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Effect of Co-pesticide on Adsorption- Desorption Process on Agricultural Soils

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Abstract**—**This work aim is to study the effect of different co-pesticides as Atrazine and propanil on adsorption processes on agricultural soil samples. The co-pesticides as Atrazine on adsorption behavior of metolachlor [2-chloro-N- (2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide)] which is nonionic herbicide, and propanil on adsorption behavior of 2,4-D (2,4- dichlorophenoxyacetic acid) as anionic herbicide have been preformed, using batch equilibrium experiments on six agricultural soil samples. Linear and Freundlich models were used to describe the competitive sorption between the pair herbicides. Variation in adsorption affinities of the soils to the pesticides was observed. Freundlich coefficient K_F values for adsorption process varied between 0.079 - 2.282 mlg^{-1} and 0.058- 0.720 mlg^{-1} for metolachlor/atrazine and 2, 4-D/propanil respectively. The sorption strength of the herbicides decreased with increasing solution concentration. A nonionic surfactant was tested for its desorption potential and was found to be fairly effective at critical micelles concentration cmc concentration with removal of more than 65% sorbed pair competitive herbicides. Freundlich coefficient for desorption process K_{Fdes} for desorption process varied between 0.209- 0.523 and 0.926- 1.296 mlg^{-1} for metolachlor/atrazine and 2,4-D/propanil respectively. To investigate the effect of adsorption-desorption in the presence of cmc concentration of the nonionic surfactant for each pesticide alone also performed by using batch equilibrium experiments on six agricultural soil samples. The Freundlich coefficient K_F in the presence of the nonionic surfactant for metolachlor and 2,4-D ranged between 0.337-0.437 and 0.001-1.012 mlg^{-1} for adsorption processes. The Freundlich coefficient K_{Fdes} values for desorption process in presence of the nonionic surfactant ranged from 0.209 to 0.689 mlg^{-1} and 0.238 to 1.442 mlg^{-1} for metolachlor and 2,4-D respectively.

Keywords**—**Atrazine, 2, 4-D, HPLC, Metalachlor Propanil.

I. INTRODUCTION

Co-application of herbicides to soil created competitive sorption between the two herbicide producing smaller partition coefficients than for separate each herbicide. The herbicides co-application on agricultural fields has the potential to increase the mobility of these herbicides in soil, thereby also increasing the risk for groundwater concentration [1&2]. Contamination of these compounds with soil and drinking water has been generally recognized as dangerous [3]. Two major factors known to influence sorption of pesticides are soil properties and molecular characteristics. Sorption of neutral organic pesticides, as atrazine depends primarily on soil organic carbon (OC) content [4]. Sorption determines whether the pesticide will persist, be transported, and pollute the underlying ground water [5]. Strongly adsorbed and persistent pesticides that have large (K_{oc}) values are likely to remain near the soil surface. In contrast, weakly adsorbed but persistent pesticides (small K_{oc}) may be readily leached through the soil and more likely to contaminate ground water [6]. Kinetic data, which are measured infrequently, have the advantage of taking into account possible time-dependent reactions for adsorption, release, or desorption. Non-equilibrium conditions may be caused by the heterogeneity of sorption sites and slow diffusion to sites within the soil matrix, or organic matter [7]. Batch equilibrium experiments and Freundlich values are usually obtained for such competes for sorption sites in soil [8]. The selected herbicides co-application atrazine [9&10] and metolachlor [11] to soil. Each herbicides were persistence in the soil, its soluble in water, and poorly bound to most soils so it leaching down towards the ground water. The two nonionic herbicides were essentially slightly decreased and desorption amount increase little. Propanil [10&12] and 2, 4-D [11] herbicides co-application to soil. The effects of propanil on the sorption of anionic herbicides are possibly caused by the enhancement of electrostatic repulsion by pre-sorbed anionic herbicide/propanil and competition for sorption on interior sorption sites of soil particles which probably leads to small smaller partition coefficients. Employing of surfactant as batch washing techniques is an ex-situ process in which the contaminated soil is first excavated [13], which cause higher desorption for the herbicides.

II. MATERIALS AND METHODS

2.1 SOLIS

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[14].

2.2 MATERIALS

Analytical grad substituted with following purities expressed in weight percent Metolachlor (purity 97.8%), and 2, 4-D (purity 98%) atrazine (purity 99.2%), propanil (purity 99.7%) respectively. Were all purchased from Riedal-de Haen, Sigma-Aldrich company ltd. A nonionic surfactant TritonX-100 (TX-100), its chemical name is [Octylphenol ethoxcylate] 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.

