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Abstract - The effect of cadmium (Cd) on adsorptiondesorption behavior of Simazine [2-chloro-4, 6 bis (ethylamine)-1,3,5-triazine] which is anionic herbicide were investigated at three different temperature 10, 25 and 40 $\pm 1^{\circ}$C on six agricultural soil samples which has different texture. The first order rate law was most fitted with the best correlation factor, the Linear, Freundlich and Langmuir models also were applied to describe the adsorption-desorption affinities to the soil samples. Values of adsorption rate constant k_a were in the range 0.836 - 1.818 h^{-1} while desorption rate constant k_{des} were in the range 0.779 - 1.376 h^{-1}. The activation energy E_a* for adsorption processes followed the range 11.041- 17.684 $KJmol^{-1}$. Values of equilibrium constant lnK_o were in the range 0.048 - 0.278. The standard free energy change ΔG^o values were in the range -0.126 to -0.655 $KJmol^{-1}$. Values of the standard enthalpy change ΔH^o followed the range -2.702 to - 4.850 $KJmol^{-1}$. The value of standard entropy change ΔS^o followed the range-7.557 to-14.965 $Jmol^{-1}k^{-1}$. The negative values revealed that the adsorption-desorption processes spontaneously, exothermic and physical in nature to some extent and chemical in others.

Keywords : adsorption-desorption isotherms, simazine, thermodynamic parameter, UV-spectro-photometer.

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Abstract - The effect of cadmium (Cd) on adsorption-desorption behavior of Simazine [2-chloro-4, 6 bis (ethylamine)-1,3,5-triazine] which is anionic herbicide were investigated at three different temperature 10, 25 and 40 ±1˚C on six agricultural soil samples which has different texture. The first order rate law was most fitted with the best correlation factor, the Linear, Freundlich and Langmuir models also were applied to describe the adsorption-desorption affinities to the soil samples. Values of adsorption rate constant k_a were in the range 0.836 - 1.818 h^{-1} while desorption rate constant k_{des} were in the range 0.779 - 1.376 h^{-1}. The activation energy E_a^* for adsorption processes followed the range 11.041- 17.684 $KJmol^{-1}$. Values of equilibrium constant lnK_o were in the range 0.048 - 0.278. The standard free energy change ΔG° values were in the range -0.126 to -0.655 $KJmol^{-1}$. Values of the standard enthalpy change ΔH° followed the range -2.702 to -4.850 $KJmol^{-1}$. The value of standard entropy change ΔS° followed the range-7.557 to-14.965 $Jmol^{-1}k^{-1}$. The negative values revealed that the adsorption-desorption processes spontaneously, exothermic and physical in nature to some extent and chemical in others. The distribution coefficient K_d values for adsorption-desorption process varied between 2.369 - 2.611 mlg^{-1}, 5.556- 22.85 mlg^{-1} respectively. Freundlich coefficient K_F ranged between 0.180-0.506 mlg^{-1} for adsorption processes. The value Freundlich coefficient for desorption process K_{Fdes} ranged from 0.107 to0.498 mlg^{-1}. Langmuir coefficient K_L for adsorption process varied between 0.027 - 0.064 mlg^{-1}. Langmuir coefficient K_{Ldes} values for desorption process from 0.014 to 0.067 mlg^{-1}. All desorption isotherms exhibited hysteresis.

Keywords : adsorption-desorption isotherms, simazine, thermodynamic parameter, UV-spectrophotometer.

I. Introduction

Estimating the behavior and fate of chemical pollutants in the environment is justified by the awareness that constitute serious risks for our health and other living organism [(1)]. The sorption of an organic chemical on a soil is complicated process, which involves many sorbent properties, besides the physic-chemical properties of the chemical itself which are the relative amount of the mineral and organic material in soil and composition [(2&3)]. The different region of a soil matrix may contain different types, amounts, and distributions of surfaces of soil organic material [(4)]. The adsorption-desorption processes of a chemical on a solid from a water solution may be seen as the result of a reversible reaction which reaches a final equilibrium condition [(5&6)]. The sorption capacity of a given sorbent may depend on a series of properties, which are grain-size distribution, specific surface area, cation exchange capacity, pH, organic matter, and mineral constituents [(7&8)]. Hysteresis or nonsingularity in the adsorption-desorption processes, and its implications in the transport of these contaminants through soil [(9&10)].

Temperature is another important factor that affected the adsorption-desorption processes, which may be occur through enthalpy-related force due to the electrostatic interactions. Or either through entropy-related force hydrophobic bonding due to London dispersion force[(11)]. Simazine is anionic herbicide which belongs to triazine group [(12&13)]. Cadmium is typical pollutants it associates with various health problems. The adsorption-desorption behavior of the heavy metal coexists with the organic pollutants interaction with soil at different temperature (10, 25 and 40 ±1C°) were investigated, the adsorption-desorption process pollutants in soil affects its transportation and bioavailability and hence is of great importance to environmental regulation and pollution control [(14)].

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 [(15)].

b) Pesticide

Analytical grad substituted Simazine (trade name Triamex), [2-chloro-4,6 bis (ethylamino)-1,3,5-triazine], (purity 98.8%), was purchased from Riedal-de Haen, Sigma-Aldrich company ltd. Cd $(NO_3)_2$ used as analytical reagent for preparing working solution. All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of the pesticides were prepared in deionised water.

