

Adsorption of Metalaxyl and Glyphosate on Six Erbilian Agricultural Soils

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A study was conducted to determine the differences in the adsorption behaviour of two non-ionic pesticides, metalaxyl [N-(2,6-dimethyl phenyl)-N-(methoxyacetyl)] and glyphosate [N-phosphonomethyl-glycine] on six agricultural soil samples from Erbil governorate. Data from batch equilibrium method revealed that the adsorption of metalaxyl and glyphosate on the selected soil samples followed the first order rate law. Glyphosate exhibited the faster rate of accumulation with 76.53 % adsorption on the soil solid matrix after 0.5 h as compared to that for metalaxyl 66.06 %. Linear, Freundlich and Langmuir models were used to describe the adsorption of both pesticides. Values of distribution coefficient (K_d) indicated moderate to strong adsorption of metalaxyl (mean calculated K_d : 5.963 mL g⁻¹) and very strong adsorption of glyphosate (mean calculated K_d : 703.716 mL g⁻¹) and consequently there is no considerable risk of ground water contamination. Wide variation in adsorption affinities of the soils to both pesticides was observed, K_d values for metalaxyl varied between 2.93 and 9.97 mL g⁻¹ and for glyphosate between 5.16 and 456.34 mL g⁻¹. A linear correlation was found between the values of adsorption coefficients of both pesticides and soil organic carbon (R^2 : 0.61 and 0.69 for metalaxyl and glyphosate, respectively).

Key Words: Metalaxyl, Glyphosate adsorption kinetics, Adsorption isotherms, Freundlich, Langmuir, HPLC.

INTRODUCTION

Pesticides have become an indispensable component of modern agricultural systems and are being increasingly used to ensure the production of an adequate supply of food and hence the quality of produce. However, the occurrence of herbicides in ground water has become an important environmental concern in many countries¹⁻⁵.

Adsorption-desorption is one of the key processes affecting the fate of agrochemicals in the sediment-water environment, so thorough understanding of adsorption is paramount for the prediction of pesticides movement in soils and aquifers^{6,7}. The sorption of uncharged organic compounds by soils has been shown to be highly correlated with soil organic carbon content⁸⁻¹² and the water solubility of the pesticides in question¹³⁻¹⁵.

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Concerning the environmental fate of pesticides, the study of the effect of pH on their adsorption is important. The pH dependency is apparent but its degree is significantly influenced by the soil properties¹⁶.

Organophosphorous herbicide glyphosate is the worlds most sold pesticide¹⁷ and in Erbil it is widely used as herbicide in agricultural as well as in private gardens and in other non-agricultural applications. Glyphosate has relatively low oral and dermal acute toxicity. Glyphosate is considered environmentally friendly, with a high biodegradability¹⁸, low toxicity¹⁹ and low leaching risk¹⁷ but in some environments, such as for examples in gravel or fractured settings, studies have shown that it may be subjected to leaching¹⁹⁻²¹.

Metalaxyl is a systematic fungicide used to control plant diseases caused by the Oomycetes or water-mold fungicide. It is used in Erbil, Iraq in many food and feed crops and on non-food, residential and greenhouse crops. Metalaxyl generally is of low acute toxicity but is a moderate eye irritant²². Earlier investigations have been carried out on the adsorption of metalaxyl to typical Cameroonian and Germanian soil²³, on its adsorption to sterile and non-sterile soils²⁴ and on modified natural clay²⁵.

Since information on the sorption behaviour of pesticides in soils is essential in predicting their leaching potential and contamination of groundwater. No data are available in literature for sorption kinetics equilibrium parameters of metalaxyl and glyphosate on Erbilian soil, studies were conducted on the sorption of the two non-ionic pesticides determining their environmental fate and understanding their soil dynamic.

