

Adsorption isotherms modeling of herbicides bispyribac- sodium and metribuzin on two common Egyptian soil types

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Abstract: The experimental adsorption isotherms of tested pesticides BPS and MBZ from aqueous solution onto clay loam soil and sandy loam soil. The order of adsorption on clay loam soil and sandy loam soil is: BPS > MBZ. Ten isotherm models: Langmuir (five linear forms), Freundlich, Temkin, Dubinin- Radushkevich (D- R), Elovich, Fowler- Guggenheim, Kiselev, Jovanovic, Harkin- Jura and Halsey models were applied to experimental data of tested pesticides; BPS and MBZ in clay loam soil and sandy loam soil. It was observed that the values of Langmuir parameters obtained from different linear expressions were different. The values of the coefficient of correlation obtained from different Langmuir expressions indicate that the soil type is the essential factor affecting on the suitable model expression. Low determination coefficient values of tested pesticides in different soils were obtained from all Langmuir expressions except the coefficient values of Langmuir 3 and 4 for MBZ in clay loam. The Freundlich model has agreement with experimental data for MBZ and BPS in clay loam soil, for MBZ and BPS in sandy loam. The adsorption data for tested pesticides in soils were analyzed by a regression analysis to test their fit with Temkin isotherm model. This model perfectly describes the adsorption isotherms of BPS in clay loam soil and sandy loam soil because of the higher coefficients of correlations and lower standard error values while it is invalid to describe the adsorption isotherm of MBZ in different tested soils. Dubinin- Radushkevich (D- R) isotherm model it was observed that the coefficient of correlation values were low, therefore, this model does not suitable to describe the equilibrium data for tested pesticides in different. Elovich model It was observed that the coefficients of correlation are low (< 0.86) for tested pesticides in tested soils indicating a bad linearity. The calculated values of θ depend on the Freundlich model are lower than 0.6. Therefore, the Fowler- Guggenheim model could be used to describe the adsorption of the tested pesticides. Jovanovic model the coefficient values of the tested pesticides BPS and MBZ were 0.7971, and 0.9130 in clay loam soil, 0.9144 and 0.9077 in sandy loam soil. The adsorption data for the tested pesticides in different tested soils were analyzed by a regression analysis to fit the equation of Harkin- Jura isotherms. Halsey isotherm is suitable for the experimental results.

Keywords: Adsorption, Langmuir, Freundlich, Temkin, Dubinin- Radushkevich, Elovich, Fowler- Guggenheim, Kiselev, Jovanovic, Harkin- Jura and Halsey, Bispyribac- sodium, Metribuzin, soil.

نمذجة الأدمصاص الحرارى لمبيدات الحشائش بيسبيرياك صوديوم والمتريببوزين على نوعين من التربة المصرية

