΔG, ΔH and ΔS constants confirmed that diazinon adsorption processes more at lower temperature and done via enthalpy effect.

To investigate the presence of copper on the adsorption process of diazinon which enhance the adsorption, K_d, K_F and K_L values varied between 4.809 - 9.454 mlg^{-1}, 1.198-1.656 mlg^{-1} and 0.008 - 0.023 mlg^{-1} respectively. Application of nonionic surfactant at critical micelles concentration cmc on the desorption for the presence of copper on the adsorption process of diazinon, K_d, KFdes and K for desorption process in presence of the nonionic surfactant ranged varied between 3.729- 8.058, 0.800- 1.207 and 0.005- 0.011 mlg^{-1} respectively. All results show a high hysteresis effect for Adsorption desorption processes.

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I. Introduction

Diazinon [O,O-diethylo-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] insecticide for agricultural and indoor pest control, it used for the control of pest in cruciferous vegetables and for controlling insect pests of tobacco plants [1&2]. Organophosphours compound tend to have the characteristic phosphoryl bond oxon P=O, and thiophosphoryl bond thion P=S [3&4]. It degrades photochemically produced hydroxyl radicals, degrading from thion to oxon compounds [5]. The detection of organophosphates based on the reaction of the unshared pair of electrons available at the nitrogen of a pyridine ring with the available pair of electrons at the positive site of the organophosphates. A displacement takes place, with the alcohol moiety being split off [6&7]. Hydrolysis of diazinon is relatively slow at pH 7 and 9, but is faster at pH 5 [8]. Diazinon has toxic degradation products, and is a clear threat to aquatic ecosystems and salmon at current use rates, it commonly detected in surface water [9]. The rate of adsorption in soil pore governed by temperature which indicated a partly physical and partly chemical[10]. The correction of solubility- temperature effect on the standard enthalpy of the pesticide adsorption processes[11].

The presence of copper enhances adsorption due to strongly coordination and complex formation or through forming a bridge between the soil and diazonin. Finally it may be via the lowering negative charge, which easily adsorbed to the negatively charged soil surface [12].

The presence of nonionic surfactant with nonpolar end at cmc concentration enhances the apparent solubility of hydrophobic organic compounds when both coexist in soil. It represent an important tool for chemical remediation of contaminated soils[13&14]). The molecule character has a great effect on adsorption and mobility through soil[15].

II. Materials and Methods

a) Soils

Fresh soil samples were taken from six soil samples were collected from six main agricultural, representing a range of physico-chemical properties. Subsamples of homogenized soils were analyzed for moisture content, organic matter content, particle size distribution, texture, pH, loss on ignition and exchangeable basic cations the detail were characterized in previous article[16].

b) Materials

Analytical grad substituted with following purities expressed in weight percent diazinon (purity 99%), were all purchased from Riedal-de Haen, Sigma-Aldrich company ltd. A nonionic surfactant TritonX 100

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(TX-100), its chemical name is [Octylphenol ethoxclyate] surfactant, its Empirical formula is $(C_8H_{17}C_6H_4O(CH_2CH_2O)_NH)$; where N=9.5, its molecular weight is 625 g mol^{-1}, and its critical micelles concentration cmc concentration 0.0002M was obtained from Fluka AG, Buchs SG, and were used without further treatments. All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of the pesticides were prepared in deionised water.

c) Adsorption-Desorption Experiments

Adsorption of the pesticides from aqueous solution was determined at temperature (25±1 C employing a standard batch equilibrium method. An aqueous stock solution of diazinon of 100 mgL^{-1} was prepared daily by diluting 1μl in 100 ml de-ionized water and methanol as co-solvent[6]. The stock and working solution were stored in the dark at 5°C or up to two days. Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (25, 50, 75, and 100 μg ml^{-1}) at the soil solution ratio 1:10. The samples plus blanks (no pesticide) and control (no soil) were thermostated and placed in shaker for 0.5, 1, 2, 2.5, 3, 3.5, 4, 6 and 24h. The tubes were centrifuged for 20 min. at 3000 rpm. One ml of the clear supernatant was removed and analyzed for the pesticide concentration. Pesticide identification was done by PerkinElmer series 200 USA family high performance liquid chromatography (HPLC) equipped with a changed loop (20μl), C_{18} reversed phase column, flow rate 1.5 ml min^{-1}, and a variable wave length UV detector at wavelength 240 nm. Separation of diazinon in aqueous phase was achieved with a mobile phase of ratio 65:35 acetonitrile to water. Under these conditions the retention time was 4.49 min. To study the effect of temperature the same experiments done at temperature (10, 25, 40 ±1 C°) employing a standard batch equilibrium method[11].

