

Kinetic Study of Adsorption-Desorption of Simazine on Agricultural Soils

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Abstract:-In this work a study for adsorption-desorption behavior of Simazine [2-chloro-4, 6 bis(ethylamine)-1,3,5-triazine] which is anionic (very weak base) herbicide have been performed by batch equilibrium experiments on six agricultural soil samples which has different texture. The adsorption processes of simazine on the soil solid matrix exhibited moderate rate of accumulation with 20.16% after 0.5h. The first order kinetic model was most agreeable with the experimental data. Values of equilibrium constant K_o for Simazine on selected soil samples were in the following from 1.893 to 1.968. The S type sorption isotherm revealed the competing reactions at soil surface and in solution. Linear, Freundlich and Langmuir models were applied to describe the adsorption-desorption of the pesticide affinities to the soil samples. The distribution coefficient K_d values for adsorption process varied between 1.924 - 2.270 mlg^{-1} , and for desorption process varied between 9.593- 14.27 mlg^{-1} . Freundlich coefficient K_F for Simazine ranged between 0.134-0.648 mlg^{-1} for adsorption processes. The value Freundlich coefficient for desorption process K_{Fdes} ranged from 0.101 to 0.269 mlg^{-1} . Organic matter free energy ΔG_{OM}^o calculated according to the values of binding Freundlich constant K_F , its negative values revealed that the adsorption of the Simazine on the six soil samples spontaneously. Langmuir coefficient K_L for adsorption process varied between 0.045 - 0.119 mlg^{-1} . Langmuir coefficient K_{Ldes} values for desorption process varied between 0.015 - 0.097 mlg^{-1} . All desorption isotherms exhibited hysteresis.

Keywords:-Adsorption- desorption isotherms, Simazine, UV-spectrophotometer.

I. INTRODUCTION

Studies elucidated that application of pesticides risk through its trace level residues present in soil, water, air, and food, may result harmful effects on human and environmental health^(1&2). Complicated mechanism of pesticides sorption by heterogeneous nature of soil components, most of pesticides have some polarity, and there is substantial evidence that polar organic compounds are sorbed by both organic and inorganic soil component^(3&4). Soil surface properties and its various components may contribute independently to sorption of pesticides although the interactions between the components are likely. The adsorption-desorption processes of pesticides in soil regulated by soil texture, and the initial reaction has been associated with diffusion of the pesticides to and from the surface of the sorbent^(5&6). A competition between the pesticides and the organic matter for the sorption sites, and affected on the type of the binding. However, physical sorption is reversible while chemisorptions irreversible. The apparent of irreversibility, or hysteresis in desorption may be due to failure to reach equilibrium during desorption. Polar organic compounds form stronger bonds with soil organic matter than with soil mineral^(7&8). Hysteresis may increase with adsorbent- adsorbate contact time^(9&10). Simazine is anionic herbicide (basic) which belongs to triazine group^(11&12), simazine molecules are weakly basic, the adsorption of the protonated species on clay may be one of the most important factors influencing persistence. Triazines have been used in several crops as pre and post herbicides⁽¹³⁾. Its adsorption is associated principally with organic matter contained in soil the interaction via hydrogen bound formation or proton transfer⁽¹⁴⁾.

II. MATERIALS AND METHODS

2.1. 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⁾.

2.2. Pesticide

Analytical grade 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, acid and base ionization equilibrium ($K_b=12.1$), octanol-water partition coefficient ($K_{oc}=269\text{mlg}_{oc}^{-1}$), (water solubility at 20°C is 6.2 mgL^{-1}), (vapor pressure 0.003mPa at 25°C), and ($t_{1/2}=90$ day). All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of the pesticides were prepared in deionised water.