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الملخص: تجارب الأدمصاص الحرارى للمبيدات المختبرة بيسبيرياك صوديوم والمتريببوزين من المحلول المائي في التربة الطينية اللومية والتربة الرملية اللومية. أدمصاص مبيد بيسبيرياك صوديوم كان أعلى من المتريببوزين في التربة الطينية اللومية والتربة الرملية اللومية. تم استخدام عشرة نماذج رياضية : نماذج لانجموير (خمسة أشكال خطية)، فراوندلخ، تيمكين، دوينين رادوسكينك، الوفيك، فولرجوجنيم، كيسيليف، جوفانيك، هاركين جورا وهاليسي تم تطبيقهم على نتائج تجارب مبيدات الحشائش بيسبيرياك صوديوم والمتريببوزين في التربة الطينية اللومية والتربة الرملية اللومية. ولوحظ أن قيم معادلة لانجموير التي تم الحصول عليها من التعبيرات الخطية مختلفة فيما بينها. تشير قيم معامل الارتباط المتحصل عليها من قيم معادلات لانجموير المختلفة إلى أن نوع التربة هو العامل الأساسي المؤثر على تطبيق النموذج المناسب. كانت قيم معامل الارتباط منخفضة للمبيدات المختبرة في الترب المختلفة في جميع معادلات لانجموير باستثناء قيم معامل الارتباط الخاصة بمعادلة لانجموير الثالثة والرابعة لمبيد المتريببوزين في التربة الطينية اللومية. وقد أظهر نموذج فراوندلخ توافقاً مع النتائج التجريبية لبسبيرياك صوديوم والمتريببوزين في تربة الطينية اللومية، بالنسبة لبسبيرياك صوديوم والمتريببوزين في التربة الرملية اللومية. نموذج تيمكين يصف تماماً أدمصاص بيسبيرياك صوديوم في التربة الطينية اللومية والتربة الرملية اللومية بسبب القيم العالية لمعامل الارتباط وانخفاض قيم الخطأ القياسي في حين أنه غير صالح لوصف ادمصاص المتريببوزين في كل من التربة الطينية اللومية والتربة الرملية اللومية. نموذج دوينين رادوسكينك لوحظ أن معامل قيم الارتباط منخفض، لذلك لا يناسب هذا النموذج وصف نتائج الأدمصاص للمبيدات المختبرة المختلفة. نموذج الوفيك لوحظ فيه أن قيم معامل الارتباط منخفضة أقل من 0.86 لمبيدات الأفات المختبرة في الترب المختبرة مشيرة إلى صورة خطية سيئة. القيم المحسوبة ل θ والتي تعتمد على نموذج فراوندلخ أقل من 0.6. لذلك، يمكن استخدام فولرجوجنيم لوصف ادمصاص المبيدات التي تم اختبارها. نموذج جوفانيك كانت قيم معامل الارتباط للمبيدات المختبرة لبسبيرياك صوديوم والمتريببوزين هي 0.7971 و 0.9130 في التربة الطينية اللومية و 0.9144 و 0.9077 في تربة الرملية اللومية. نماذج هاركين جورا وهاليسي مناسبة لوصف النتائج التجريبية المتحصل عليها.

الكلمات المفتاحية: لانجموير، فراوندلخ، تيمكين، دوينين رادوسكينك، الوفيك، فولرجوجنيم، كيسيليف، جوفانيك، هاركين جورا، هاليسي، بيسبيرياك صوديوم، المتريببوزين، التربة.

INTRODUCTION

Pesticide emission from the soil- plant system and their behaviour in the environment is evaluated by using mathematical models, which may provide a certain degree of prediction (Sumon et al., 2016; Jones et al., 2017; Kah et al., 2018). Various pesticide- soil models had been developed in the past decade, so there is considered to be a useful tool in the evaluation of environmental risks of pesticides (Leistra et al., 2001). A simulation models may be classified either as "research models", "screening models", or "management models" (Wagenet and Rao 1985). For agricultural and environmental management neither research nor screening models are necessarily very useful. Although, the pesticides have many hazards either direct or indirect impact on humans and environment, it is impossible today stopping pesticide application, because the use of pesticides is essential in agricultural practice in all countries (Mishra et al., 2015; Sánchez- Bayo et