The adsorption of diazinon-copper experiments done in the presence of 40 mgL^{-1}copper, the samples were shaken for 24h, and the amounts of Cu adsorbed were calculated from the difference before and after equilibrium. Each sample was injected twice to determine the pesticide content by integrating the obtained peak with the respective standard pesticides. The pesticide content was average of two measurements, with no more than 5% deviation between the measurements. Desorption processes were done at 25 ±1 C and done as each test tube was placed in a thermostated shaker after equilibration for 24 h with different pesticide concentrations the samples were centrifuged 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of surfactant and this were repeated for four times [12&17].

III. Data Analysis

a) Adsorption Kinetics

The rate constants for adsorption of each pesticide on soils were calculated using the first order rate expression[18]:

$$Log(C_\circ - C_t) = \log C_\circ - \frac{k}{2.303}t \qquad (1)$$

Where k is the rate constant (hour^{-1}), t the time (hour), C_o the concentration of pesticide added(μg ml^{-1}) and C_t the amount adsorbed (μg ml^{-1}) at time t. In all cases, first order equation provided satisfactory fit for the data by a linear plots of log ($C_o - C_t$) against t as shown in (Table 1).

Power function equation used to describe the pesticides adsorption-desorption from soils is given as[19]:

$$Ln(C_t) = \ln C_\circ - k \ln t \qquad (2)$$

Where C_t is the amount of the pesticides released at time t. A plot lnC_t versus ln (t) should give a straight line with a slope (k) and the intercept is ln (C_o) where the value of slope of straight line is coefficient of release rate as shown in (Table 1).

b) Adsorption-Desorption Isotherms

i. Linear Adsorption Coefficient (Distribution Coefficient)

The distribution coefficient (K_d) was calculated using the equation [17&20]:

$$C_s = K_d C_e \qquad (3)$$

The distribution coefficient (K_d) was calculated by taking the ratio of adsorption concentration in soil (C_s) and equilibrium concentration in solution (C_e). The results were summarized in (Table 2, 3, 4, and 6).

ii. Freundlich Adsorption Isotherm

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation[21]:

$$LogC_s = \log K_F + \frac{1}{n} \log C_e \qquad (4)$$

C_s and C_e were defined previously, K_F is Freundlich adsorption coefficients, and n is a linearity factor, it is also known as adsorption intensity, 1/n is the slope and logK_F is the intercept of the straight line resulting from the plot of logC_s versus logC_e. The values of K_F and 1/n calculated from this regression equation showed that Freundlich adsorption model effectively describes isotherms for both pesticides in all cases. The results were summarized in (Table 2, 3, 4, and 6).

iii. Langmuir Adsorption isotherm

Data from the batch adsorption conform to Langmuir equation[22]:

$$\frac{C_e}{C_s} = \frac{1}{C_m K_L} + \frac{C_e}{C_m} \qquad (5)$$

C_m is the maximum amount of pesticide adsorbed (adsorption maxima, $\mu g \ ml^{-1}$), it reflects the adsorption strength and K_L is the Langmuir adsorption coefficient, binding energy coefficient. The results were summarized in (Table 2, 3, 4, and 6).

The same equations (3, 4 and 5) used to describes the process of desorption in all experiments and on all soil samples [23]. Where k is k_{des} is the desorption rate constant (h^{-1}), Ct is the amount of released pesticides at time t and C is C_e is the amount of released pesticides at equilibrium the results was demonstrated in (Table 6).

c) Thermodynamic parameters
i. Standard free energy change

Values of binding Langmuir constant K_L, can be expressed in terms of the standard Gibbs or free energy for adsorption (ΔG) [24].

$$\Delta G = -RTLnK_L \qquad (6)$$

The results were summarized in table 5.

ii. Standard enthalpy change

The standard enthalpy change of adsorption (ΔH) represents the difference in binding energies between the solvent and the soil with the pesticides. Values of ΔH determined graphically from the following equation[25]:

$$LnK_L = \frac{\Delta H}{RT} + cons \tan t \qquad (7)$$

Plotting $-lnK_L$ against 1/ T, a straight line is expected the standard enthalpy change (ΔH) of adsorption were determined from the slope as shown in Fig1. The results were summarized in table 5.

iii. Standard entropy change

The entropy changeΔS for each system were determined by using the equations bellow [26].

$$\Delta G = \Delta H - T\Delta S \qquad (8)$$

The values of ΔS were summarized in table 5.

d) Hysteresis coefficient

Hysteresis coefficients (H), can be determined by using the following equation[27].

$$H_1 = \frac{n_a}{n_{des}} \qquad (9)$$

Where n_a and n_{des} ratio for Ferundlich adsorption and desorption constants, respectively, indicating the greater or lesser irreversibility of adsorption in all samples, the highest values corresponding for which the highest adsorption constant was obtained. The coefficient H_1 is a simple one and easy to use, Data in table 7 demonstrated H_1 values the selected soil samples.