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c) Adsorption-Desorption Experiments

The effect of cadmium on adsorption-desorption of Simazine from aqueous solution were determined at temperatures (10, 25, 40±1 C°) employing a standard batch equilibrium method [11&16]. Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (3, 5, 10, and 15 μg ml^{-1}) and (3, 5, 10, and 15 μg ml^{-1}) for Cd, at the soil solution ratios 2:10 in 16 ml glass tube fitted with Teflon-lined screw caps. The samples plus blanks (no pesticide) and control (no soil) were thermostated and placed in shaker for 0.5, 1, 3, 6, 9, 12 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 [14&17]. Simazine identification was done by spectrophotometer UV detector at wavelength 220 nm. Desorption processes were done as each test tube was placed in a thermostated shaker at (10,25,40 ±1 C°) after equilibration for 24 h with different pesticide concentrations (3, 5, 10 and 15 μg ml^{-1}) and (3, 5, 10, and 15 μg ml^{-1}) for Cd, the samples were centrifuged, 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of water and this repeated for four times [18]. The resuspended samples were shaken for mentioned time previously for the kinetic study Simazine.

III. Data Analysis

a) Adsorption-Desorption Kinetics & Equilibrium constant

The rate constants for the effect of cadmium on adsorption-desorption of Simazine on soils were calculated using the first order rate expression [19&20]:

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

Where k is k_a is the rate constant for adsorption (h^{-1}), t the time (h) C is 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 as linear plots of log (Co–Ct) against t for the effect of cadmium on adsorption desorption of Simazine demonstrated in (Table 1). The same equation used to describe the process of desorption in all experiments and on all soil samples [21]. Where k is k_{des} is the desorption rate constant (h^{-1}), C_t is the amount of released pesticides at time t and C is C_e is the amount of released pesticides at equilibrium and k_{des} is the slope of straight line which is equal to coefficient release rate of k_{des}. A plot of log (C_e - C_t) versus t should give a straight line with slope -k_{des}/2.303 and intercept of log C_e for the effect of cadmium on adsorption-desorption of Simazine demonstrated in (Table 1).

Considering the experimental equilibrium constant k_o can be conducted by the ratio of adsorption rate constant k_a is to the desorption rate constant k_{des}, K_o were calculated using the following expression [21].

$$K_o = \frac{k_a}{k_{des}} \qquad (2)$$

i. *Arrhenius activation energy*

The Arrhenius activation energy **E_a** for the adsorption and desorption processes for the effect of cadmium on adsorption-desorption of Simazine on soils were calculated by linearized Arrhenius equation [22&23]:

$$\ln k = \ln A - \frac{E_a}{RT} \qquad (3)$$

Where k; adsorption rate constant or desorption rate constant, E_a; the activation energy, R; gas constant 8.314J (Kmol)$^{-1}$, and T; absolute temperature, A; preexponential factor, the plot of lnk against the reciprocal of absolute temperature resulted in straight lines for each system. The activation energies were evaluated from the slope of each linear plot as shown in table 2 for the effect of cadmium on adsorption-desorption of Simazine.

ii. *Activations parameters*

A plot of ln (k/T) against the reciprocal of absolute temperature for the effect of cadmium on adsorption-desorption of Simazine were shown in figure 1, the enthalpy of activation, ΔH^*, and the entropy of activation, ΔS^* were calculated from Eyring equation [24&25]:

$$\ln\frac{k}{T} = \ln\frac{\mathbf{k}}{h} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \qquad (4)$$

Where k; adsorption rate constant or desorption rate constant: ΔH^*; enthalpy of activation, ΔS^*; entropy of activation, **k**; Boltzmann's constant 1.38.10^{-23} JK^{-1}, h; Plank's constants h=6.6.10^{-34} Js. As shown in figure 3, the enthalpy of activation, ΔH^*, and the entropy of activation, ΔS^* were calculated from the slope and the intercept of each linear plot as shown in table2 for the effect of cadmium on adsorption-desorption of Simazine.

The free energies of activation, ΔG^* for each system were determined by using the equations bellow [26].

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

The values of ΔG* were determined at a T value which is equal to 298.15K, and these values are included in table 2 for the effect of cadmium on adsorption-desorption of Simazine.

iii. *Isosteric enthalpy of Adsorption*

The isosteric enthalpy of adsorption is the standard enthalpy of adsorption at a fixed surface coverage. Values of isosteric heat of the adsorption as a function of the amount of the chemical adsorbed (x) was calculated by the expression [6]:

$$\Delta H = R\left[\frac{dLnC_e}{d\left(\frac{1}{T}\right)}\right]x \qquad (6)$$

Where C_e is the equilibrium concentration, and the average were calculated for each concentration, The results were summarized in table 2 for the effect of cadmium on adsorption-desorption of Simazine.

iv. *Standard free energy change*

Adsorptions equilibrium constant (K_o), can be expressed in terms of the standard Gibbs or free energy for adsorption (ΔG^o) [6] .

$$\Delta G^o = -RTLnK_o \qquad (7)$$

The results were summarized in table 3 for the effect of cadmium on adsorption-desorption of Simazine.

v. *Standard enthalpy and entropy change*

The standard enthalpy change of adsorption (ΔH^o) represents the difference in binding energies between the solvent and the soil with the pesticides. Values of ΔH^o and standard entropy change (ΔS^o) also determined graphically from the following equation [6&10]:

$$LnK_o = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad (8)$$

Plotting $-\ln K_o$ against 1/ T, a straight line is expected the standard enthalpy change (ΔH^o) of adsorption were determined from the slope, and the intercept equal to $\Delta S^o/R$ as shown in figure 2, the results were summarized in table 3.