EXPERIMENTAL

Soils: Fresh soil samples were taken from plough layer (0-15 cm depth), after removal of stones and debris, air dried under shade, ground then sieved through 2 mm sieve and stored in black plastic container in dark^{26,27}. The 6 soil samples were collected from six main agricultural locations in Erbil governorate 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 (Table-1a and b). All these analysis were performed in Laboratories of Division of Agricultural and Environmental Science, University of Nottingham, NG7, 2RD.UK.

Pesticides: Analytical grade substituted anilide fungicide metalaxyl and organo-phosphorous herbicide glyphoste were both purchased from Riedal-de Haen, Sigma-Aldrich company ltd. With following purities expressed in weight per cent metalaxyl > 99.99 % [CAS-No. 57837-19-1] and glyphosate > 99.2 % [CAS-No. 1071-83-6].

All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of both pesticides were prepared in deionized water.

TABLE-1a
SOME PHYSICO-CHEMICAL PROPERTIES OF THE SELECTED SOIL SAMPLES

No.	Soil	SOM (%)	Moisture (%)	Loss on ignition (%)	pH		Exchangeable basic cations (mg/kg)			
					In distilled water	In CaCl ₂	Mg ²⁺	K ⁺	Na ⁺	Ca ²⁺
S1	Khabat	0.99	1.773	3.401	7.91	7.01	1520	121	823	13054
S2	Shaklawā	2.25	2.013	5.043	7.76	6.96	1434	447	658	13940
S3	Enkawa	1.22	3.175	5.739	7.94	7.13	2076	457	769	16524
S4	Qushtapa	0.86	2.526	2.063	7.29	6.74	1930	222	714	15261
S5	Harer	4.50	3.065	8.861	8.04	7.29	2796	586	693	15353
S6	Salahaddin	2.25	2.802	2.559	7.68	6.78	2294	465	621	13513

TABLE-1b
PARTICLE SIZE DISTRIBUTION AND THE TEXTURE OF THE SELECTED SOIL SAMPLES

No.	Soil	Sand (%)	Silt (%)	Clay (%)	Texture
S1	Khabat	46.815	40.485	12.700	Loam
S2	Shaklawā	18.124	58.242	23.633	Silt loam
S3	Enkawa	7.558	81.408	11.033	Silt loam
S4	Qushtapa	8.301	51.598	40.100	Silty clay
S5	Harer	9.847	53.485	36.666	Silty clay loam
S6	Salahaddin	38.408	30.958	30.633	Clay loam

Adsorption experiments: Adsorption of pesticides from aqueous solution was determined at ambient laboratory temperature (22 ± 2 °C) employing a standard batch equilibrium method^{26,27}. Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (2, 5, 10 and 15 mg L⁻¹ for metalaxyl and 50, 75, 100 mg L⁻¹ for glyphosate) at the soil solution ratios 1:5 and 1:10 for metalaxyl and glyphosate, respectively, in 16 mL glass tube fitted with Teflon-lined screw caps. The samples plus blanks (no soil) and control (no pesticide) were thermostated and placed in shaker for 0.5, 1, 2, 4, 6, 8, 24 and 48 h for metalaxyl and 0.5, 1, 2, 2.5, 3, 3.5, 4, 6 and 24 h for glyphosate. The tubes were centrifuged for 20 min at 3500 rpm. 20 µL of the clear supernatant was removed and analyzed for the pesticide concentration²⁸.

Pesticide identification was done by high performance liquid chromatography (HPLC) equipped with a 20 µL fix loop, C₁₈ reversed phase column, flow rate 1.4 mL min⁻¹ and a variable wave length UV detector (model S2500) at wavelength 220 and 156 nm for metalaxyl and glyphosate, respectively. Separation of metalaxyl in aqueous phase was achieved with a mobile phase of 50 % acetonitrile and 50 % water (no acidic modifiers were required). While the separation of glyphosate was achieved with mobile phase of 12 % methanol and 88 % water (phosphate buffer at pH 2.0).

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.