The extent of hysteresis was quantified by using hysteresis coefficient (ω), it was defined on the discrepancy between the sorption and desorption isotherms, and calculated by using Freundlich parameters estimated from sorption and desorption isotherms separately, (ω) expressed as[28]:

$$\omega = (\frac{n_a}{n_{des}} - 1)x100 \qquad (10)$$

Recently Zhu et. al [23] proposed an alternative hysteresis coefficient (λ) based on the difference in the areas between adsorption and desorption isotherms, they derived the following expression for the parameter λ for the traditional isotherms:

$$\lambda = (\frac{n_a + 1}{n_{des} + 1} - 1)x100 \qquad (11)$$

e) Organic matter normalized adsorption coefficient

The linear or distribution coefficient (K_d) is related to soil organic carbon (OC) and soil organic matter (OM) by the following equations[21]:

$$\%OC = \frac{\%OM}{1.724} \qquad (12)$$

$$K_{OM} = \frac{100K_d}{\%OM} \qquad (13)$$

$$K_{OC} = \frac{100K_d}{\%OC} \qquad (14)$$

IV. Results and Discussion

Data in Table 1 showed the values of rate constant for the adsorption of diazinon on different soil samples using two models first order rat law and power function equations, the values were in the range from 0.967 to 2.139 h^{-1} and 0.104 to 0.244h^{-1} for the two equations respectively, and the value of standard error (S.E.) from 0.129 to 0.185 and from 0.132 to 0.214 for the two equations respectively. Diazinon has a high octanol water partition coefficient ($logK_{ow}$= 3.81) exhibited the moderate rate of accumulation with 14.1 % adsorption on the soil solid matrix after 0.5 hours. The

adsorption of diazinon in all cases followed first order rate law as reported in literature [29]. The non-linear adsorption isotherms might be expected for diazinon which competes with a limited number of cation exchange sites contributes significantly to adsorption process. The magnitude of the Kd is moderate were ranged between 3.261 - 6.413 mlg^{-1}. as shown in Fig2$_{-a}$. These findings are in agreement with the hydrophobicity of the pesticide as represented by octanol-water partition coefficient value [29].

The Freundlich adsorption model effectively describes isotherm for diazinon on all soil samples as shown in Fig2-b, values of K_F were varied from 1.194 1.506 mlg-1. Values of KF   for diazinon was in the order of S3>S4>S5>S1>S6>S2, the difference in the behavior of diazinon toward the soil samples is due to the difference in the type of interaction with the soil which it is likely due to the binding of its phosphoric side moiety to cation on the clay or organic matter, adsorption is correlated with unoqupied phosphate adsorption capacity of a soil. The values of n all n>1 the variable slopes of the adsorption isotherm obtained for different soil systems studied reveal that diazinon adsorption on soil is complex phenomena involving different types of adsorption sites with different surface energies[20].

Langmuir adsorption model effectively describes isotherm for diazinon on all soil samples as shown in Fig2-c, with regression factor R^2 ranged between 0.704- 0.948, values of K_L ranged from 0.017 to 0.020 mlg^{-1} the maximum amount of diazinon adsorption (C_m) ranged from 333.33 to 1000 mg g^{-1} the high C_m values on the examined soil samples could be explained by the high affinity of diazinon to bind to soil organic matter and clay values of K_L for diazinon was in the order of $S_4>S_1>S_3>S_6>S_5>S_2$. The different value of adsorption coefficients for the same pesticide with different soils is due to soil organic carbon and clay content. A significant differences in the chemistry of the soil organic carbon may be encountered from soil to soil in its polarity, elemental composition, aromaticity, and condensation evolution from loss polymer to condensed cool –like structures[30&31]. Therefore, soil organic carbon and clay are not adequate to estimate different soil adsorption capacity, but also their quality and their chemical nature are important.