b) Adsorption-Desorption Isotherms

i. *Distribution Coefficient*

The distribution coefficient (K_d) was calculated by the using the following expression [6&19].

$$C_s = K_d C_e \qquad (9)$$

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), and averaged across all equilibrium concentration to obtain a single estimate of K_d for the effect of cadmium on adsorption-desorption of Simazine demonstrated in (Table 4 fig 3a). The same equations (9) used to describes the process of desorption in all experiments and on all soil samples the results was demonstrated in (Table 4 & fig 4a).

ii. *Freundlich Coefficient*

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation [19]:

$$\log C_s = \log K_F + \frac{1}{n}\log C_e \qquad (10)$$

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 $\log K_F$ is the intercept of the straight line resulting from the plot of $\log C_s$ versus $\log C_e$ as shown in (fig 3b). The values of K_F and 1/n calculated from this regression equation showed that Freundlich adsorption model effectively describes isotherms for Simazine in all cases. Desorption isotherms of pesticide was fitted to the linearzed form of the Freundlich equation [19]:

$$\log C_s = \log K_{Fdes} + \frac{1}{n_{des}}\log C_e \qquad (11)$$

Where C_s is the amount of pesticides still adsorbed (μg g^{-1}), C_e is the equilibrium concentration of pesticides in solution after desorption (μg mL^{-1}), and K_{Fdes} (μg $g^{1-nfdes}$ /ml^{nfdes} g^{-1}) and n_{fdes} are two characteristic constants of Simazine desorption [23]. The value of the K_{Fdes} and n_{fdes} constants of Simazine demonstrated in (Table 4 & fig 4b).

iii. *Langmuir Adsorption Isotherm*

Data from the batch adsorption conform to Langmuir equation [19]:

$$\frac{C_e}{C_s} = \frac{1}{C_m K_L} + \frac{C_e}{C_m} \qquad (12)$$

C_m is the maximum amount of pesticide adsorbed (adsorption maxima, μg ml^{-1}), it reflects the adsorption strength and K_L is the Langmuir adsorption coefficient, binding energy coefficient. The results were summarized in (Table 4 & fig 3c).

The same equations (12) used to describes the process of desorption in all experiments and on all soil samples [20] the results was demonstrated in (Table 4 & fig 4c).

c) Hysteresis Coefficient

A study for the effect of cadmium on adsorption-desorption of Simazine isotherms show positive hysteresis coefficients H_1 on the six selected soil samples. Hysteresis coefficients (H_1) can be determined by using the following equation [27].

$$H_1 = \frac{n_a}{n_{des}} \qquad (13)$$

Where n_a and n_{des} are 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 5 demonstrated H_1 values for simazine.

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 [20]:

$$\omega = (\frac{n_a}{n_{des}} - 1)x100 \qquad (14)$$

Zhu et. al [28] 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:

$$\lambda = (\frac{n_a + 1}{n_{des} + 1} - 1)x100 \qquad (15)$$

IV. Results and Discussion

Adsorption-desorption processes of simazine alone were discussed in our previous article [13], but in this study to investigate the effect of cadmium on adsorption-desorption behavior of Simazine depend on the interaction between the two that affected by the texture of the soil [9]. The values of adsorption rate constant k_a were in the range 0.836-1.818 while, desorption rate constant k_{des} were in the range 0.779 - 1.376 for the effect of cadmium on adsorption-desorption of Simazine respectively as shown in Table 1. The nitrogen lone-pair electrons, side-chain NH group vise basic triazine ring N, and the Cl atom at the 2-position on the triazine rings all were available to formed complexes with Cd^{+2} ion and finally formation of adducts with organic matter of the soil [14&29]. The Values of adsorption rate constant were greater than desorption constant indicating that adsorption processes was faster than desorption, and the values of adsorption-desorption rate constant decreased by increasing the temperature.

The activation energy E_a for adsorption processes followed the range 11.041-17.684 $KJmol^{-1}$, while for desorption processes followed the range 6.917-13.111 $KJmol^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively. As the values of E_a for adsorption processes were higher than desorption. As shown from figures 1 a & b the values of R^2 in range 0.874 to 0.999 for adsorption process and 0.776 to 0.972 for desorption process, which supported our investigation that adsorption rate constant and amount adsorbed increased with the increase in organic matter content of soil, and an exothermic binding reaction and a reversible relation between temperature and the activation energy [20&26].

The Values enthalpy of activation, ΔH^* for adsorption-desorption followed the range-13.518 to-20.161 $KJmol^{-1}$, -12.247 to -15.589 $KJmol^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively. The negative values of ΔH^* showing that the interaction of pesticides, heavy metal with the soil is an energetically stable exothermic process and the adsorption occurred through a bonding mechanism. As shown from figures the values of R^2 in range 0.821 to 0.980 which supported our investigation [25]. The values of isosteric enthalpy of adsorption were followed the range 959.04-1, 066.6 $kJmol^{-1}$, on selected soil samples. The values of isosteric heat of adsorption as a function of amount of chemical adsorbed, relatively small and were of the order which was consistent with a physical type of adsorption [10].

Data in table 2 demonstrated the values of entropy of activation ΔS^* followed the range-287.99 to -308.36 $Jmol^{-1}$ k^{-1}, -275.33 to -296.39 $Jmol^{-1}$ k^{-1} for the effect of cadmium on adsorption-desorption behavior of Simazine respectively which suggest that the interaction done via the formation of ion-ion and hydrophobic interactions leading the decrease in the standard entropy [27].