2.3 ADSORPTION-DESORPTION EXPERIMENTS

Adsorption of the pesticides from aqueous solution was determined at temperature (25±1 C°) employing a standard batch equilibrium method. Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (1, 2, 4 and 8 µg ml^{-1}) were for metolachlor/Atrazine 2,4-D/propanil, which the ratio of each pair were 1:1. 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 for metolachlor/Atrazine and 0.5, 1, 1.5,2, 2.5, 3, 3.5, 4, 6 and 24h for 2,4-D/propanil. 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) for each pesticide concentration. The detailed information about the soil characteristics and their sorption process has been reported in previous work [11]. Desorption processes were done as each test tube was placed in a thermostated shaker at (25±1 C°) after equilibration for sufficient time as mentioned above with different pesticide concentrations (1, 2, 4 and 8 µg ml^{-1}) the samples were centrifuged, 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of a nonionic surfactant at cmc concentration and this repeated for four times [15]. Adsorption-desorption of two pesticides each alone done in presence of nonionic surfactant at cmc concentration as mentioned above [16]. The resuspended samples were shaken for mentioned time previously for the kinetic study for each pesticide.

III. DATA ANALYSIS

3.1 ADSRPTION-DESORPTION ISOTHERM

3. 2.1 DISTRIBUTION COEFFICIENT

The distribution coefficient (K_d) was calculated by the using the following expression [17].

$$C_s = K_d C_e \qquad (1)$$

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 the pesticides demonstrated in (Table 1-4)

3. 2.1 FREUNDLICH COEFFICIENT

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation [17]

$$\log C_s = \log K_F + \frac{1}{n}\log C_e \qquad (2)$$

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 as shown in fig 1-4 . The values of K_F and 1/n calculated from this regression equation showed that Freundlich adsorption model effectively describes isotherms for the pesticides in all cases. Desorption isotherms of the pesticides were fitted to the linearzed form of the Freundlich equation [18].

$$\log C_s = \log K_{Fdes} + \frac{1}{n_{des}}\log C_e \qquad (3)$$

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 the pesticides desorption [19]. The value of the K_{Fdes} and n_{fdes} constants of the pesticides demonstrated in (Table1-4).

3. 3 HYSTERESIS COEFFICIENT

A study of the pesticides 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 [18].

$$H_1 = \frac{n_a}{n_{des}} \quad (4)$$

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&6 demonstrated H_1 values for metolachlor, and 2, 4-D respectively. 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].

$$\omega = (\frac{n_a}{n_{des}} - 1)x100 \quad (5)$$

Recently Zhu et. al [21] 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.

$$\lambda = (\frac{n_a + 1}{n_{des} + 1} - 1)x100 \quad (6)$$

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 [22].

$$\%OC = \frac{\%OM}{1.724} \quad (7)$$

$$K_{OM} = \frac{100K_d}{\%OM} \quad (8)$$

$$K_{OC} = \frac{100K_d}{\%OC} \quad (9)$$

IV. RESULTS AND DISCUSSION

The K_d values for adsorption process for metolachlor/atrazine varied between 1.384 - 2.832 mlg^{-1} while the regression coefficient R^2 value ranging from 0.705 to 0.895 with standard error S.E. value between 0.012 – 0.096. The K_d values for adsorption process for 2,4-D/propanil varied between 2.209- 5.542 mlg^{-1}, while the value of R^2 ranging from 0.704 to 0.783 with standard error S.E. value between 0.019 – 0.058, the regression equations relating that the highest values are the most fitted model. The competitive effect of pair pesticides sorption by soil generally decreased with increasing initial herbicide concentrations because of the saturation of sorption sites in soil, our results agreed with research [2].The each two pair pesticides are widely used for pest control in agricultural crops[23&24].

The desorption experiments were conducted with a nonionic surfactant TritonX-100 at concentration 0.1cmc, cmc and 20cmc on metolachlor and 2,4-D sorbed soil corresponding to initial concentration 4 µg mL^{-1} the comparative results shown in table 7, present that the degree of desorption of each pesticides from soil into surfactant solution was 46 % for 0.1cmc concentration; 65% for cmc concentration and 68% for 20cmc concentration. The cmc concentration gave the best results as there was only a normal increase in desorption at the concentration of 3%. So the used surfactant solution is therefore fairly effective in desorption of metolachlor and 2, 4-D from the contaminated soil. The dynamics are believed to be highly related to the adsorption of the four herbicides used, could be partially explained by the unoccupied sites in each soil more by the total sorption capacity [25]. Although results of the research showing an important role to the organic matter in the adsorption process[26]. Another explanation of the mechanism for adsorption process was the formation of adducts between the pair herbicide used and the and the constituent of the soil [27].