2.3. Adsorption Experiments

Adsorption of Simazine from aqueous solution was determined at temperature (25 ± 1 C°) employing a standard batch equilibrium method^(16, 17). Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (3,

5, 10, and 15 $\mu\text{g ml}^{-1}$) were for the pesticides 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^(13&18). 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 ($25\pm 1\text{ }^\circ\text{C}$) after equilibration for 24 h with different pesticide concentrations (3, 5, 10 and 15 $\mu\text{g ml}^{-1}$) 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⁽¹⁹⁾. The resuspended samples were shaken for mentioned time previously for the kinetic study for each pesticide.

III. DATA ANALYSIS

3.1. Adsorption-Desorption Kinetics & Equilibrium constant

The rate constants for adsorption-desorption of Simazine on soils were calculated using the first order rate expression^(19&20):

(1)

Where k_a is the rate constant for adsorption (h^{-1}), t the time (h), C is C_o the concentration of pesticide added ($\mu\text{g ml}^{-1}$) and C_t the amount adsorbed ($\mu\text{g ml}^{-1}$) at time t . In all cases, first order equation provided satisfactory fit for the data as linear plots of $\log(C_o - C_t)$ against t 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 $\log C_e$ 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 to the desorption rate constant k_{des} , K_o were calculated using the following expression⁽²¹⁾.

(2)

It indicates that adsorption in the systems studied may be viewed as a reaction in which a solute molecule collides with an adsorption site to form the adsorption complex. Desorption may be viewed as "unimolecular" process by which the adsorption complex dissociates to a free site and solute molecule. The large difference in the equilibrium adsorption arise mainly from the difference in the rate of desorption.

3.2. Adsorption-Desorption Isotherms

3.2.1. Distribution Coefficient

The distribution coefficient (K_d) was calculated by the using the following expression^(20&22).

(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), and averaged across all equilibrium concentration to obtain a single estimate of K_d of Simazine demonstrated in(Table 2 & fig1a). The same equations (3) used to describes the process of desorption in all experiments and on all soil samples the results was demonstrated in (Table 2 & fig2 a).

3.2.2. Freundlich Coefficient

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation⁽²²⁾:

(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 $\log K_F$ is the intercept of the straight line resulting from the plot of $\log C_s$ versus $\log C_e$ as shown in (fig 1b). 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 linearized form of the Freundlich equation⁽²²⁾:

(5)

Where C_s is the amount of pesticides still adsorbed ($\mu\text{g g}^{-1}$), C_e is the equilibrium concentration of pesticides in solution after desorption ($\mu\text{g mL}^{-1}$), and K_{Fdes} ($\mu\text{g g}^{1-n_{fdes}} / \text{ml}^{n_{fdes}} \text{g}^{-1}$) 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 (Table2 & fig2b).

3.2.3. Langmuir Adsorption isotherm

Data from the batch adsorption conform to Langmuir equation⁽²²⁾:

(6)

C_m is the maximum amount of pesticide adsorbed (adsorption maxima, $\mu\text{g ml}^{-1}$), it reflects the adsorption strength and K_L is the Langmuir adsorption coefficient, binding energy coefficient. The results were summarized in (Table 2 & fig1c). The same equations (6) used to describes the process of desorption in all experiments and on all soil samples⁽²³⁾ the results was demonstrated in (Table 2 & fig2 c).

3.3. Hysteresis coefficient

A study of Simazine desorption 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⁽²³⁾.

(7)

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 3 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⁽²³⁾:

(8)

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:

(9)

3.4. 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⁽²⁴⁾:

(10)

(11)

(12)

Organic matter free energy (ΔG_{OM}°) of adsorption of simazine was calculated by using the following equation⁽²⁴⁾:

(13)

Where ΔG_{OM} organic matter normalized free energy change (KJ mol^{-1}), R gas constant $8.314 \text{ J}(\text{K}.\text{mol})^{-1}$ and T Kelvin temperature.