Data in table 2 demonstrated the values of free energy change ΔG^* values were in the range -96.79 to -109.95 $KJmol^{-1}$, and -88.99 to -101.1 $KJmol^{-1}$ for the effect of cadmium on adsorption-desorption behavior of Simazine respectively, indicating that the interactions were spontaneous with a high preference of the soil surface and adsorption occurred through a bonding mechanism[28].

Data in table 1 demonstrated the values of equilibrium constant K_o equilibrium constant for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine on selected soil samples were in the following from 1.049 to 1.321, while the values of equilibrium constant lnK_o were in the range 0.048 - 0.278, as shown in figure 2 confirming that K_o values were decreased with rise in temperature.

Data in table 3 demonstrated the free energy change ΔG^o values were in the range -0.126 to -0.655 $KJmol^{-1}$, all the values were negative and decreased with the rise in temperature, and thermodynamically spontaneous process and adsorption occurred through a bonding mechanism [29&30].

The values of enthalpy change ΔH^o followed the range -2.702 to -4.850 $KJmol^{-1}$, the results were summarized in table 3. The values of R^2 were in the range 0.812 to 0.941 which supported the linear nature of the plot. The negative enthalpy indicating an exothermic binding reaction [31&32], thus low values of ΔH^o pointed towered chemisorptions, hence the heavy metal and the herbicides adsorption may be due to coordination and /or protonation, hydrogen bonding and dipole association or van der Waal's forces, and metal ion bridged mechanism between the clay and / or organic molecules occur with or without a water bridge. Our results showed that the negative values of ΔH^o decrease with temperature. This indicates that the interactions between the pesticides and the studied soil samples were stronger at lower temperature.

The results were summarized in table 3 where the value of entropy change ΔS^o followed the range-7.557 to -14.965 $Jmol^{-1}\ k^{-1}$, a negative slope as shown in fig 2 $-\Delta H^o/T$ corresponds to positive change of entropy of the surroundings, and favors the adsorption. When temperature is raised $-\Delta H^o/T$ decreases and the increasing entropy of the surroundings which result, the equilibrium lies less to the adsorption process. The negative values of entropies pointing to the formation of the complexity by coordination or association of the herbicides and an exchangeable cation with the resultant of the loss in the degree of freedom of the pesticide [33&34]. The increase of the temperature from 288.15 to 308.15k leads to increase the thermal energy for the reactant and products combined with the decrease in the rate of adsorption reaction. On the other side, the increase in the thermal energy of the reactant and product leads to increase the disorder of reactant and product which decrease the bond energy formation for products of the reaction (adsorption).

Data in Table 4 demonstrates The distribution coefficient K_d values for adsorption process varied between 2.369 - 2.611 mlg^{-1}, and for desorption process varied between 5.556- 22.85 mlg^{-1} for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine respectively, and the value of R^2 for adsorption-desorption process on selected soil samples ranged from 0.754 to 0.984 and from 0.752 to 0.968 respectively. The value of standard error (S.E.) for adsorption-desorption process ranged from 0.012to 0.087 and from 0.016 to 0.087 respectively, our result agreed with article [35] .

Coefficient K_F for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine ranged between 0.180-0.506 mlg^{-1} and 0.107-0.489 mlg^{-1} respectively. The value of n indicating a linear relationship as shown in figure 3 b & 4 b, the value of n ranged between 1.153-1.357, while Freundlich the value of n_{fdes} ranged between 1.071-1.807. The value of R^2 for adsorption-desorption process on selected soil samples ranged from 0.882 to 0.999 and from 0.764 to 0.998 respectively The value of standard error (S.E.) for adsorption-desorption processes ranged from 0.027to 0.033 and from 0.026 to 0.043 respectively [36].

Langmuir coefficient K_L for adsorption process varied between 0.027 - 0.064 mlg^{-1} while Langmuir coefficient K_{Ldes} values for desorption process varied between 0.014 - 0.067 mlg^{-1}. The values of C_m, S.E and R^2 demonstrated in table 4 for the effect of cadmium (Cd) on adsorption-desorption behavior of Simazine on selected soil sample. The, C_m, S.E, and R^2 ranged from, 8.929-18.18 μgg^{-1}, 0.030-0.037, and 0.760-0.935 for adsorption process respectively. While C_m, S.E, and R^2 ranged from 0.719-7.813μgg^{-1}, 0.031-0.033, and 0.640-0.985 for desorption processes respectively [37].

Data in table 5 demonstrated (H_1) values for the effect of cadmium on adsorption-desorption behavior of Simazine from the selected soil samples in the range from 0.638-1.137, indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases, and indicate the increased difficulty of the sorbed analyte to desorb from the matrix. The calculated values of hysteresis coefficient (ω) for adsorption-desorption of for si for the effect of cadmium on adsorption-desorption of Simazine on the selected soil samples were summarized in table 5 ranged from 3 to 36. Whereas hysteresis coefficient (ω) is only applicable for the traditional type isotherms of the successive desorption[38]. The data in table 5 demonstrated hysteresis coefficient (λ) for the effect of cadmium on adsorption-desorption of Simazine from the selected soil samples were ranged from 2 to 23.