The K_d values for desorption process in the presence of cmc concentration of the surfactant varied between for metolachlor/atrazine 3.498- 14.43 mlg^{-1} while the value of R^2 ranging from 0.726 to 0.957 with standard error S.E. value between 0.016 – 0.090. The K_d values for desorption process in the presence of cmc concentration of the surfactant for 2,4-D/propanil varied between 18.25- 52.46 mlg^{-1} while the value of R^2 ranging from 0.763 to 0.996 with standard error S.E. value between 0.005 – 0.091. The Ferundlich nonlinear sorption isotherm showed a good fit to the measured data for all soil samples for metolachlor/atrazine and 2,4-D/propanil. The K_F values for adsorption process for metolachlor/atrazine varied between 0.079 - 2.282 mlg^{-1} , the R^2 value ranging from 0.758 to 0.889 with S.E. 0.032-0.039 and the value of the nonlinearity reneging between n_F 1.515-2.392. The K_F values for adsorption process for2,4-D/propanil 0.058- 0.720 mlg^{-1}, the R^2 value ranging from 0.799 to 0.987 with S.E. 0.032-0.038 and the value of the nonlinearity reneging between n_F 0.543-2.198. The values of K_F less for the two pair as the two pesticides were used alone. Freundlich coefficient for desorption process K_{Fdes} for metolachlor/atrazine in the presence of cmc concentration of the surfactant varied between 0.209- 0.523 mlg^{-1} the R^2 value ranging from 0.770 to 0.941 with S.E. 0.044-0.054, the values of n_{Fdes} 1.209-3.968. The K_{Fdes} for 2, 4-D/propanil in the presence of cmc concentration of the surfactant between 0.926- 1.296 mlg^{-1} the R^2 value ranging from 0.725 to 0.996 with S.E. 0.068-0.083, values of n_{Fdes} 0.588-1.342. The K_d values for adsorption process in the presence of cmc concentration of the surfactant varied between for metolachlor 1.000- 1.226 mlg^{-1} while the value of R^2 ranging from 0.703 to 0.901 with standard error S.E. value between 0.154 – 0.252. The K_d values for adsorption process in the presence of cmc concentration of the surfactant for 2,4-D varied between 1.332- 3.712 mlg^{-1} while the value of R^2 ranging from 0.693 to 0.965 with standard error S.E. value between 0.025 – 0.068. The K_d values for desorption process in the presence of cmc concentration of the surfactant varied between for metolachlor 4.431- 13.01 mlg^{-1} while the value of R^2 ranging from 0.768 to 0.957 with standard error S.E. value between 0.010 – 0.031. The K_d values for desorption process in the presence of cmc concentration of the surfactant for 2,4-D varied between 1.081- 57.48 mlg^{-1} while the value of R^2 ranging from 0.707 to 0.965 with standard error S.E. value between 0.023 – 0.086. The K_F values for adsorption process in the presence of cmc concentration of the surfactant for metolachlor varied between 0.337 - 0.437 mlg^{-1} , the R^2 value ranging from 0.752 to 0.880 with S.E. 0.041-0.049 and the value of the nonlinearity reneging between n_F 1.600-2.387. The K_F values for adsorption process in the presence of cmc concentration of the surfactant for 2, 4-D 0.001- 1.012 mlg^{-1}, the R^2 value ranging from 0.849 to 0.992 with S.E. 0.0324-0.039 and the value of the nonlinearity reneging between n_F 0.808-2.028. Freundlich coefficient for desorption process K_{Fdes} for metolachlor in the presence of cmc concentration of the surfactant varied between 0.209- 0.689 mlg^{-1} the R^2 value ranging from 0.776 to 0.998 with S.E. 0.027-0.063, the values of n_{Fdes} 0.709-1.828. The K_{Fdes} for 2, 4-D in the presence of cmc concentration of the surfactant 0.238- 1.442 mlg^{-1} the R^2 value ranging from 0.735 to 0.976 with S.E. 0.021-0.089 ,the values of n_{Fdes} 0.888-1.486. The size of the organic is considered to play an important role in its rate of adsorption, Baily and white 1970[28]. et. al. summarized the of molecular size as follows: a)Adsorption of noneletrolytes by nonpolar adsorbents increases as molecular weights of the substances increases. b) Van der Waals forces of adsorption increases with increasing molecular size. c) Adsorption decreases because of steric hindrance. The evidence available also shows the presence of a maximum limit in molecular size in adsorption of organic compounds. Larger molecules (chain length greater than five units) may be adsorbed only in the presence of excess water. However very large molecules difficulties in adsorption due to adverse molecular configuration. The use of mixture for the each pair herbicides, This indicated that atrazine and propanil competed with the two herbicides for sorption sites in soil[29]. The differences in adsorption coefficient between samples were statistically significant, for soils with organic content for that readily sorbed propanil than the other, thereby being more competitive in soils with greater soil organic matter content. The Ferundlich slope of the isotherm was always less than unity and indicating that the affinity between the herbicides used alone and soil was greatest at initial herbicides concentrations and decreased as increasing the herbicides concentrations [30].

Data in table 5 demonstrated H_1 values for metolachlor/atrazine and 2,4-D/propanil from the selected soil samples in the range from 0.615-1.751 and 0.594-2.524 respectively**.** The calculated values of hysteresis coefficient (ω) for adsorption-desorption of for metolachlor/atrazine and 2, 4-D/propanil on the selected soil samples ranged from -43 to -75 and from -41 to 152 respectively. Whereas hysteresis coefficient (ω) is only applicable for the traditional type isotherms of the successive desorption [31&32]. The hysteresis coefficient (λ) for metolachlor/atrazine and 2,4-D/propanil from the selected soil samples were ranged from -10 to 148 and from 29 to 1662 respectively. The H_1 values for metolachlor and 2, 4-D alone in the presence of cmc surfactant as summarized in table 6 from the selected soil samples in the range from 1.144-2.687 and 0.869-2069 respectively**,** indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases, and indicate the increased difficulty of the sorbed analytic to desorbed from the matrix. The calculated values of hysteresis coefficient (ω) for adsorption-desorption of for metolachlor and 2,4-D on the selected soil samples ranged from 14 to 169 and from -13 to -107 respectively. The hysteresis coefficient (λ) for metolachlor and 2, 4-D from the selected soil samples were ranged from -40 to -94 and from -6 to 1441 respectively.