IV. RESULTS AND DISCUSSION

4.1. Adsorption-Desorption Rate

Adsorption-desorption processes of simazine depend on types of clays and exchanged cations. The pH of the bulk solution is important for the protonation of a weakly basic organic compound, and determines the ability to exchange with a metal cation on clays⁽⁹⁾. They concluded that nitrogen lone-pair electrons delocalize into the triazine ring, thereby creating significant polarity [acidic side- chain NH group vise basic triazine ring N] and a high propensity for hydrogen bonding to

or from the molecule. Thus, particularly strong complexes are expected between simazine and either amide or carboxylic proton catalysis, possible that the Cl atom at the 2-position on the triazine rings sufficiently electron-withdrawing to inhibit its electron-donating capacity and thereby to prevent the formation of charge-transfer complexes with organic matter, its adsorption is associated via hydrogen bond formation or proton transfer^(14&15). The key properties controlling pesticide behavior in soil include ionization potential, water solubility, vapor pressure, soil retention (K_{oc}) and persistence $T_{1/2}$ ⁽²⁵⁾. The commonly proposed adsorption mechanism for Uncharged herbicide (simazine above pH 4) to clay minerals in the neutral pH range are under Vande Waals forces and hydrophobicity. Authors has been proposed that nitroaromatic compounds an electron donor-acceptor complex [ie., a pi (π) –complex] . Data in Table 1 showed that adsorption –the pesticides in all cases followed first order rate law^(26, 27), values of rate constants for adsorption-desorption of simazine on selected soil samples were in the range from 1.078 to 1.932 h^{-1} and 0.512 to 0.951 h^{-1} respectively, and the value of R^2 for adsorption-desorption of simazine on selected soil samples ranged from 0.756 to 0.983 and from 0.833 to 0.994 respectively. The value of standard error (S.E.) for adsorption-desorption of simazine on selected soil samples ranged from 0.193 to 0.216 and from 0.184 to 0.213 respectively. The values of rate constant for adsorption k_a for the pesticide was greater than desorption rate constant k_{des} , the desorption during the first few hours is likely to come from the or more accessible sites and /or from the low-energy –release sorption mechanisms, whereas simazine sorbed on less accessible sites and/or more strongly adsorbed sites is not susceptible to desorption initially and is subsequently subject to slow release over time^(28, 29). Data in table 1 demonstrated the values of equilibrium constant K_o equilibrium constant for simazine on selected soil samples were in the following from 1.893 to 1.968.

4.2. Adsorption-Desorption Isotherms

K_d values for simazine adsorption-desorption process varied between 1.924 - 2.270 mlg^{-1} and 9.593- 14.27 mlg^{-1} respectively, and the value of R^2 for simazine adsorption-desorption on selected soil samples ranged from 0.830 to 0.977 and from 0.798 to 0.982 respectively. The value of standard error (S.E.) for simazine adsorption-desorption ranged from 0.021 to 0.084 and from 0.012 to 0.091 respectively. The distribution coefficient K_{OM} and K_{OC} were related to soil organic matter and carbon content⁽³⁰⁾ as expressed in equation 10, 11, and 12. Values of K_{OC} ranged between 66-20 mlg^{-1} , while the values K_{OM} ranged between 1.139-3.487 mlg^{-1} .

The values of organic matter normalized free energy ΔG_{OM}^0 as expressed in equation 13, (Table 2) were in the range -9.96 to -23.29 $KJmol^{-1}$ for Simazine. The negative values of ΔG_{OM}^0 revealed that the adsorption of the Simazine in the six soil samples are spontaneous process and the adsorption is partly physical nature⁽²²⁾ and partly chemical, hence the herbicides adsorption may be due to coordination, 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. Thus constant partitioning of the pesticide between soil and solution, and water molecules do not pose strong competition for the adsorption sites, and also more affinity of the studied pesticides towards soil particulate matter than soil solution. Because most of the available sites in these soils are probably present at the surface of SOM and are therefore readily available for adsorption.