V. Conclusion

The interaction of the heavy metal and organic pollutant bound to soil particles and its thermodynamic investigations important to pay more attention and more study to solve these problem. Adsorption-desorption experiments were conducted at 10, 25, and 40°C to study the parameter, which generally ascribed to H-bonding, van der Walls forces, electrostatic attraction, and coordination reactions with the active surfaces of the soil matrix, and also occur through the diffusion phenomena even through forming a bridge between the soil and the pollutant.

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Table 1 : Adsorption rate constants k_a, desorption rate constants k_d and equilibrium rate constants k_o for the effect of cadmium coexist with Simazine on the selected soil samples

Temp(K)	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
283.15K	k_a (calc) h^{-1}	1.565	1.818	1.636	1.631	1.513	1.730
	k_d (calc) h^{-1}	1.284	1.376	1.284	1.324	1.289	1.340
	K_o	1.219	1.321	1.274	1.232	1.173	1.291
298.15K	k_a (calc) h^{-1}	1.301	1.272	1.329	1.409	1.360	1.449
	k_d (calc) h^{-1}	1.109	1.139	1.205	1.260	1.174	1.302
	K_o	1.173	1.117	1.104	1.119	1.158	1.158
313.15K	k_a (calc) h^{-1}	0.842	0.909	1.042	0.956	0.892	0.836
	k_d (calc) h^{-1}	0.794	0.836	0.966	0.884	0.849	0.779
	K_o	1.059	1.087	1.079	1.082	1.049	1.073

Table 2 : Thermodynamic parameters for the effect of cadmium on the adsorption-desorption Simazine at three temperatures and Isosteric heat change on the selected soil samples

Soil	E_a ($kJmol^{-1}$) , R^2		ΔH_a^* ($kJmol^{-1}$), R^2		ΔS_a^* ($Jmol^{-1}.K^{-1}$)		ΔG_a^* ($KJmol^{-1}$)		average X(KJ/mol) Isosteric heat change
	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption	
S_1	-15.115 0.934	-11.714 0.938	-17.584 0.950	-14.184 0.956	-302.46	-292.24	-105.04	-98.68	970.64
S_2	-17.027 0.999	-12.180 0.972	-19.496 0.999	-14.658 0.980	-308.36	-293.40	-108.66	-99.49	973.88
S_3	-11.041 0.994	-6.917 0.890	-13.518 0.995	-9.387 0.935	-287.99	-275.33	-96.79	-88.99	959.04
S_4	-12.995 0.920	-9.768 0.818	-15.464 0.941	-12.247 0.874	-294.65	-284.92	-100.66	-94.63	1,119.4

S_5	-12.837 0.874	-10.134 0.890	-15.314 0.907	-12.612 0.924	-293.64	-286.58	-100.51	-95.48	1,025.8
S_6	-17.684 0.902	-13.111 0.776	-20.161 0.922	-15.589 0.821	-301.53	-296.39	-109.95	-101.1	1,066.6

Table 3 : Equilibrium constants and standard free energy change at three different temperatures, Standard enthalpy change and standard entropy change (determined graphically) for the effect of cadmium on the adsorption-desorption Simazine on the selected soil samples

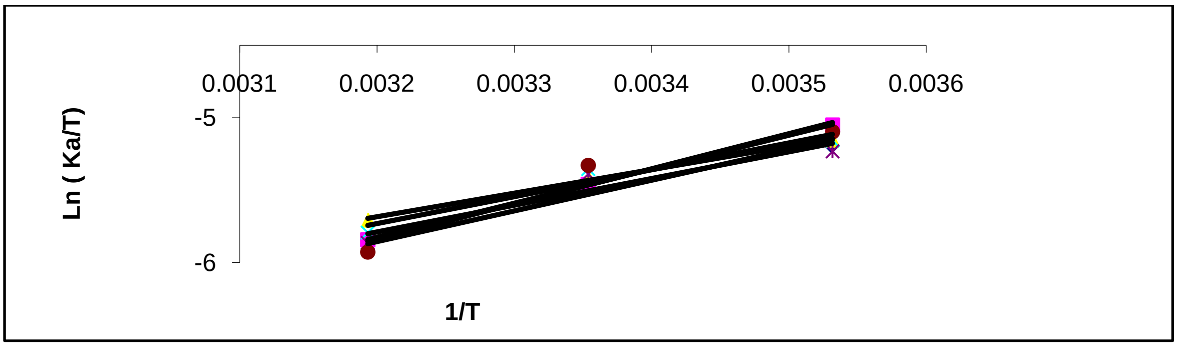
Soil	283.15 K		298.15K		313.15K				
	$\ln K_0$	ΔG^o (KJ/mol)	$\ln K_0$	ΔG^o (KJ/mol)	$\ln K_0$	ΔG^o (KJ/mol)	$\Delta H^o{}_{cal}$ (KJ/mol)	R^2	$\Delta S^o{}_{cal}$ J/(mol.k)
S_1	0.198	-0.465	0.159	-0.396	0.058	-0.152	-3.397	0.919	-10.259
S_2	0.278	-0.655	0.111	-0.274	0.083	-0.217	-4.845	0.872	-14.965
S_3	0.242	-0.570	0.099	-0.244	0.076	-0.197	-4.128	0.870	-12.712
S_4	0.209	-0.491	0.112	-0.278	0.079	-0.204	-3.220	0.941	-9.711
S_5	0.159	-0.376	0.147	-0.364	0.048	-0.126	-2.702	0.812	-8.089
S_6	0.255	-0.601	0.107	-0.266	0.071	-0.184	-4.572	0.909	-7.557