V. CONCLUSION

The using of each pair of herbicides metolachlor/atrazine and 2,4-D/propanil may increase herbicides leaching to depth relative to the use of each one alone on the six agricultural soil samples. The cmc concentration gave the best results in desorption. So the used surfactant solution is therefore fairly effective in desorption of metolachlor, 2, 4-D from the contaminated soil and for each pair.

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Table 1: Adsorption of the co-application metolachlor/atrazine and their desorption in the presence of TritonX-100 at cmc concentration, the linear and Freundlich models isotherm parameters on the selected soil samples.

Ads-des Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	2.832	1.618	1.599	1.384	1.870	1.956
	S.E	0.075	0.072	0.096	0.012	0.075	0.095
	R^2	0.705	0.821	0.794	0.890	0.893	0.755
	K_{OC}(mL/g)	101	156	50	59	98	130
	K_{OM}(mL/g)	1.744	2.685	0.863	1.013	1.684	2.235
Freundlich (ads)	K_F(mL/g)	0.079	0.199	0.233	0.282	0.155	0.218
	S.E	0.034	0.037	0.038	0.039	0.032	0.035
	n_F	2.392	1.515	1.761	1.789	1.563	2.257
	R^2	0.864	0.835	0.810	0.889	0.776	0.758
Des.Distr. coffi.	K_d (calc)	4.158	8.386	3.498	14.43	6.116	4.366
	S.E	0.019	0.027	0.023	0.016	0.090	0.024
	R^2	0.940	0.780	0.957	0.780	0.759	0.726
Freundlich(des)	K_{Fdes}(mL/g)	0.244	0.461	0.209	0.464	0.523	0.252
	S.E	0.044	0.046	0.045	0.054	0.051	0.047
	n_F	1.366	2.463	1.178	2.463	1.209	3.968
	R^2	0.941	0.838	0.906	0.838	0.913	0.770

Table 2: Adsorption of metolachlor alone and it's desorption in the presence of TritonX-100 at cmc concentration, the linear and Freundlich models isotherm parameters on the selected soil samples.

Ads-des Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	1.142	1.160	1.099	1.000	1.226	1.014
	S.E	0.252	0.127	0.122	0.242	0.154	0.250
	R^2	0.741	0.800	0.901	0.703	0.777	0.721
	K_{OC}(mL/g)	40.8	112	34	42	64	67
	K_{OM}(mL/)	0.703	1.924	0.593	0.732	1.104	1.158
Freundlich (ads)	K_F(mL/g)	0.385	0.340	0.348	0.419	0.337	0.437
	S.E	0.045	0.042	0.041	0.045	0.043	0.049
	n_F	2.092	1.718	1.600	2.387	1.905	2.325
	R^2	0.771	0.880	0.879	0.856	0.854	0.752
Des.Distr. coffi	K_d (calc)	11.11	13.01	4.431	7.109	8.069	12.17
	S.E	0.016	0.017	0.031	0.027	0.012	0.010
	R^2	0.868	0.768	0.859	0.781	0.957	0.811
Freundlich(des)	K_{Fdes}(mL/g)	0.658	0.659	0.209	0.488	0.614	0.689
	S.E	0.057	0.063	0.044	0.027	0.062	0.061
	n_F	1.828	0.987	1.178	2.049	0.709	1.451
	R^2	0.981	0.803	0.906	0.776	0.998	0.856

Table 3: Adsorption of the co-application of 2,4-D/propanil and their desorption in the presence of TritonX-100 at cmc concentration, the linear and Freundlich models isotherm parameters on the selected soil samples.

Ads-des Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	2.678	3.362	2.209	5.542	4.565	3.519
	S.E	0.058	0.019	0.064	0.029	0.035	0.033
	R^2	0.704	0.783	0.771	0.742	0.728	0.737
	K_{OC}(mL/g)	96	324	69	235	238	233
	K_{OM}(mL/g)	1.649	5.578	1.191	4.055	4.112	4.020
Freundlich (ads)	K_F(mL/g)	0.720	0.100	0.135	0.203	0.122	0.058
	S.E	0.034	0.035	0.033	0.038	0.036	0.037
	n_F	0.543	1.484	1.988	2.151	2.198	1.795
	R^2	0.799	0.987	0.920	0.872	0.935	0.806
Des.Distr. coffi.	K_d (calc)	18.25	30.15	27.56	28.04	52.46	21.56
	S.E	0.091	0.074	0.033	0.005	0.027	0.035
	R^2	0.835	0.838	0.912	0.996	0.763	0.828
Freundlich(des)	K_{Fdes}(mL/g)	0.926	1.296	1.096	1.131	1.291	1.022
	S.E	0.068	0.079	0.074	0.073	0.083	0.069
	n_F	0.914	0.588	1.114	1.043	1.342	0.968
	R^2	0.782	0.932	0.891	0.996	0.725	0.897

Table 4: Adsorption of 2,4-D alone and its desorption in the presence of TritonX-100 at cmc concentration, the linear and Freundlich models isotherm parameters on the selected soil samples.