al., 2016). However, the information about the behaviour of pesticides under Egyptian conditions is poor. Therefore, the aim of the present work is to understand the behaviour of some pesticides in the common Egyptian soil types and optimization of their persistence and disappearance to decrease the agricultural microenvironment contamination using laboratory and bench- scale experiments. The adsorption characteristics of bispyribac sodium, a pyrimidinyloxybenzoic herbicide, in 21 types of soil collected from different locations in the U.S., Italy, Spain, Greece, France, U.K., the Netherlands, Germany, and India were evaluated under laboratory conditions. It was showed that the Freundlich equation fits its adsorption well, and the Freundlich adsorption constant values (K_f) ranged from 0.3 to 5.6 mL g⁻¹. Adsorption isotherms were nonlinear, with $1/n_f$ values <1 (Chirukuri and Atmakuru 2015). Bispyribac sodium was poorly adsorbed in four Indian soil types and adsorption decreased with an increase in the herbicide concentration in solution. Freundlich adsorption coefficient (K_f) values for bispyribac sodium ranged between 0.37 and 0.87. Slope ($1/n$) values varied from 0.2 to 0.31 suggesting that BPS adsorption was highly dependent on its initial concentration in solution (Singh and Singh 2015). The distribution coefficients of metribuzin varied from 0.56 for the sandy loam soil to 31.67 for the most highly adsorptive muck soil. Most of the adsorbed metribuzin was desorbed from the mineral soils after six aqueous extractions, however substantial amounts of the herbicide remained adsorbed on the muck soils after aqueous extraction (Jones et al., 2017; Wood and Goulson, 2017). The herbicide was relatively mobile in mineral soils but was immobile in the muck soils (Sharom and Stephenson 1976). The adsorption of some pesticides with different physico- chemical properties in sediments has been studied employing a batch technique. Atrazine and bifenoxy showed different competitive effects: the adsorption of the relatively weak sorbing atrazine was slightly reduced in the presence of the stronger adsorbing bifenoxy, whereas the sorption of bifenoxy was less affected by competition of atrazine (Gao et al., 1998).

MATERIALS AND METHODS

Tested pesticides

Bispyribac- sodium(BPS)

IUPAC name: Sodium 2, 6- bis [(4, 6- dimethoxypyrimidin- 2- yl)oxy] benzoate, Pyrimidinyloxybenzoic acid. The chemical structure: **Figure 1**. Technical 95% a.i. Solubility (20 °C): Water 7330 mg/L. Production Company: AGROCHEM, Egypt.

Metribuzin (MBZ)

IUPAC name: 4- amino- 6- terbutyl- 3- methylsulfanyl- 1, 2, 4- triazin- 5- one, Triazinone. Technical 97.0% a.i. Solubility (20 °C): Water 1200 mg/L. Production Company: Egyptian Chemical Industries Kima, Egypt.

Tested soils

Two types of the common Egyptian soils were tested in this study. The soil samples were collected from the top (0- 30 cm) layers of the soil profiles from different locations in Agricultural Research Station, Abis, alluvial soil (clay loam) and Bangar Elsokar region, calcareous soil (sandy loam). The physical and chemical properties were determined at the Department of Soil and Water Sciences, Faculty of Agriculture, University of Alexandria according to Gee et al., 1986; Nelson et al., 1996 and the data are presented in **Tables 1 and 2**. Soils were air- dried, ground and passed through a 2- mm sieve prior to use.

Table (1) Physical properties of the tested soils

Soil code	Soil type	Particle size distribution (%)			Texture class	Water holding capacity (mL)
		Clay	Silt	Sand		
A	Alluvial	42	18	40	Clay loam	46
B	Calcareous	14	11	75	Sandy loam	35

Table (2) Chemical properties of the tested soils

Chemical properties	Soil A	Soil B
EC (m mohs/cm) at 25°C	1.32	2.33
Soil pH	8.25	8.20
Organic matter content (%)	3.31	1.32
Total carbonate (%)	7.87	40.09
Soluble cations conc. (meq/L):		
Ca ⁺⁺	3.8	8.8
Mg ⁺⁺	5.0	7.0
Na ⁺	9.4	15.3
K ⁺	0.5	2.4

Chemical properties	Soil A	Soil B
Soluble anions conc. (meq/L):		
CO_3^{--}	1.6	1.6
HCO_3^-	2.6	3.4
Cl^-	8.5	16.5
SO_4^{--}	0.6	1.8

Determination of tested pesticides

Each pesticide standard solutions (0.1- 100 $\mu\text{g}/\text{mL}$) were prepared by the stepwise dilution of the pesticide stock solution (0.5 g/L). The tested pesticide concentrations in different experiments were analyzed by a UV- Vis Spectrophotometer (Thermo Corporation, Nicolet, evolution 100). To determine the optimum wavelength (λ_{max}) that is specific for each tested pesticide with minimum interference, a scanning range of 200- 400 nm was used to generate a for 5 $\mu\text{g}/\text{mL}$ pesticide solution. The standard calibration curve (C- D curve) was created by plotting triplicates ($n = 3$) of known pesticide concentrations (0.1- 100 $\mu\text{g}/\text{mL}$) against its corresponding absorbance at the optimum obtained λ_{max} (**Figures 1 and 2**). For quality assurance and control, triplicate samples including controls and blanks were used (Abdo et al., 2010). To test the validity of this spectrophotometer method, guidelines for limit of blank (LOB), limit of detection (LOD) and limit of quantitation (LOQ) were according to Chang (2011).