Adsorption kinetics: The rate constants for adsorption of each pesticide on soils were calculated using the first order rate expression²⁸:

$$\log(C_0 - C_t) = \log C_0 - \frac{k}{2.303} t \quad (1)$$

where k is the rate constant (h^{-1}), t the time (h), C_0 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 shown by a linear plots of $\log(C_0 - C_t)$ against t (Figs. 1 and 2).

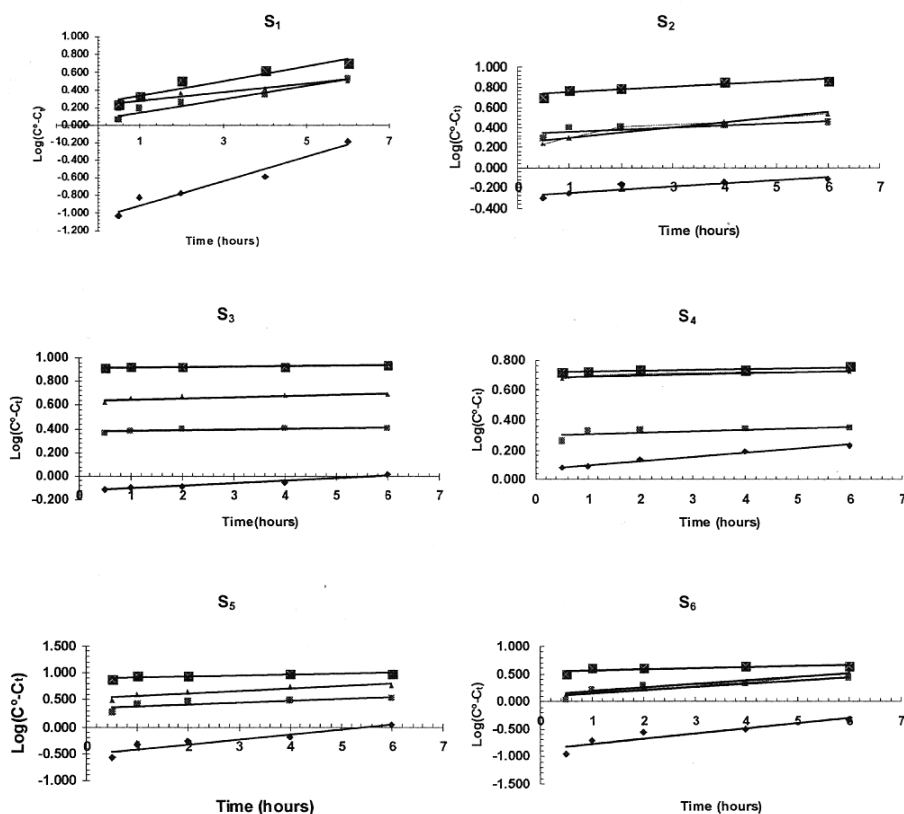


Fig. 1. Variation of concentrations of metalaxyl with time (Application of 1st order rate law) on the selected soil samples (\blacklozenge 2, \blacksquare 5, \blacktriangle 10 and \bullet 15 mg metalaxyl).