Ads-des Models	Parameter	Soils					
		S_1	S_2	S_3	S_4	S_5	S_6
Ads.Distr. coffi.	K_d (calc)	1.332	1.801	1.401	3.712	3.037	2.212
	S.E	0.068	0.025	0.067	0.042	0.041	0.033
	R^2	0.965	0.791	0.977	0.693	0.825	0.703
	K_{OC}(mL/g)	48	173	44	158	159	147
	K_{OM}(mL/g)	0.820	2.988	0.756	2.716	2.736	2.527
Freundlich (ads)	K_F(mL/g)	0.253	1.012	0.266	0.059	0.001	0.110
	S.E	0.038	0.036	0.037	0.039	0.035	0.034
	n_F	1.420	0.808	1.678	2.028	1.838	1.773
	R^2	0.930	0.977	0.992	0.905	0.849	0.922
Des.Distr. coffi.	K_d (calc)	1.081	21.27	13.54	16.77	57.48	27.954
	S.E	0.056	0.029	0.060	0.086	0.028	0.023
	R^2	0.965	0.932	0.888	0.707	0.838	0.802
Freundlich(des)	K_{Fdes}(mL/g)	0.238	1.031	0.754	0.784	1.442	1.064
	S.E	0.038	0.067	0.021	0.026	0.089	0.071
	n_{Fdes}	1.443	0.929	1.504	1.486	0.888	1.340
	R^2	0.976	0.927	0.999	0.735	0.796	0.932

Table 5: Hysteresis effect for the co-application of each pair metolachlor/atrazine, and 2,4-D/propanil on the selected soil samples.

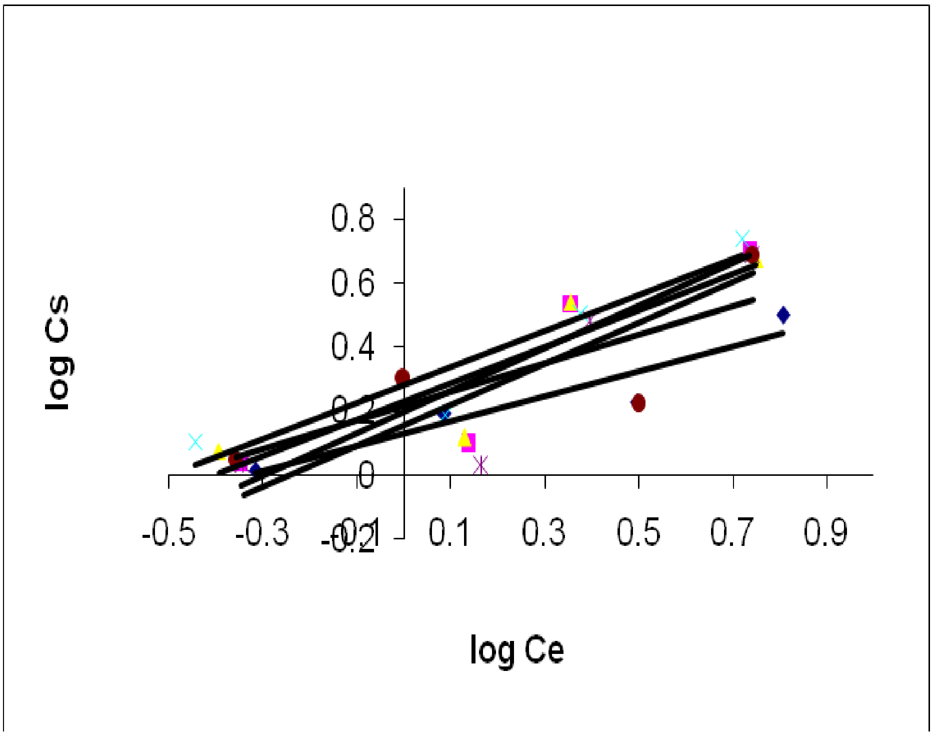
Soil	Metolachlor /atrazine			2,4-D/propanil		
	H_1	ω	λ	H_1	ω	λ
S_1	1.751	75	184	0.594	-41	29
S_2	0.615	-39	109	2.524	152	1196
S_3	1.495	49	-10	1.785	79	712
S_4	0.726	-27	63	2.062	106	457
S_5	1.293	29	237	1.638	64	958
S_6	0.569	-43	16	1.854	85	1662

Table 6: Hysteresis effect for metolachlor and, 2,4-D each one alone on the selected soil samples.