Freundlich coefficient K_F for simazine adsorption-desorption behavior ranged between 0.134-0.648 mlg^{-1} and 0.101-0.269 mlg^{-1} respectively. Freundlich desorption isotherms K_{Fdes} values indicate that a small proportion of the chemical has desorbed into solution^(31,32). The value of n indicating a linear relationship as shown in fig 1 b & 2 b, the value of n ranged between 1.171-1.595. The variable slopes of the adsorption isotherm obtained for different soil systems studied reveal that the Simazine adsorption on soil complex phenomena involving different types of adsorption sites with different surface energies. The value of n_{des} describes nonlinearity curvature in the desorption isotherm and is often used as an index of hysteresis^(33, 34), the values of n_{des} ranged between 1.092-1.686. The value of R^2 for simazine adsorption-desorption on selected soil samples ranged from 0.884 to 0.978 and from 0.792 to 0.981 respectively. The value of standard error (S.E.) for simazine adsorption-desorption ranged from 0.028 to 0.036 and from 0.031 to 0.038 respectively.

The values of K_L , C_m , S.E and R^2 demonstrated in table 2 for simazine adsorption-desorption on selected soil sample. The K_L , C_m , S.E, and R^2 ranged from 0.045- 0.119 mlg^{-1} , 6.711-7.937 μgg^{-1} , 0.029-0.039, and 0.718-0.954 for adsorption of simazine respectively. While K_L , C_m , S.E, and R^2 ranged from 0.015-0.097 mlg^{-1} , 1.095-6.250 μgg^{-1} , 0.031-0.033, and 0.714-0.859 for desorption of simazine respectively.

Data in table 3 demonstrated H_1 values for simazine from the selected soil samples in the range from 0.738-1.376, 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 simazine on the selected soil samples were summarized in table 3 ranged from 7 to 38. Whereas hysteresis coefficient (ω) is only applicable for the traditional type isotherms of the successive desorption^(35, 36). The data in table 3 demonstrated hysteresis coefficient (λ) according to equation 9 for adsorption-desorption of for simazine from the selected soil samples were ranged from 4 to 20.

V. CONCLUSION

According to our results significant amounts of triazines the Uncharged herbicide (simazine above pH 4) may be stored in soil after application. The persistence of the herbicide bound to soil particles can be mobilized and leading to wide spread contamination. All desorption isotherms exhibited hysteresis. Hysteresis, which represents differences between sorption-desorption isotherms it could be due to the change in sorption capacity, or to incomplete equilibrium and to degradation or transformation of the pesticide during experimentation. Adsorption processes of the pesticide are generally ascribed to H-bonding, van der Waals forces, electrostatic attraction, and coordination reactions with the active surfaces of the soil matrix, and also occur through the diffusion phenomena.

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Table1: Adsorption-Desorption rate constants and Equilibrium constant for Simazine on the selected soil samples.