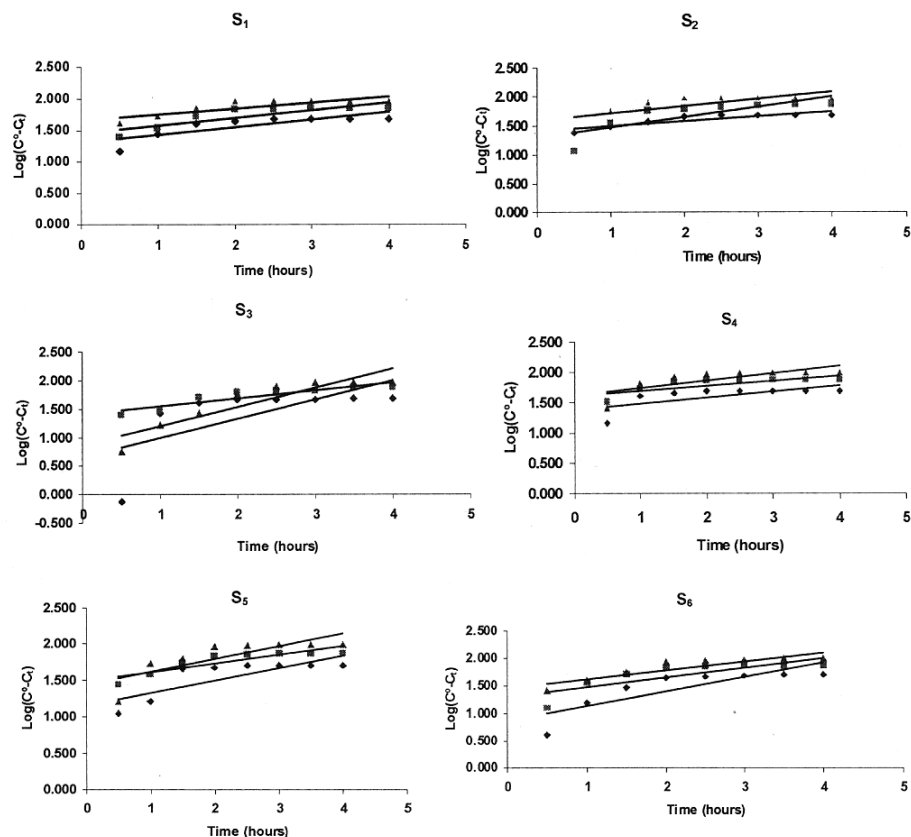


Fig. 2. Variation of concentrations of glyhosate with time (Application of 1st order rate law) on the selected soil samples (◆ 50, ■ 75 and ▲ 100 mg glyhosate)

Adsorption isotherms: During adsorption studies, equilibrium concentration of pesticide in solution (C_e) was determined by direct analysis of the solution and amount of pesticide adsorbed on soil (C_s) was computed by the difference between the initial and the equilibrium concentration in the aqueous phase. Analysis of control samples showed that, in the absent of soil, pesticide concentration remained constant during the course of the batch experiments. The adsorption data were used to construct the following linear forms of isotherms²⁸.

Linear adsorption coefficient (distribution coefficient):

$$C_s = K_d C_e \quad (2)$$

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 (Table-2).

TABLE-2
 ADSORPTION RATE CONSTANTS FOR METALAXYL AND
 GLYPHOSATE ON THE SELECTED SOIL SAMPLES

Soil	Initial conc. (mg/L)	Metalaxyl		Initial conc. (mg/L)	Glyphosate	
		K (mathm.) (h ⁻¹)	k (graph) (h ⁻¹)		K (mathm.) (h ⁻¹)	k (graph) (h ⁻¹)
S ₁	2	2.134	2.156	50	0.364	0.253
	5	0.983	0.840	75	0.380	0.394
	10	1.313	1.276	100	0.310	0.384
	15	1.513	1.379	–	–	–
S ₂	2	0.996	0.805	50	0.242	0.278
	5	0.631	0.478	75	0.537	0.486
	10	1.266	1.282	100	0.394	0.247
	15	0.779	0.742	–	–	–
S ₃	2	0.612	0.549	50	1.033	0.988
	5	0.498	0.465	75	0.415	0.553
	10	0.552	0.553	100	0.993	0.629
	15	0.400	0.399	–	–	–
S ₄	2	0.304	0.367	50	0.310	0.396
	5	0.628	0.504	75	0.238	0.286
	10	0.483	0.436	100	0.375	0.372
	15	0.699	0.610	–	–	–
S ₅	2	0.170	0.125	50	0.480	0.335
	5	0.526	0.225	75	0.345	0.214
	10	0.681	0.473	100	0.521	0.526
	15	0.414	0.432	–	–	–
S ₆	2	1.688	1.648	50	0.748	0.667
	5	0.862	0.842	75	0.526	0.588
	10	1.228	1.272	100	0.473	0.413
	15	0.963	0.879	–	–	–

Freundlich adsorption isotherm: Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation²⁹:

$$\log C_s = \log K_F + \frac{1}{n} \log C_e \quad (3)$$

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 $\log C_e$.