Soil	metolachlor			2,4-D		
	H_1	ω	λ	H_1	ω	λ
S_1	1.144	14	71	0.984	-2	-6
S_2	1.740	74	94	0.869	-13	2
S_3	1.358	36	- 40	1.116	12	183
S_4	1.164	16	16	1.365	37	1228
S_5	2.687	169	82	2.069	107	1441
S_6	1.602	60	58	1.323	32	867

Table 7: Desorption data at initial sorbate concentration 4 µg ml^{-1} and pH=6 for metolachlor and, 2,4-D each one alone at different surfactant concentration.

Agitation Time (h)	Metolachlor at different Surfactant Concentration			2,4-D at different Surfactant Concentration		
	0.1cmc	cmc	20cmc	0.1cmc	cmc	20cmc
0.5	15.99	19.55	21.66	12.56	16.43	18.87
1	19.11	30.78	36.25	16.32	27.45	33.31
2	26.65	40.23	43.27	23.32	37.13	40.67
3	37.68	46.74	47.34	34.22	43.11	44.87
4	40.43	48.86	50.22	37.34	44.23	47.89
6	41.56	50.44	51.46	38.17	47.55	48.43
24	41.65	50.89	51.85	38.74	47.74	48.89



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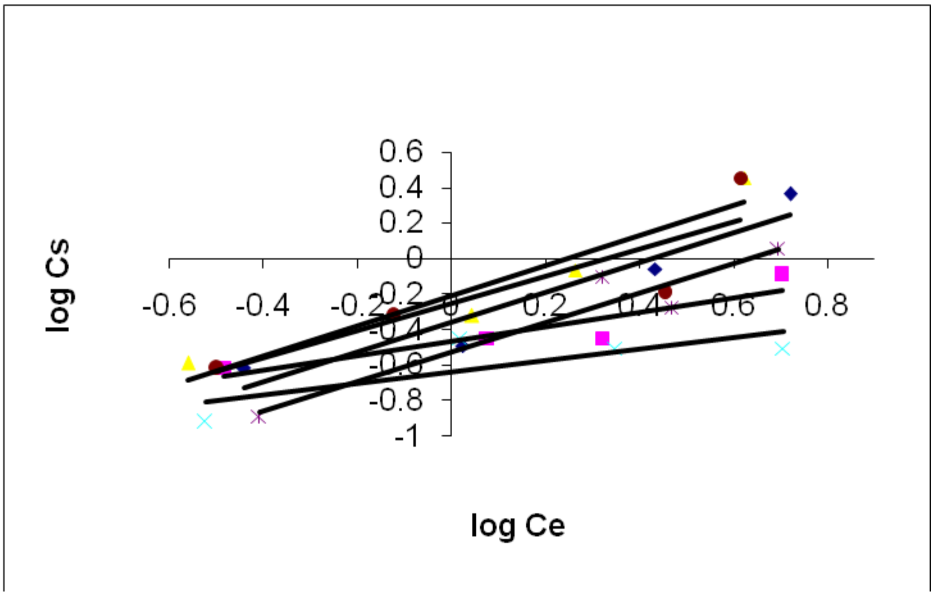
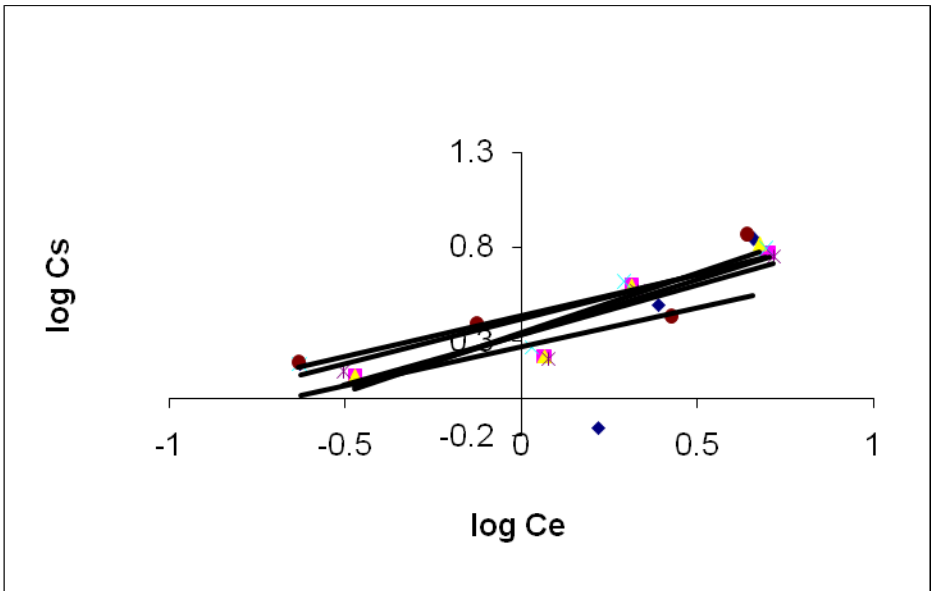


b-

Fig. 1: Fitted Ferundlich model for co-application of metolachlor/atrazine (a) adsorption (b) desorption isotherm in the presence of nonionic surfactant on selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6).