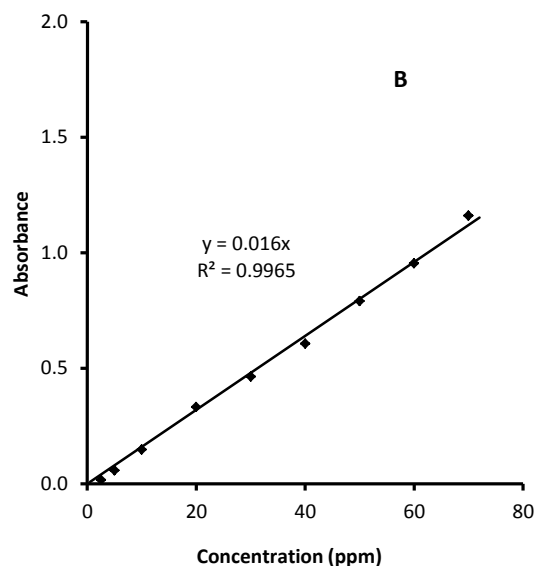
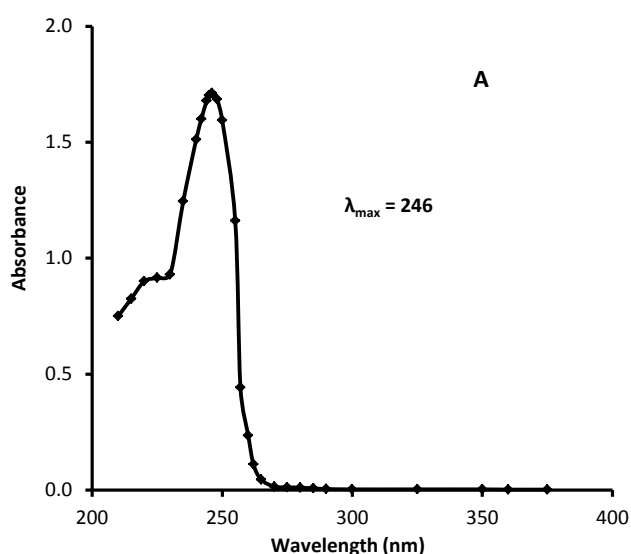


Figure (1) Spectral- Density (S- D) curve of bispyribac- sodium (A). 200 to 400 nm spectra are plotted and clearly show the maximum wavelength is 246 nm and Calibration- Density (C- D) curve of bispyribac- sodium (B) at 246 nm by UV- Spectrophotometric method.