Data in Table 2, 3, and 4 shows the effect of temperature on the adsorption of diazinon on different soil samples. The values of free energy change ΔG for adsorption of the studied pesticides on the selected soil samples at 283.15, 298.15 and 313.15K were summarized in tables 5. The negative value of ΔG and decreased with the rise in temperature, indicating that at all experimental temperatures; the interactions of diazinon on soils were spontaneous [32]. The ΔG values were in the range -5.888 to -11.742 KJmol^{-1}. The negative values of ΔH indicated the exothermic

behaviors of the reaction, as the temperature increases the negative values of ΔH is decreased. The linear nature of the plot indicates that the mechanism of adsorption is not changed as temperature is changed. The values of enthalpy change ΔH followed the range -7.892 to -47.887 KJmol^{-1}. The values of R^2 were in the range 0.816 to 0.996. The negative enthalpy of adsorption for partition coefficient, indicating an exothermic binding reaction, showing that the interaction of pesticides with the soil is an energetically stable exothermic process and the adsorption occurred through a bonding mechanism[11&33]. The negative values of entropy change ΔS followed the range -65.600 to -194.48 Jmol^{-1} k^{-1}.

The presence of copper on the adsorption process of diazinon which enhance the adsorption as shown in table 6, K_d, K_F and K_L values for adsorption process varied between 4.809 - 9.454 mlg^{-1}, 1.198-1.656 mlg-1 and 0.008- 0.023 mlg^{-1} respectively. The regression coefficient R^2 value ranging between 0.697-0.766, 0.853-0.993, and 0.713-0.987 for each model respectively, the standard error S.E. value between 0.118 – 0.372, 0.424-0.569, and 0.231-0.287. The regression equations relating that the highest values are the most fitted model, our results agreed with research[13]. The desorption experiments were conducted with a nonionic surfactant TritonX-100 at concentration 0.1cmc, cmc and 20cmc on diazinon sorbed soil[17&34]. The K_d values for desorption process in the presence of cmc concentration of the surfactant varied between 3.729- 8.058mlg^{-1} while the value of R^2 ranging from 0.874 to 0.979 with standard error S.E. value between 0.165 – 0.630. Freundlich coefficient for desorption process K_{Fdes} for diazinon in the presence of cmc concentration of the surfactant varied between 0.800- 1.207 mlg^{-1}, the R^2 value ranging from 0.982 to 0.998 with S.E. 0.404-0.607, the values of n_{Fdes} 1.166-1.348. Langmuir desorption coeffecient K_L ranged from 0.005- 0.011 mlg^{-1} the maximum amount of diazinon desorption (C_m) ranged from 500 to 1000 mg g^{-1} the R^2 value ranging from 0.636 to 0.989 with S.E. 0.138-0.219.

Data in table 7 demonstrated H1 values for diazinon from the selected soil samples in the range from 1.236-1.714. The calculated values of hysteresis coefficient (ω) for adsorption-desorption for diazinon on the selected soil samples ranged from 23.6 to 71.4. Whereas hysteresis coefficient (ω) is only applicable for the traditional type isotherms of the successive desorption[35&36].The hysteresis coefficient (λ) for diazinon from the selected soil samples were ranged from -22.3 to 47.8 .

V.   CONCLUSION

The batch kinetics experiments were used to investigate the behavior of diazinon in six agricultural soil samples. The soil OC and clay content and the chemical

nature of both constituents determined the adsorption affinity of the soil. The using of pesticide diazinon may increase pesticides leaching to depth relative to the use on agricultural soil samples. The cmc concentration gave the best results in desorption. So the used surfactant solution is therefore fairly effective in desorption of diazinon from the contaminated soil. Thermodynamics and kinetic investigations of clay and soils are limited. Adsorption experiments were conducted at 10, 25, and 40°C to study the thermodynamic parameter, associated with the adsorption of the studied pesticides on the selected soil samples.

VI. Acknowledgements

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Table 1 : Adsorption rate constants for diazinon adsorption on the selected soil samples.