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.

Langmuir adsorption isotherm: Data from the batch adsorption conform to Langmuir equation³⁰:

$$\frac{C_e}{C_s} = \frac{1}{C_m K_L} + \frac{C_e}{C_m} \quad (4)$$

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.

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 equations³¹:

$$K_{OC} = \frac{100K_d}{\%OC} \quad (5)$$

$$K_{OM} = \frac{100K_d}{\%OM} \quad (6)$$

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

The free energy change during adsorption as influenced by organic matter was calculated from the following equation^{29,32}:

$$\Delta G_{OM} = -RT \ln K_{OM} \quad (8)$$

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

RESULTS AND DISCUSSION

Adsorption rate: Data in Table-2 showed that the adsorption of both pesticides in all cases followed first order rate law as reported in literature^{33,34}. Values of rate constant for the adsorption of glyphosate on different soil samples and at all experimental concentrations were greater than that for metalaxyl. Metalaxyl has a higher octanol water partition coefficient ($\log K_{ow} = 1.75$) than glyphosate ($\log K_{ow} = -4.47$). Thus glyphosate exhibited the faster rate of accumulation with 76.53 % adsorption on the soil solid matrix after 0.5 h as compared to that for metalaxyl 66.06 %. The different values of the rate constants for adsorption of metalaxyl (or glyphosate) on the selected soil samples during this study revealed the different characteristics of the studied soil samples.

Adsorption isotherms: Data in Table-3 indicated that the linear model not fitted properly most experimental data with both pesticides. The non-linear adsorption isotherms might be expected for the compounds for which competition for a limited number of cation exchange sites contributes significantly to adsorption process. The magnitude of the K_d is indicative of moderate to strong adsorption for metalaxyl (mean K_d calculated = 5.963 mL g^{-1}) and very strong adsorption for glyphosate (mean K_d calculated = $703.716 \text{ mL g}^{-1}$). These findings are in agreement with the hydrophobicity of the pesticides as represented by octanol-water partition coefficient values, which supports the comments by Calvet³⁴ about the use of ($\log K_{ow}$) to predict the adsorption of organic compound in soil. The great extents of adsorption of glyphosate by the soil samples is in agreement with the failure to observe these compounds at significant concentrations in the storm water run off from the sites despite their high water solubility³⁵.

TABLE-3
 ADSORPTION ISOTHERM PARAMETERS FOR THE LINEAR, FREUNDLICH AND
 LANGMUIR MODELS TO COMPARE THE SELECTED SOIL SAMPLES FOR
 METALAXYL AND GLYPHOSATE ADSORPTION CAPACITY

Pesticide	Absorption model	Parameter	Soils					
			S ₁	S ₂	S ₃	S ₄	S ₅	S ₆
Metalaxyl	Linear	K _d (mL/g)	2.821	4.22	6.313	3.739	7.752	2.466
		K _d (calc)	4.692	4.408	5.826	9.974	7.946	2.933
		R ²	0.373	0.79	0.885	0.492	0.916	0.76
	Freundlich	K _F (mL/g)	5.685	4.275	5.236	11.914	7.591	2.564
		K _{OC} (mL/g)	1525.409	541.451	591.371	2423.022	828.306	337.493
		K _{OM} (mL/g)	26831.23	12664.6	11294.33	20337.6	10912.27	13164.82
		N	0.664	0.984	1.087	0.373	1.019	1.019
		R ²	0.534	0.85	0.968	0.792	0.911	0.743
	Langmuir	K _L (mL/g)	0.073	0.01	-0.028	0.347	-0.004	-0.009
		C _m (µg/g)	60.241	400	-185.185	37.313	-1666.67	-263.158
		R ²	0.226	0.008	0.184	0.746	0.002	0.006
	Glyphosate	Linear	K _d (mL/g)	150.2	118.59	5.165	293.56	456.34
K _d (calc)			352.229	625.528	354.607	861.504	1365.23	663.202
R ²			-0.626	-3.107	1	-0.05	-0.726	-0.896
Freundlich		K _F (mL/g)	546.64	330.13	5.165	379.29	764.57	661.56
		N	0.242	0.266	1	0.422	0.228	0.29
		R ²	0.889	0.751	1	1	0.935	0.992
Langmuir		K _L (mL/g)	1.111	1.8	0.9	1.4	3	1.5
		K _{OC} (mL/g)	124.928	239.649	90	140	320.959	151.271
		K _{OM} (mL/g)	112.23	80.00	73.77	162.79	66.66	66.66
		C _m (µg/g)	1000	1111.11	1111.111	1428.571	1111.111	111.111
		R ²	0.93	0.994	0.99	0.992	0.953	0.983