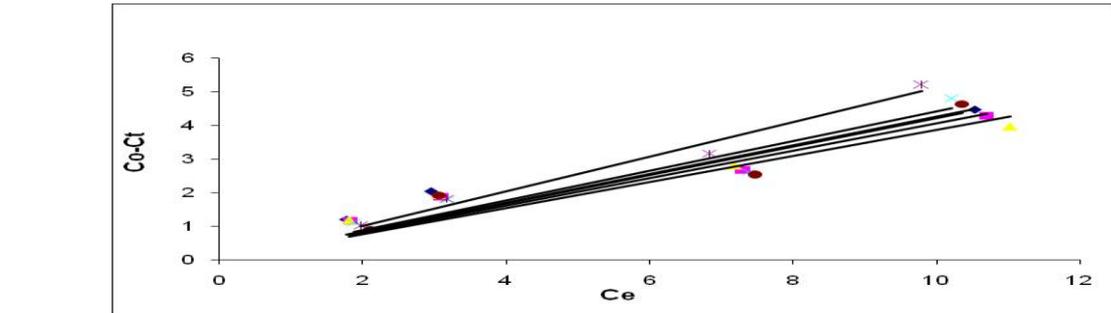
Soil	Conc. ppm	adsorption			desorption			K_0
		K_{ads} (calic (h ⁻¹))	S.E	R ²	K_{des} (calic (h ⁻¹))	S.E	R ²	
S ₁	3	1.361	0.199	0.816	0.771	0.209	0.863	1.968
	5	1.078	0.196	0.924	0.512	0.208	0.971	
	10	1.471	0.200	0.812	0.635	0.211	0.885	
	15	1.428	0.203	0.852	0.792	0.212	0.960	
S ₂	3	1.362	0.198	0.912	0.697	0.203	0.956	1.903
	5	1.299	0.199	0.756	0.602	0.205	0.936	
	10	1.370	0.197	0.973	0.719	0.210	0.931	
	15	1.211	0.195	0.950	0.737	0.211	0.905	
S ₃	3	1.463	0.201	0.926	0.647	0.203	0.981	1.916
	5	1.240	0.198	0.849	0.520	0.206	0.881	
	10	1.321	0.197	0.905	0.668	0.209	0.930	
	15	1.313	0.197	0.914	0.951	0.211	0.930	
S ₄	3	1.932	0.216	0.893	0.592	0.202	0.959	1.893
	5	1.176	0.193	0.854	0.815	0.184	0.925	
	10	1.394	0.198	0.860	0.737	0.210	0.913	
	15	1.146	0.196	0.983	0.839	0.211	0.960	
S ₅	3	1.774	0.201	0.820	0.754	0.204	0.978	1.957
	5	1.158	0.196	0.854	0.709	0.206	0.937	
	10	1.291	0.196	0.876	0.697	0.210	0.986	
	15	1.326	0.200	0.806	0.621	0.211	0.943	
S ₆	3	1.578	0.202	0.863	0.805	0.207	0.994	1.947
	5	1.116	0.196	0.875	0.923	0.206	0.963	
	10	1.452	0.198	0.855	0.859	0.189	0.973	
	15	1.252	0.197	0.879	0.898	0.213	0.833	

Table 2: Adsorption-desorption isotherm parameters, linear, Freundlich and Langmuir models for Simazine on the selected soil samples.