Soil	Conc. ppm	First order rate equation			Power –function equation		
		(calc h⁻¹)		R^2	(calc h⁻¹)	S.E	R^2
S_1	25	1.288	0.148	0.884	0.244	0.135	0.963
	50	1.372	0.144	0.824	0.121	0.174	0.932
	75	1.500	0.143	0.967	0.108	0.197	0.998
	100	1.320	0.153	0.813	0.123	0.208	0.918
S_2	25	1.442	0.144	0.978	0.107	0.142	0.917
	50	1.566	0.143	0.958	0.157	0.179	0.801
	75	1.605	0.144	0.910	0.135	0.200	0.984
	100	1.083	0.138	0.997	0.131	0.214	0.892
S_3	25	1.071	0.129	0.848	0.172	0.133	0.980
	50	1.329	0.129	0.939	0.185	0.175	0.973
	75	1.454	0.130	0.959	0.170	0.197	0.898
	100	1.429	0.130	0.984	0.186	0.211	0.858
S_4	25	0.967	0.131	0.986	0.152	0.132	0.839
	50	1.197	0.134	0.937	0.180	0.173	0.946
	75	1.395	0.134	0.930	0.146	0.198	0.707
	100	1.411	0.139	0.985	0.182	0.211	0.913
S_5	25	1.092	0.135	0.863	0.136	0.135	0.994
	50	1.166	0.133	0.974	0.185	0.172	0.934
	75	1.422	0.139	0.979	0.171	0.197	0.831
	100	1.518	0.145	0.950	0.184	0.212	0.952
S_6	25	1.117	0.130	0.985	0.160	0.138	0.928
	50	1.596	0.145	0.969	0.106	0.179	0.960
	75	2.139	0.185	0.945	0.109	0.202	0.908
	100	1.579	0.142	0.991	0.104	0.214	0.931

Table 2 : Adsorption of diazinon linear, Freundlich and Langmuir models isotherm parameters on the selected soil samples at 283.15 K.

Adsorption Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	12.927	6.976	8.773	10.441	6.931	8.814
	S.E	0.376	0.279	0.329	0.286	0.132	0.127
	R^2	0.724	0.764	0.778	0.810	0.788	0.893
Freundlich	K_F(mL/g)	1.678	1.601	1.641	1.567	1.288	1.288
	S.E	0.639	0.499	0.551	0.592	0.509	0.558
	n_F	1.730	2.079	1.969	1.647	1.412	1.311
	R^2	0.991	0.938	0.951	0.998	0.963	0.987
Langmuir. coffi.	K_L (ml/g)	0.024	0.076	0.061	0.018	0.011	0.082
	S.E	0.205	0.263	0.242	0.219	0.282	0.225
	C_m(μg/g)	1000	500	1000	1000	1000	1000
	R^2	0.999	0.833	0.841	0.956	0.937	0.965

Table 3 : Adsorption of diazinon linear, Freundlich and Langmuir models isotherm parameters on the selected soil samples at 298.15 K.

Adsorption Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	6.413	3.261	5.503	6.107	5.200	3.559
	S.E	0.161	0.899	0.224	0.229	0.140	0.117
	R^2	0.862	0.737	0.725	0.784	0.720	0.730
	K_{OC}(mL/g)	229	314	172	259	272	236
	K_{OM}(mL/g)	3.949	5.411	2.968	4.469	4.682	4.066
Freundlich	K_F(mL/g)	1.353	1.194	1.506	1.494	1.357	1.291
	S.E	0.487	0.347	0.449	0.473	0.441	0.362
	n_F	1.572	1.754	2.045	1.912	1.724	1.893
	R^2	0.977	0.947	0.871	0.900	0.990	0.954
Langmuir. coffi.	K_L (ml/g)	0.019	0.017	0.019	0.020	0.018	0.019
	S.E	0.257	0.313	0.279	0.269	0.282	0.309
	C_m(µg/g)	1000	333.3	500	500	500	333.3
	R^2	0.855	0.796	0.704	0.708	0.948	0.854

Table 4 : Adsorption of diazinon linear, Freundlich and Langmuir models isotherm parameters on the selected soil samples at 313.15 K.

Adsorption Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	3.326	1.757	2.299	2.585	3.019	1.719
	S.E	0.141	0.399	0.602	0.369	0.725	0.335
	R^2	0.712	0.741	0.741	0.812	0.671	0.756
Freundlich	K_F(mL/g)	1.363	0.865	1.067	0.747	1.096	0.805
	S.E	0.346	0.249	0.284	0.317	0.335	0.248
	n_F	2.173	1.608	1.773	1.261	1.628	1.531
	R^2	0.777	0.934	0.957	0.952	0.917	0.940
Langmuir. coffi.	K_L (ml/g)	0.016	0.011	0.017	0.007	0.015	0.015
	S.E	0.316	0.343	0.333	0.321	0.317	0.345
	C_m(μg/g)	333.3	250	250	500	333.3	200
	R^2	0.745	0.761	0.879	0.776	0.778	0.905

Table 5 : Free energy change, standard entropy change and standard enthalpy change at three temperatures for adsorption of diazinon on the selected soil samples.