Table 4 : Linear, Freundlich and Langmuir models for the effect of cadmium on the adsorption-desorption of Simazine at 298.15K on the selected soil samples

Models		Parameter	Soils					
			S_1	S_2	S_3	S_4	S_5	S_6
Adsorption	Distr	K_d (calc)	2.409	2.508	2.611	2.571	2.369	2.437
		S.E	0.052	0.047	0.041	0.012	0.087	0.029
		R^2	0.901	0.920	0.971	0.959	0.984	0.754
	Freu	K_F(mL/g)	0.506	0.487	0.421	0.500	0.180	0.360
		S.E	0.033	0.032	0.031	0.028	0.027	0.029
		n_F	1.357	1.353	1.238	1.189	1.153	1.198
		R^2	0.947	0.960	0.952	0.973	0.999	0.882
	Lang	K_L (ml/g)	0.064	0.060	0.047	0.043	0.027	0.033
		S.E	0.030	0.033	0.031	0.032	0.032	0.037
		C_m(μg/g)	8.929	9.010	10.41	9.091	18.18	9.000
		R^2	0.761	0.935	0.760	0.845	0.870	0.765
Desorption	Distr	K_d (calc)	18.28	22.85	13.89	10.08	5.556	10.13
		S.E	0.085	0.079	0.016	0.027	0.087	0.038
		R^2	0.808	0.765	0.917	0.864	0.968	0.752
	Freu	K_{Fdes}(mL/g)	0.432	0.449	0.107	0.261	0.498	0.209
		S.E	0.042	0.045	0.034	0.033	0.026	0.027
		n_F	1.223	1.389	1.089	1.071	1.807	1.717
		R^2	0.884	0.806	0.844	0.998	0.764	0.922
	Lang	K_L (ml/g)	0.056	0.067	0.028	0.014	0.015	0.053
		S.E	0.078	0.011	0.063	0.034	0.035	0.050
		C_m(μg/g)	1.285	1.155	0.755	7.813	1.022	0.719
		R^2	0.643	0.640	0.932	0.748	0.960	0.985

Table 5 : Hysteresis effect on desorption for cadmium coexist with Simazine on the selected soil samples

Soil	298.15K		
	H_1	ω	λ
S_1	1.110	11	6
S_2	0.974	3	2
S_3	1.137	14	7
S_4	1.110	11	6
S_5	0.638	36	23
S_6	0.698	30	19



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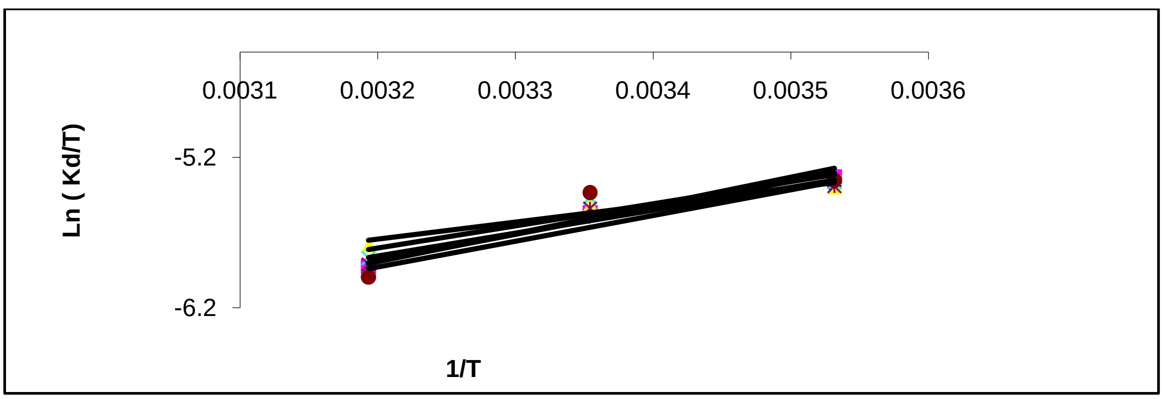

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Figure 1 : Variation of ln (K_a /T) with 1/T for the effect of cadmium coexist with Simazine of, (a) adsorption (b) desorption on the selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6)