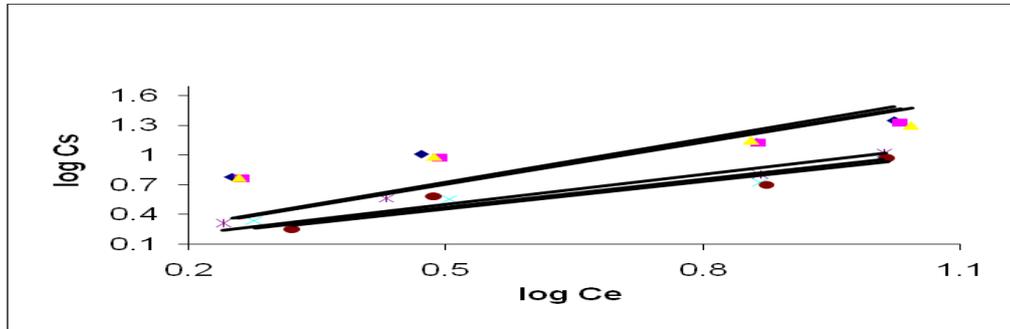
Models	Parameter	Soils						
		S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	
Adsorption	Distr. coffi	K _d (calc)	1.984	2.102	2.113	2.092	1.924	2.270
		S.E	0.084	0.070	0.077	0.021	0.022	0.024
		R ²	0.830	0.876	0.977	0.906	0.964	0.854
		K _{OC} (mL/g)	71	202	66	89	101	150
		K _{OM} (mL/g)	1.222	3.487	1.139	1.531	1.733	2.593
	Freundlich	K _F (mL/g)	0.648	0.607	0.636	0.134	0.147	0.556
		S.E	0.036	0.035	0.034	0.028	0.031	0.029
		n _F	1.548	1.490	1.595	1.285	1.212	1.171
		R ²	0.951	0.962	0.978	0.939	0.963	0.884
		ΔG ^o _{OM} (KJ/mol)	-17.99	-23.29	-17.13	-9.96	-11.68	-20.66
	Langmuir	K _L (ml/g)	0.105	0.092	0.119	0.051	0.076	0.045
		S.E	0.033	0.031	0.039	0.036	0.029	0.035
		C _m (μg/g)	7.634	7.937	6.711	12.04	7.143	6.993
		R ²	0.718	0.755	0.935	0.933	0.842	0.954
		K _d (calc)	14.27	9.59	10.70	12.09	12.31	10.55
Desorption	Distr.coffi	S.E	0.012	0.017	0.091	0.017	0.018	0.057
		R ²	0.798	0.852	0.951	0.842	0.813	0.982
		K _{Fdes} (mL/g)	0.262	0.101	0.239	0.111	0.128	0.269
	Freundlich	S.E	0.038	0.033	0.036	0.033	0.032	0.031
		n _F	1.404	1.374	1.159	1.686	1.642	1.092
		R ²	0.901	0.899	0.963	0.952	0.792	0.981
		K _L (ml/g)	0.097	0.079	0.038	0.019	0.015	0.016
	Langmuir	S.E	0.033	0.030	0.031	0.032	0.031	0.031
		C _m (μg/g)	1.094	1.855	2.923	1.095	1.956	6.250
		R ²	0.746	0.713	0.859	0.835	0.714	0.739

Table 3: Hysteresis effect on desorption of Simazine on the selected soil samples.

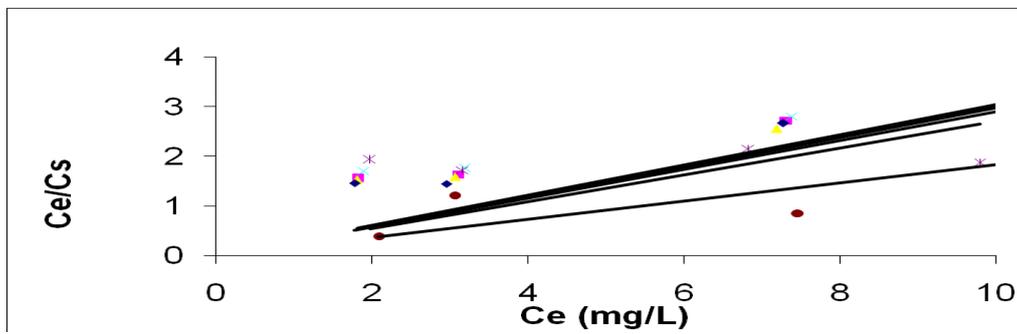
Soil	metolachlor		
	H ₁	ω	λ
S ₁	1.103	10	6
S ₂	1.084	8	5
S ₃	1.376	38	20
S ₄	0.762	24	15
S ₅	0.738	26	16
S ₆	1.072	7	4