| Parameter	Soils					
	S_1	S_2	S_3	S_4	S_5	S_6
ΔG (kJ/mol	-8.780	-6.067	-6.584	-9.457	-10.617	-5.888
ΔS (J/mol. K)	-66.260	-190.55	-135.57	-113.60	-65.600	-169.89
ΔG (kJ/mol	-9.824	-10.100	-9.824	-9.697	-9.958	-9.824
ΔS (J/mol. K)	-66.429	-194.48	-139.62	-108.69	-59.872	-174.56
ΔG (kJ/mol	-10.766	-11.742	-10.608	-12.918	-10.934	-10.934
ΔS(J/ mol. K)	-66.254	-190.42	-135.43	-113.77	-60.119	-169.74
ΔH (kJ/mol)	-9.9812	-47.887	-31.803	-22.709	-7.892	-42.219
R^2	0.996	0.924	0.836	0.839	0.816	0.872

Table 6 : Adsorption of diazinon in the presence of 40ppm of copper and desorption in the presence of TritonX-100 at cmc concentration, the linear, Freundlich and Langmuir models isotherm parameters on the selected soil samples.

Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
linear.Distr. coffi.	K_d (calc)	9.454	4.809	6.623	8.578	6.274	5.410
	S.E	0.257	0.131	0.291	0.372	0.143	0.118
	R^2	0.766	0.750	0.697	0.733	0.762	0.766
Freundlich coffi.	K_F(mL/g)	1.553	1.328	1.599	1.656	1.340	1.198
	S.E	0.569	0.424	0.487	0.544	0.482	0.452
	n_F	1.689	1.727	2.137	2.045	1.567	1.441
	R^2	0.991	0.993	0.890	0.853	0.955	0.907
Langmuir. coffi.	K_L (ml/g)	0.017	0.017	0.023	0.015	0.011	0.008
	S.E	0.231	0.287	0.267	0.245	0.265	0.275
	C_m(µg/g)	1000	500	500	1000	1000	1000
	R^2	0.987	0.945	0.766	0.713	0.941	0.820
Des.Distr. coffi	K_d (calc)	8.058	3.739	3.729	4.532	4.371	4.001
	S.E	0.165	0.630	0.583	0.620	0.465	0.349
	R^2	0.932	0.874	0.968	0.979	0.979	0.975
Freundlich coffi.	K_{Fdes}(mL/g)	1.207	0.921	0.842	0.865	0.857	0.800
	S.E	0.566	0.404	0.426	0.607	0.436	0.414
	n_F	1.348	1.328	1.248	1.193	1.191	1.166
	R^2	0.982	0.983	0.991	0.990	0.996	0.998
Langmuir. coffi.	K_L (ml/g)	0.011	0.011	0.010	0.005	0.005	0.005
	S.E	0.138	0.219	0.200	0.173	0.189	0.201
	C_m(µg/g)	1000	500	500	1000	1000	1000
	R^2	0.767	0.963	0.731	0.636	0.851	0.989