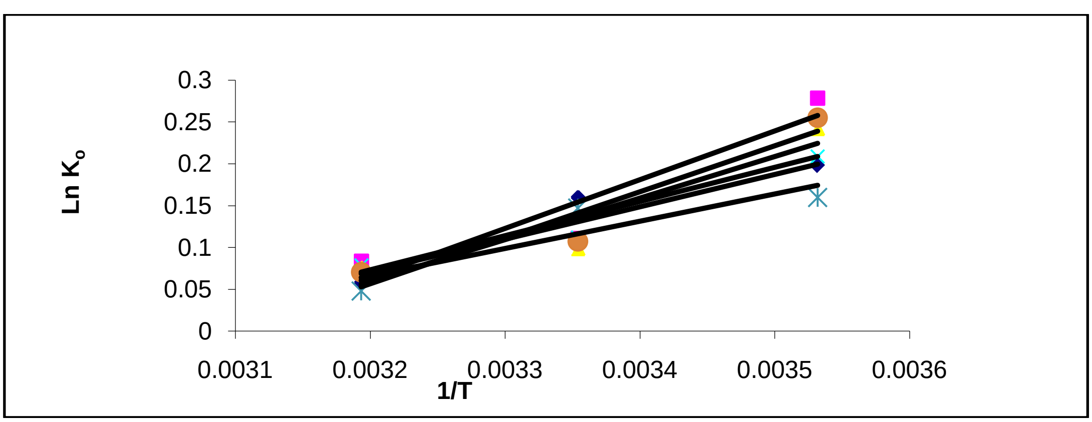
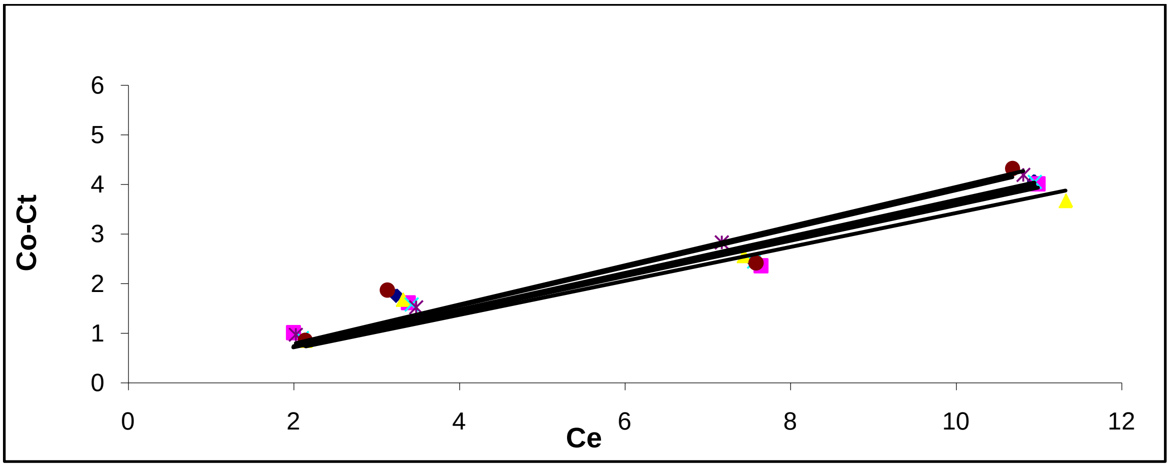


Figure 2 : Variation of ln K_o with 1/T for the effect of cadmium on the adsorption-desorption Simazine on the selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6)



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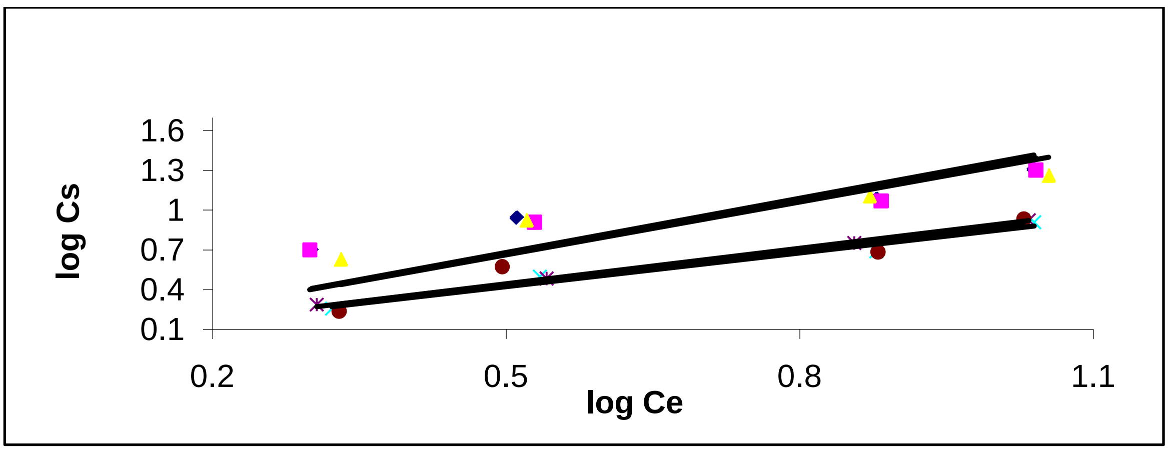

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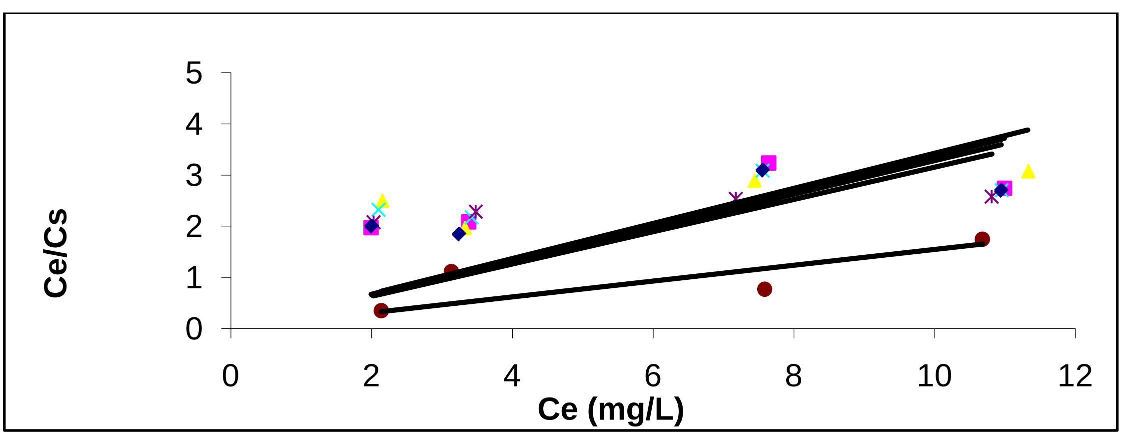