a-

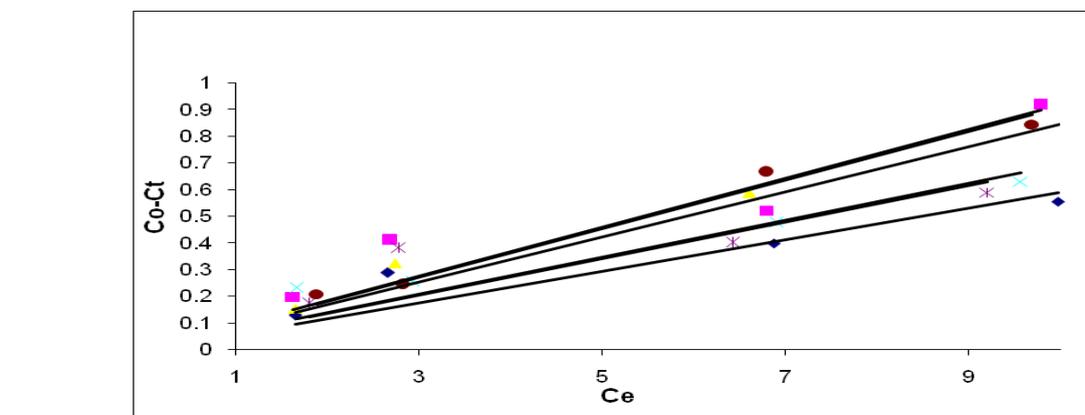


b-

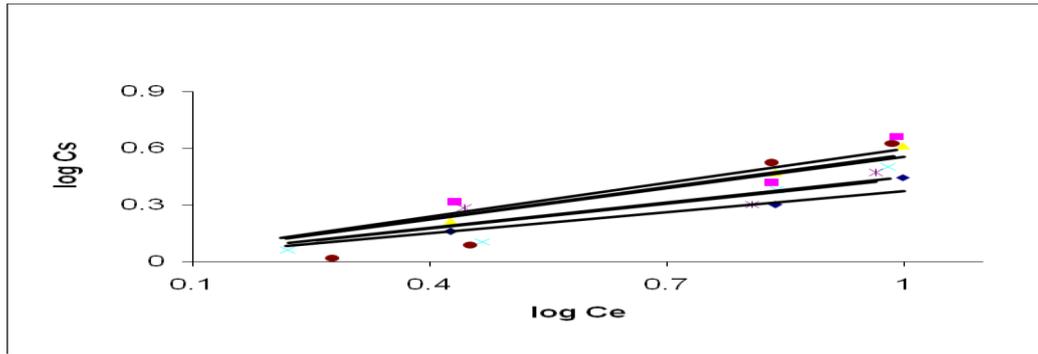


c-

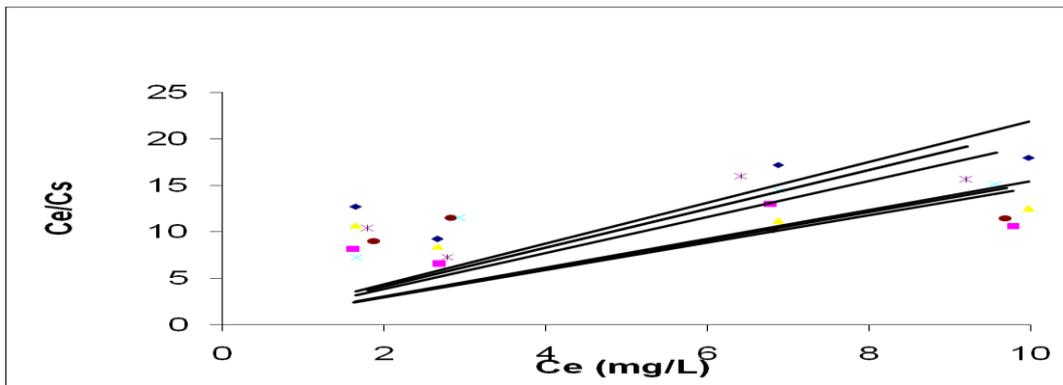
Fig. 1: Fitted models for Simazine adsorption (a)Linear (b)Freundlich (c)Langmuir, isotherms on selected soil samples (♦ S₁, ■ S₂, ▲ S₃, x S₄, * S₅, ● S₆).



a-



b-



c-

Fig. 2: Fitted models for Simazine desorption (a)Linear (b)Ferundlich (c)Langmuir, isotherms on selected soil samples (♦ S₁, ■ S₂, ▲ S₃, x S₄, * S₅, ● S₆).