Table 7 : Hysteresis effect for Adsorption of diazinon in the presence of 40ppm of copper and desorption in the presence of TritonX-100 at cmc concentration on the selected soil samples.
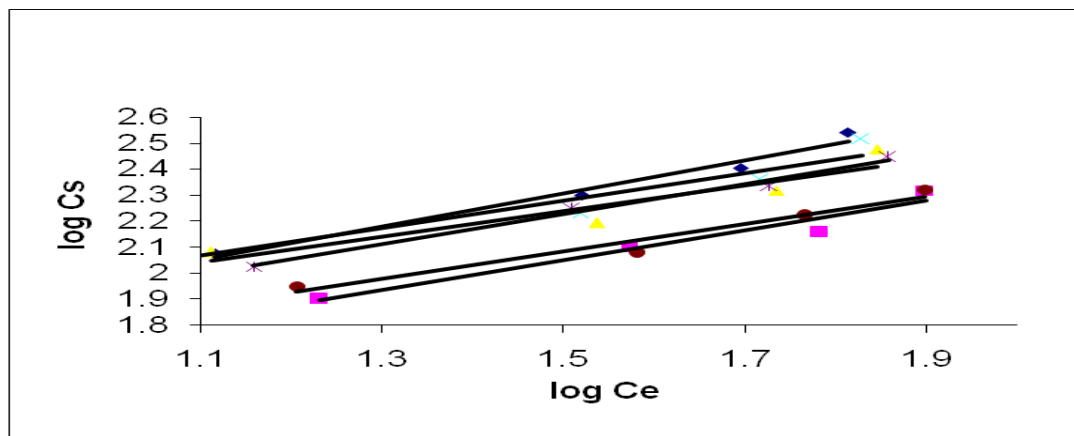
Soil	Diazinon		
	H_1	ω	λ
S_1	1.252	25.3	-22.3
S_2	1.300	30.1	-30.7
S_3	1.712	71.2	-47.3
S_4	1.714	71.4	-47.8
S_5	1.316	31.6	-36.0
S_6	1.236	23.6	-33.2
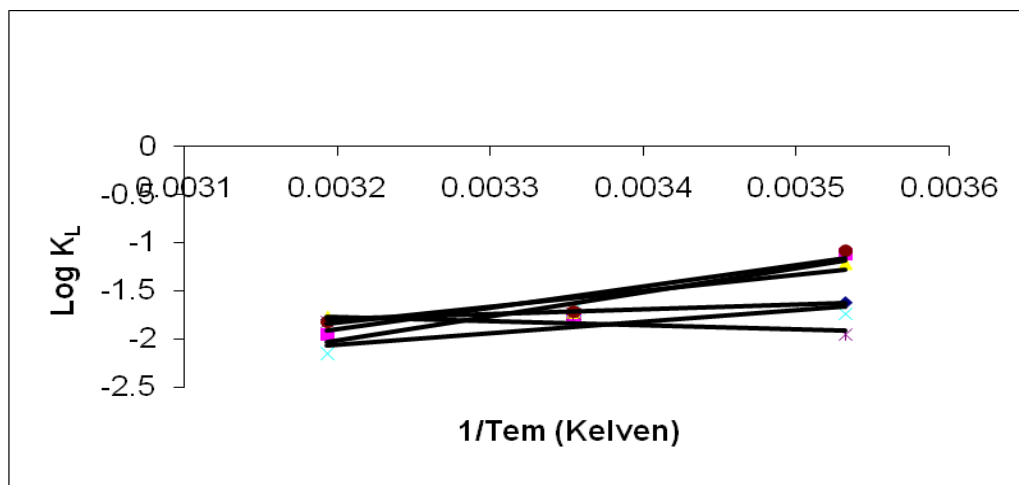
Figure 1 : Variation of log K_L with 1/T for adsorption of diazinon on the six soil samples(♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5 ●S_6).