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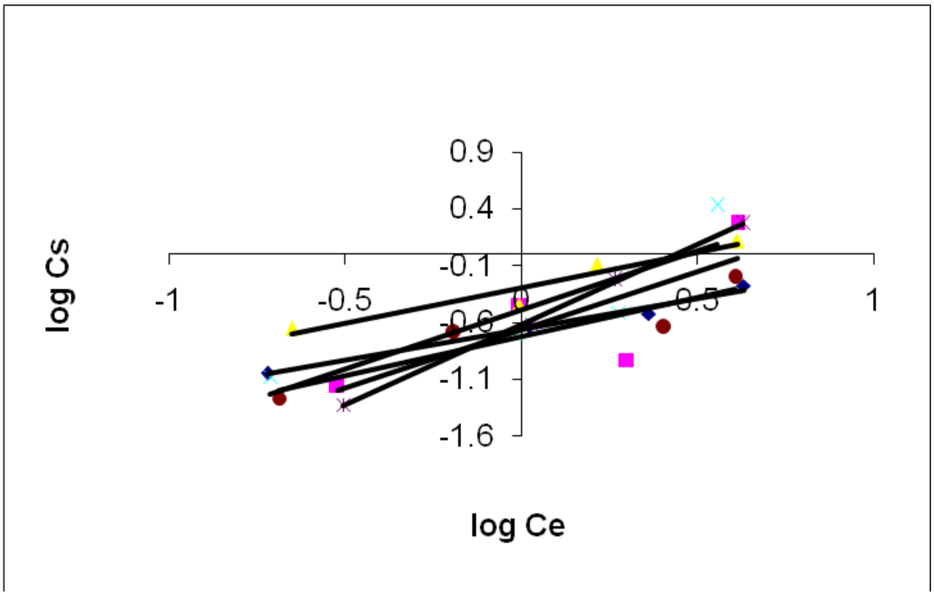
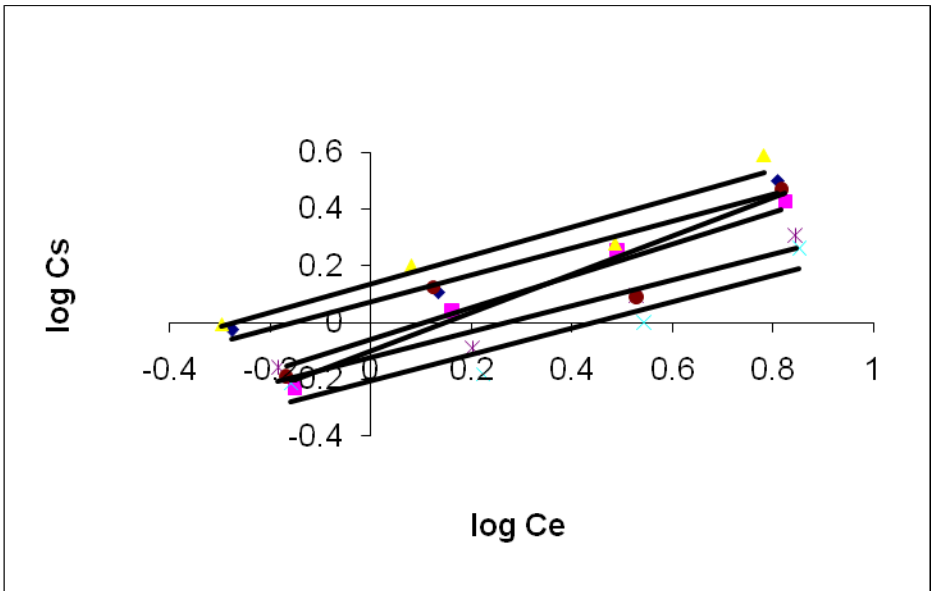


b-

Fig. 2: Fitted Ferundlich model for metolachlor alone in presence of nonionic surfactant (a) adsorption (b) desorption isotherm selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ● S_6).