Values of K_d for metalaxyl adsorption by soil samples varied between 2.93 and 9.97 mL g⁻¹ and for glyphosate between 5.16 and 456.34 mL g⁻¹ so the values K_d for metalaxyl were generally higher than the values predicted by Andreus *et al.*³⁶

Data in Table-3 indicated that, Freundlich adsorption model effectively describes isotherm for metalaxyl on all soil samples, values of K_F were varied from 2.56 to 11.91 mL g⁻¹ and from 5.1 to 764.5 mL g⁻¹ for metalaxyl and glyphosate respectively. Values of K_F for metalaxyl was in the order of S₄ > S₅ > S₁ > S₃ > S₂ > S₆ and for glyphosate in the order of S₅ > S₆ > S₁ > S₄ > S₂ > S₃ the difference in the behaviour of metalaxyl than that of glyphosate toward the same soil samples is due to the difference in the type of interaction of the both pesticides with the same soil which reveals the characteristics of each pesticide. For glyphosate it is likely due to the binding of its phosphoric side moiety to cation on the clay or organic matter³⁷. Alferness and Iwate³⁸ showed that the glyphosate adsorption is correlated with phosphate adsorption capacity of a soil.

In present study, the values of n were less than unity for S_1 , S_2 and S_4 indicating non-linear relationship between concentration of metalaxyl and its adsorption in to these soils. A linear relationship between concentration of metalaxyl and adsorption to other soils (S_3 , S_5 and S_6) was shown in the values of $n > 1$. The variable slopes of the adsorption isotherm obtained for different soil systems studied reveal that metalaxyl adsorption on soil is complex phenomena involving different types of adsorption sites with different surface energies³⁹.