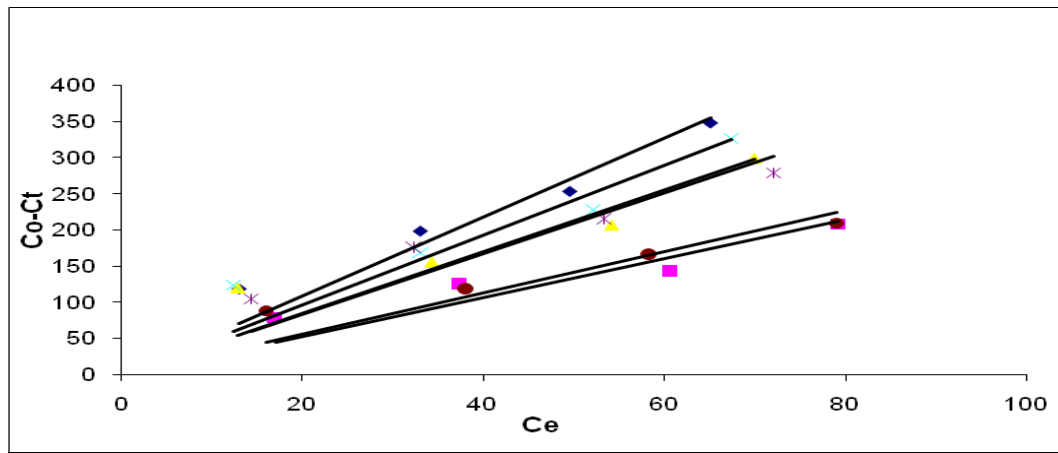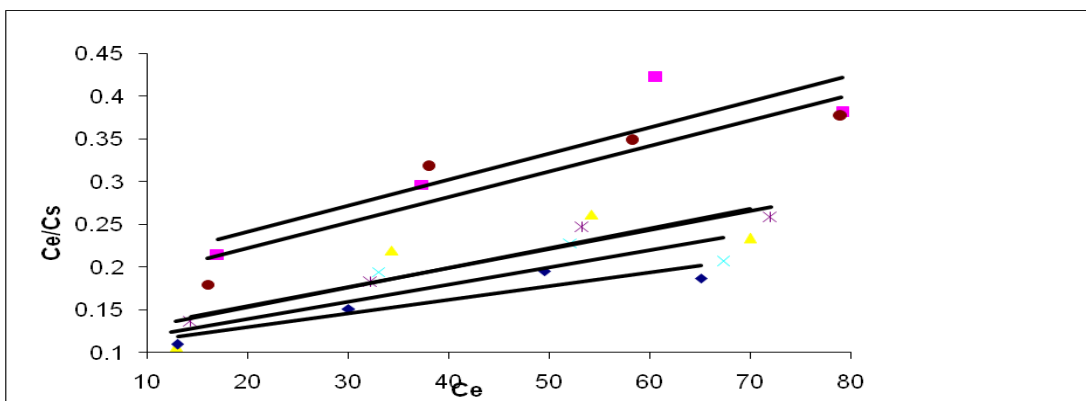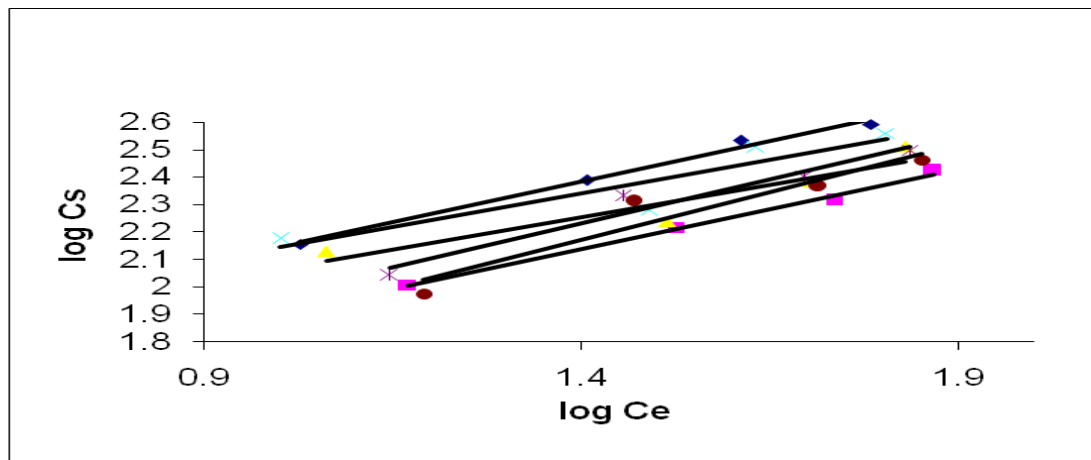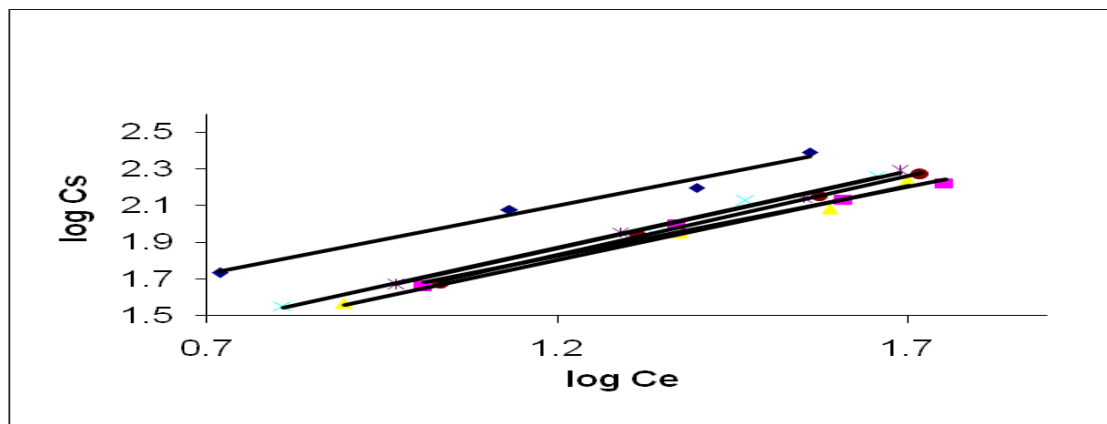
a-

b-

c-

Figure 2 : Fitted models for diazinon adsorption (a) Linear(b) Ferundlich (c)Langmuir, isotherms on selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6).

a-

b-

Figure 3 : Fitted Ferundlich model for diazinon alone in presence of 40ppm of copper (a) adsorption (b) desorption in presence of nonionic surfactant, isotherms selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6).