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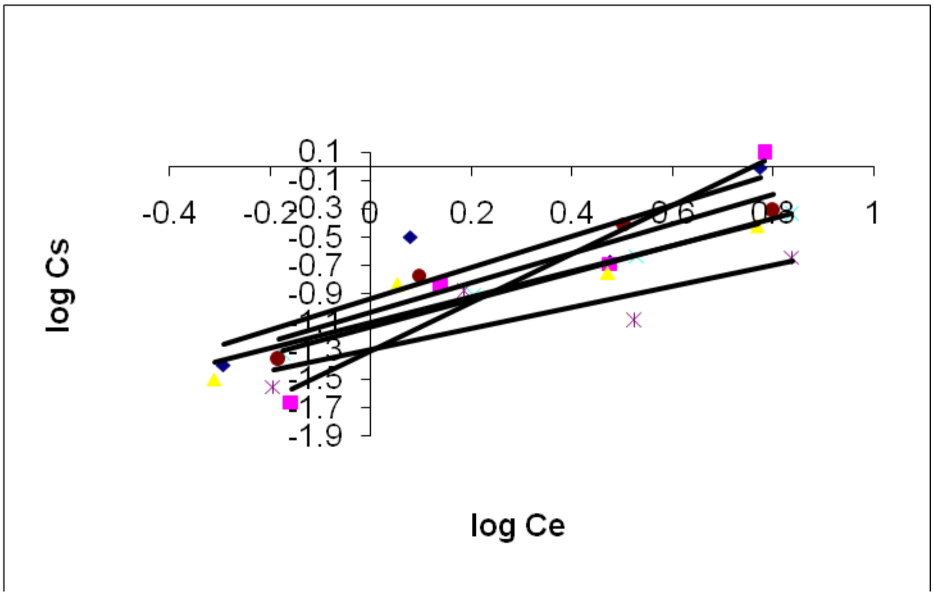
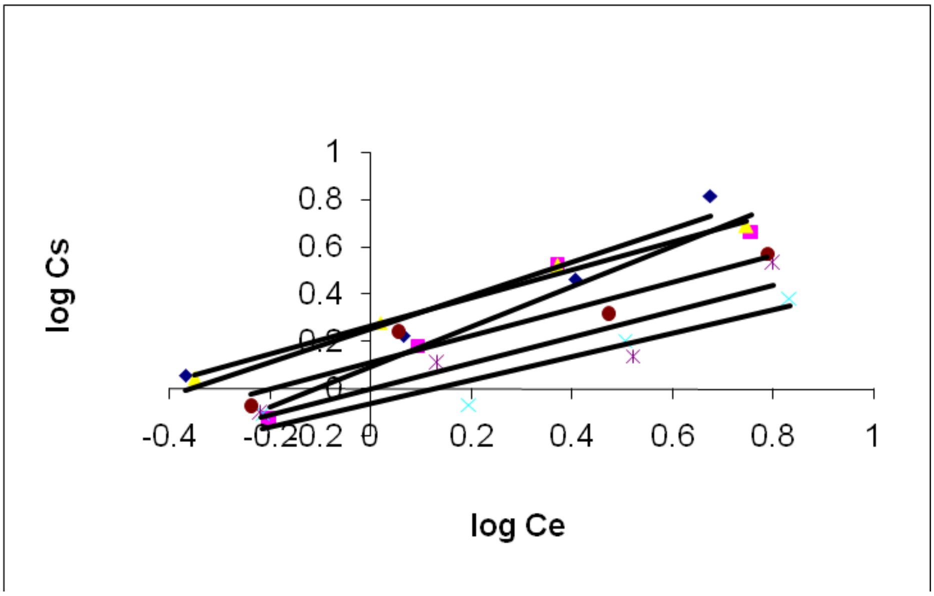


b-

Fig. 3: Fitted Ferundlich model for co-application of 2,4-D/propanile (a) adsorption (b) desorption isotherm in the presence of nonionic surfactant on selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6).



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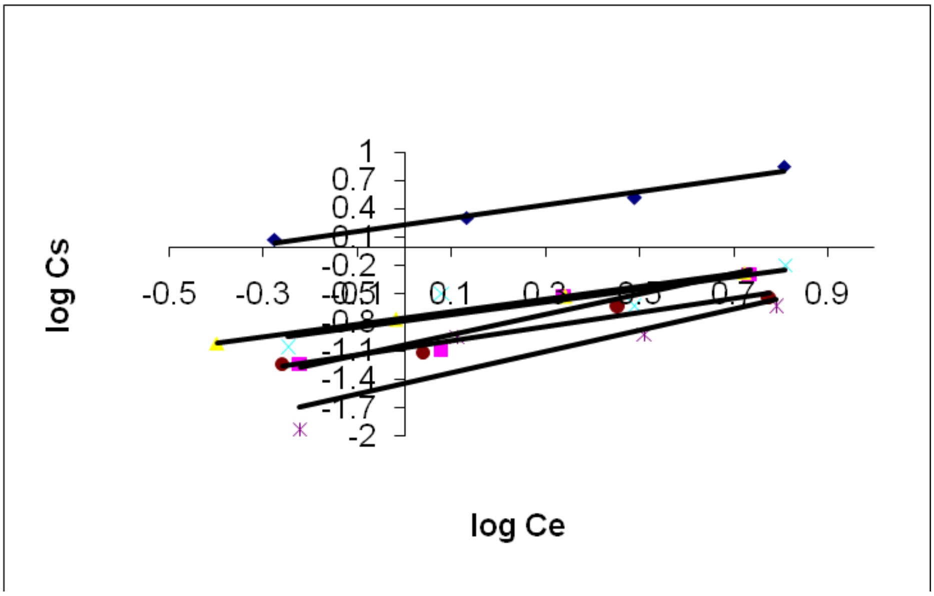

b-

Fig. 4: Fitted Ferundlich model for 2,4-D alone in the presence of nonionic surfactant (a) adsorption (b) desorption isotherm on selected soil samples (♦ S_1, ■ S_2, ▲ S_3, x S_4, * S_5, ●S_6).