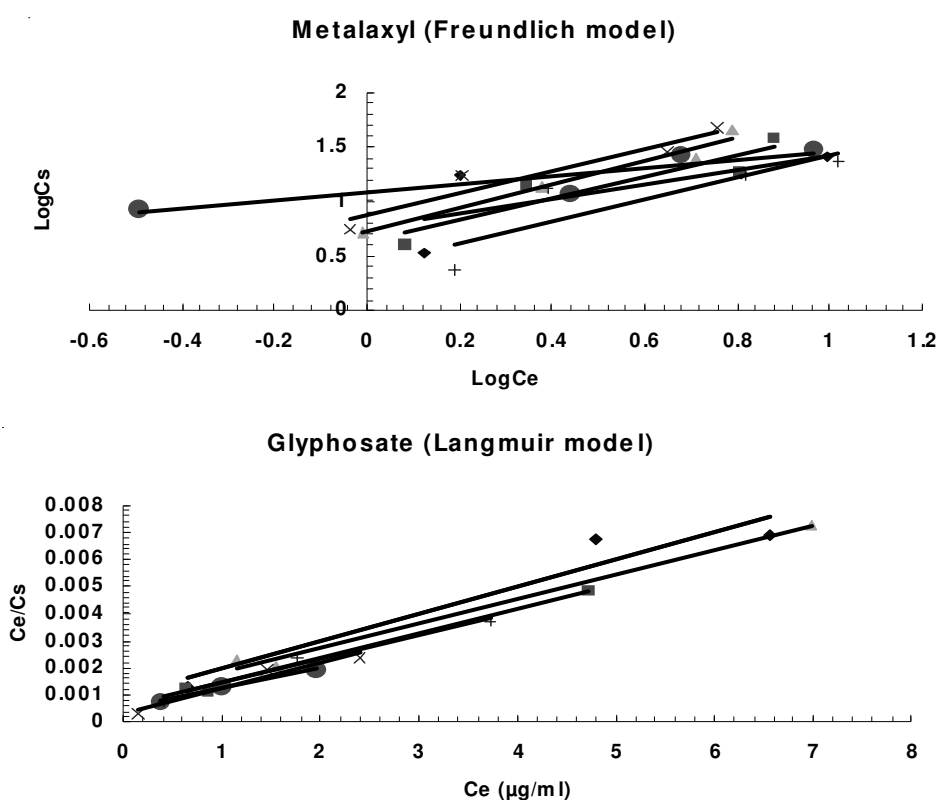


Fig . 3. Fitted adsorption isotherm models for (a) metalaxyl and (b) glyphosate

Data in Table-3 indicated, Langmuir adsorption model effectively describes isotherm for glyphosate on all soil samples, with regression factor $R^2 \geq 0.93$ values of K_L ranged from 0.90 to 3.00 mL g^{-1} . The maximum amount of glyphosate adsorption (C_m) ranged from 1000 to 1428.57 mg g^{-1} the high C_m values found for glyphosate on the examined soil samples could be explained by the high affinity of glyphosate bind to soil organic matter and clay values of K_L for glyphosate was in the order of $S_5 > S_2 > S_6 > S_4 > S_1 > S_3$. The different values of adsorption coefficients for the same pesticides with different soils is due (to some extent) to soil

organic carbon^{40,41} and clay content⁸. For example, soil 5 has high clay content 36.66 % and a very high exchangeable cation contents (19428.43 mg kg⁻¹) among the selected soil samples. It has a highest adsorption coefficients towards both pesticides thus present results are in agreement with that reported in literatures^{8,42,43}. In contrast, S₄ has highest clay content 40.1 and very high exchangeable cation concentration (18127 mg kg⁻¹) but it has a lower K_F values as compared to other soil samples, which is due to a significant differences 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 structures⁴⁴. 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.

In the present study, the values of K_F for metalaxyl and K_L for glyphosate obtained for different soils correlated to soil organic matter with regression factor R² = 0.61 and 0.69 for metalaxyl and glyphosate, respectively. Linear correlations between soil organic carbon and adsorption coefficients, have often been reported for many non-ionic compounds^{28,34} which is in agreement with present results for both pesticides.

The negative values of organic matter normalized free energy change (ΔG_{OM}) of adsorption revealed that the adsorption of both pesticides on the selected soil samples are spontaneous process and the adsorption has physical nature. The results of this study was in agreement with those reported by Suman and Gajbhiye²⁸, which complies that there is a constant partitioning of both pesticide between soil and solution and water molecules do not pose strong competition for the adsorption sites and also more affinity of the studied pesticide towards soil particulate mater than soil solution.

Conclusion

The batch kinetics experiments were used to differentiate the behaviour of two pesticides in 6 agricultural soil samples. The adsorption studies demonstrated that glyphosate has stronger affinity to all the selected soil samples than metalaxyl and the soils varied widely in their adsorption capacities for metalaxyl and glyphosate. It is found that soil organic carbon and clay content and the chemical nature of both constituents determined the adsorption affinity of the soil. Since the current level understanding the role of the chemical composition of soil organic carbon in determining pesticide fate and behaviour in soils of Iraq is in adequate. Efforts must continue to develop better understanding of role of chemistry of soil organic carbon in governing pesticide adsorption and explaining different types of soil pesticide interactions.

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