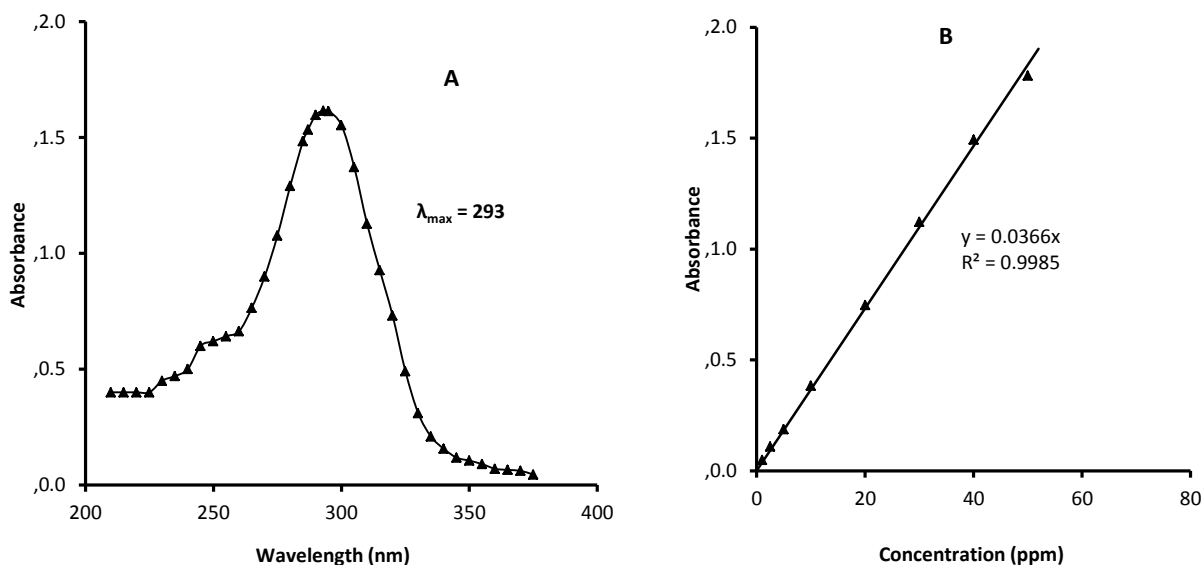


Figure (2) Spectral- Density (S- D) curve of metribuzin (A). 200 to 400 nm spectra are plotted and clearly show the maximum wavelength is 293 nm and Calibration- Density (C- D) curve of metribuzin (B) at 293 nm by UV- Spectrophotometric method.

Adsorption isotherm of tested pesticides

Adsorption isotherms of tested herbicides by soil were quantified using the batch equilibration technique (Khuntong et al., 2010). Experiments were carried out in duplicate with a sorbent mass to pesticide solution ratio of 1:5 for soil. Initial pesticide concentrations of in 1.0- 100 $\mu\text{g}/\text{mL}$ range were prepared in 0.01 M CaCl_2 and equilibrated with soil in 25- mL polypropylene centrifuge tubes. The tubes were shaken mechanically at 150 rpm at room temperature for 24 hours to achieve equilibrium and centrifuged at 4000 rpm for 15 min. The pesticide concentration in supernatants was determined by spectrophotometer at the proper λ_{max} . Control samples (no pesticide) containing only adsorbent substances and 0.01 M CaCl_2 were included in each series of experiments. Blanks containing pesticide solution with no adsorbents indicated that sorption onto reaction tube was insignificant. The amount of pesticide sorbed, C_s , by solid phase after equilibrium was calculated,

$$C_s = (C_i - C_e)X \frac{V}{M_s}$$

where C_s is the concentration or amount of pesticide sorbed per mass unit of adsorbent ($\mu\text{g/g}$), C_i is the initial concentration of pesticide ($\mu\text{g/mL}$), C_e is the equilibrium concentration of the pesticide per mass unit of solution ($\mu\text{g/mL}$), V is the volume of added solution (mL) and M_s is the weight of the adsorbent sample (g) (Sun et al., 2006). Experimental data are presented as mean \pm standard error and the statistical analysis was performed by the SPSS program (ver. 21.0, USA).

Modeling sorption isotherm

To find the model that can describe with precision, the experimental results of adsorption isotherms and specify the parameters that can be calculated and used to compare pesticides sorption behaviour. It was utilized the linear least- squares optimization program in order to obtain best- fit parameters which provide the best description of the adsorption data. The equilibrium data were modeled with the Langmuir (five linear forms), Freundlich, Temkin, Dubinin- Radushkevich (D- R), Elovich, Fowler- Guggenheim, Kiselev, Jovanovic, Harkin- Jura and Halsey models (Hamdaoui and Naffrechoux 2007).