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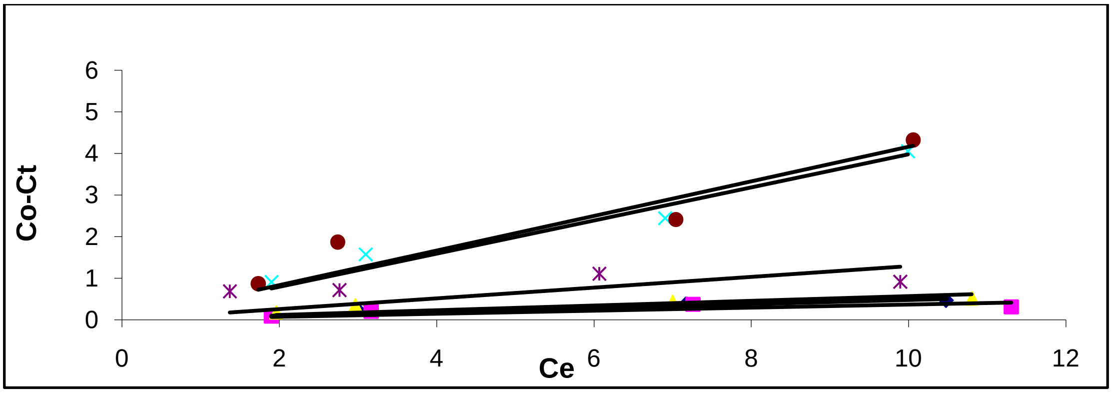
Figure 3 : Fitted models for the effect of cadmium on the Simazine adsorption (a) Linear (b) Ferundlich (c) Langmuir, on the selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6)



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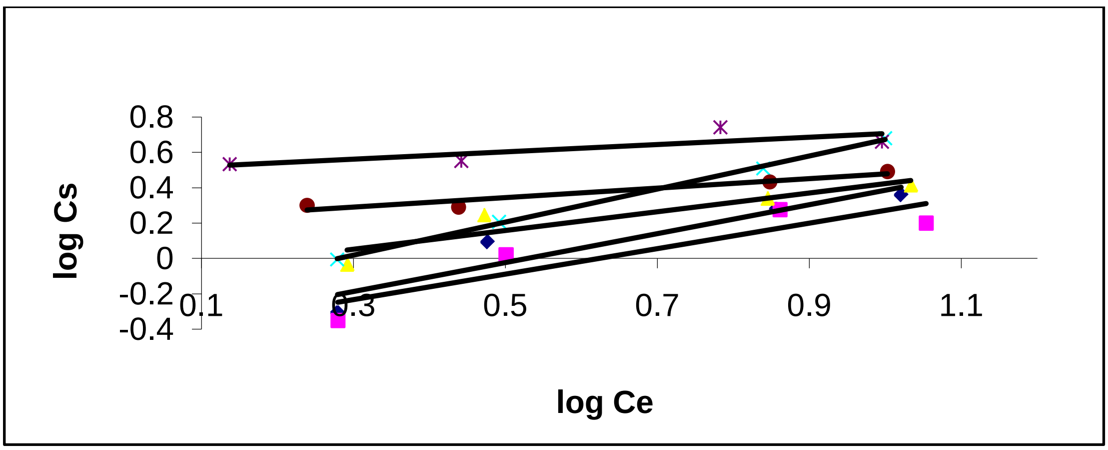

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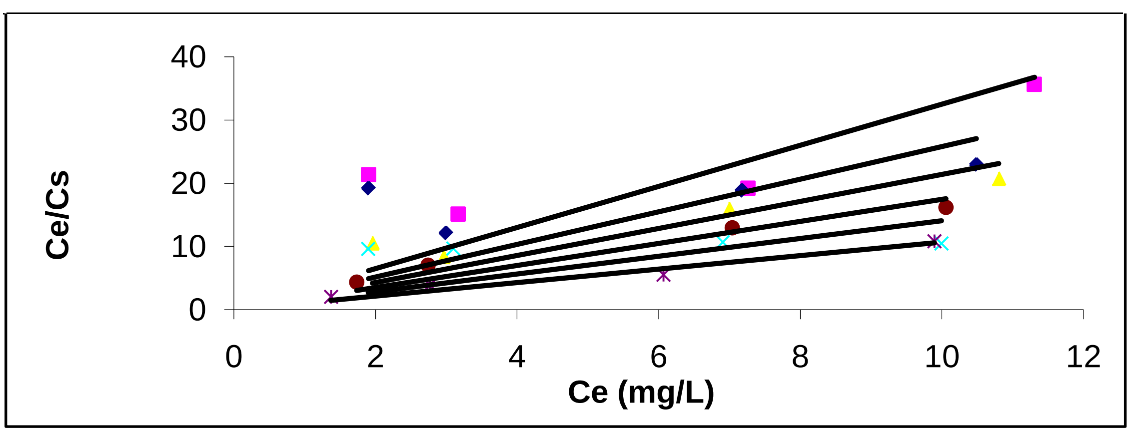

c-

Figure 4 : Fitted models for the effect of cadmium on the Simazine desorption (a) Linear (b) Ferundlich (c) Langmuir, on the selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6)