RESULTS AND DISCUSSION

Adsorption isotherms

The experimental adsorption isotherms of tested pesticides BPS and MBZ from aqueous solution onto clay loam soil and sandy loam soil are presented in Fig. (3). The order of adsorption on clay loam soil and sandy loam soil is: BPS > MBZ. The shape of the isotherms is the first experimental tool to diagnose the nature of a specific adsorption phenomenon. The isotherms have been classified according to the classification of (Giles et al., 1960). They have classified adsorption isotherms into four main groups; S, L, H and C. According to this classification, the some isotherms displayed an L- type isotherm. While, the other isotherms of other pesticides displayed an S- type isotherm. The L shape of the adsorption isotherm means that there is no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites (Hamdaoui and Naffrechoux 2007). It is characterized by decrease in the pesticide adsorption at higher aqueous concentrations of the compound. This indicated greater competition for adsorption sites which become limited as solute concentration in the solution increased (Singh and Singh 2015). The shape of the S- type means that in the case of low concentration, the adsorption affinity of the surface is low then the adsorption affinity increases with increasing of concentration.

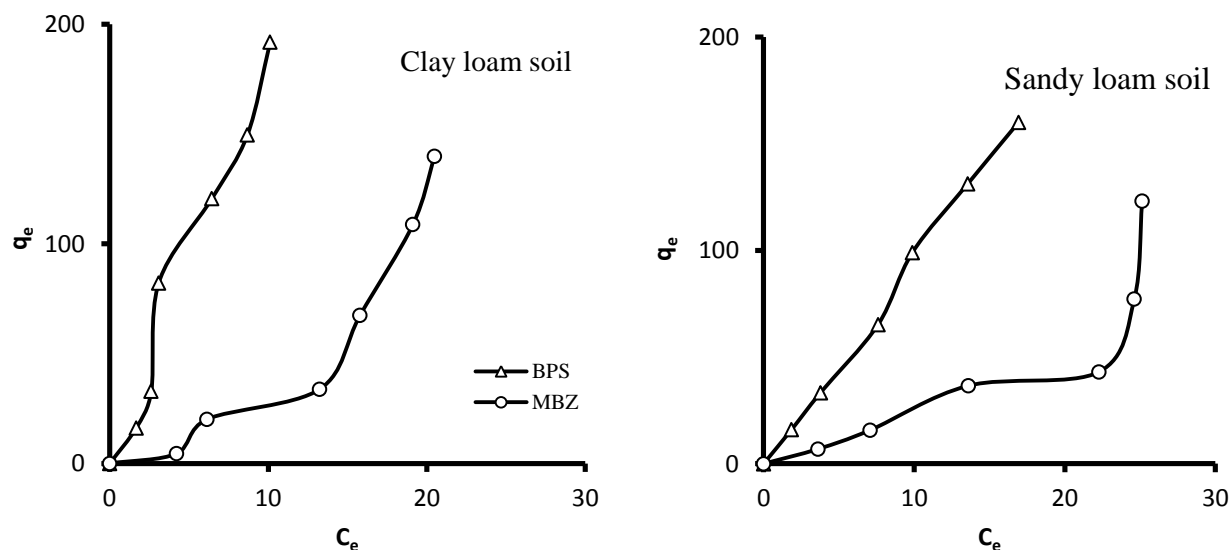


Fig. (3) Adsorption isotherm of BPS and MBZ in clay loam and sandy loam soil.

(C_e : equilibrium concentration of insecticide ($\mu\text{g}/\text{mL}$), q_e : adsorbed insecticide on soil ($\mu\text{g}/\text{g}$ soil))

Mathematical models:

Several mathematical models can be used to describe experimental data of adsorption isotherms (Eris and Azizian, 2017; Gonzalez- Ortega and Guzman, 2018). To find the model and to determine the characteristic parameters for the pesticide adsorption process, ten isotherm models: Langmuir (five linear forms), Freundlich, Temkin, Dubinin- Radushkevich (D- R), Elovich, Fowler- Guggenheim, Kiselev, Jovanovic, Harkin- Jura and Halsey models were applied to experimental data of tested pesticides; BPS and MBZ in clay loam soil and sandy loam soil. The experimental values of q_e (the amount of solute adsorbed) and C_e (equilibrium concentration) for each pesticide in each soil are initially treated with the linearized equations in order to determine the models parameters and the isotherms are reconstituted using the determined values. The isotherm curves showed the superposition of experimental data (points) and the theoretical calculated points (lines) (Ali et al., 2014; Chen, 2015). Linear correlation coefficients (R^2) presented the fit between experimental data and linearized forms of model equations. Its value may vary from 0 to 1 (Kumar and Sivanesan 2006). The adsorption isotherm models and their empirical and linear forms are presented in Table (3).

Table (3) Adsorption isotherm models and their linear forms

Models	Empirical formula	Linear form	Plot
Langmuir- 1		$\frac{1}{q_e} = \frac{1}{bq_m} \frac{1}{C_e} + \frac{1}{q_m}$	$\frac{1}{q_e}$ vs. $\frac{1}{C_e}$

Models	Empirical formula	Linear form	Plot
Langmuir- 2		$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$	$\frac{C_e}{q_e}$ vs. C_e
Langmuir- 3	$q_e = \frac{q_m b C_e}{1 + b C_e}$	$q_e = -\frac{1}{b} \frac{q_e}{C_e} + q_m$	q_e vs. $\frac{q_e}{C_e}$
Langmuir- 4		$\frac{q_e}{C_e} = -bq_e + b q_m$	$\frac{q_e}{C_e}$ vs. q_e
Langmuir- 5		$\frac{1}{C_e} = bq_m \frac{1}{q_e} - b$	$\frac{1}{C_e}$ vs. $\frac{1}{q_e}$
Freundlich	$q_e = K_F C_e^{1/n}$	$\log q_e = \frac{1}{n} \log C_e + \log K_F$	$\log q_e$ vs. $\log C_e$
Temkin	$q_e = \frac{RT}{b} \ln(K_t C_e)$	$q_e = \beta_T \ln C_e + \beta_T \ln A_T$	q_e vs. $\ln C_e$
Dubinin-Radushkevich	$q_e = X_m \exp(-\beta \epsilon^2)$	$\ln q_e = -\beta \epsilon^2 + \ln X_m$	$\ln q_e$ vs. ϵ^2
Elovich	$\frac{q_e}{q_m} = K_E C_e \exp(-\frac{q_e}{q_m})$	$\ln \frac{q_e}{C_e} = -\frac{q_e}{q_m} + \ln(K_E q_m)$	$\ln \frac{q_e}{C_e}$ vs. q_e
Fowler-Guggenheim	$K_{FG} C_e = \frac{\theta}{1 - \theta} \exp(\frac{2\theta W}{RT})$	$\ln \left[\frac{C_e (1 - \theta)}{\theta} \right] = \frac{2\theta W}{RT} - \ln K_{FG}$	$\ln \left[\frac{C_e (1 - \theta)}{\theta} \right]$ vs. θ
Kiselev	$K_1 C_e = \frac{\theta}{(1 - \theta)(1 + K_n \theta)}$	$\frac{1}{C_e(1 - \theta)} = \frac{K_1}{\theta} + K_1 K_n$	$\frac{1}{C_e(1 - \theta)}$ vs. $\frac{1}{\theta}$
Jovanoic	$q_e = q_m (1 - \exp(-K_J C_e))$	$\ln q_e = -K_J \ln q_m C_e + \ln q_m$	$\ln q_e$ vs. C_e
Harkins-Jura	$\frac{1}{q_e^2} = \left(\frac{B_{HJ}}{A_{HJ}} \right) - \left(\frac{1}{A_{HJ}} \right) \log C_e$	$\frac{1}{q_e^2} = \left(\frac{B_{HJ}}{A_{HJ}} \right) - \left(\frac{1}{A_{HJ}} \right) \log C_e$	$\frac{1}{q_e^2}$ vs. $\log C_e$
Halsey	$q_e = \exp \left[\frac{(\ln K_H - \ln C_e)}{n_H} \right]$	$\ln q_e = -\left[\frac{1}{n_H} \ln \frac{1}{C_e} \right] + \left[\left(\frac{1}{n_H} \right) \ln K_H \right]$	$\ln q_e$ vs. $\ln \frac{1}{C_e}$

Langmuir model:

The Langmuir model (Langmuir 1916) assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the adsorbent surface. The Langmuir equation may be written as;

$$q_e = \frac{q_m b C_e}{1 + b C_e}$$

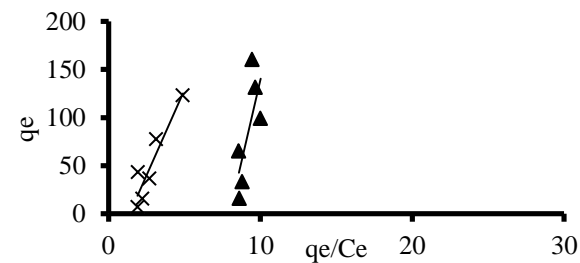
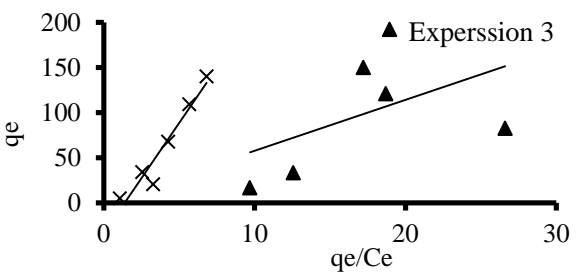
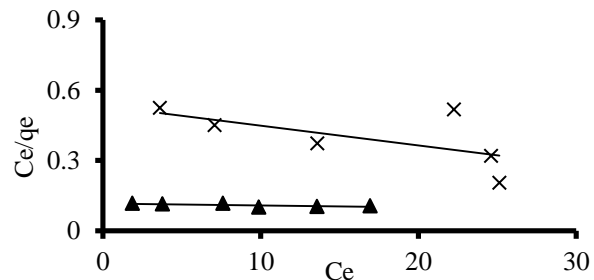
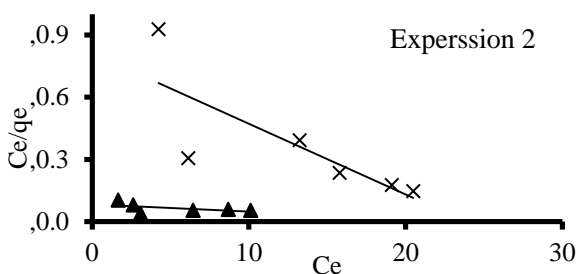
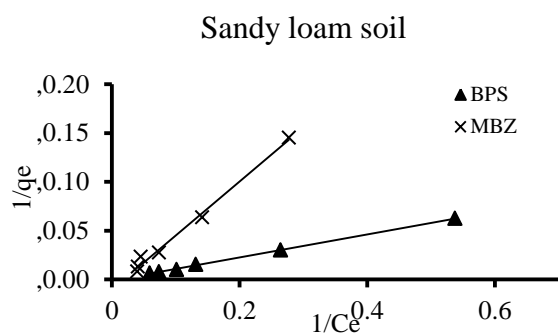
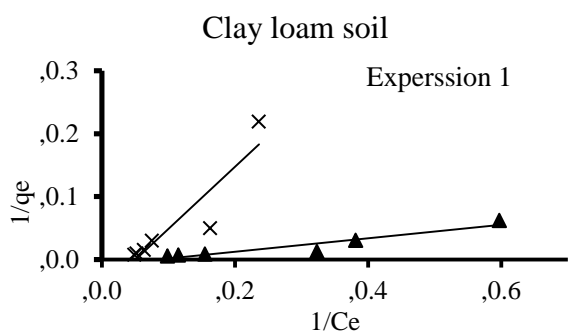
Where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium ($\mu\text{g g}^{-1}$), C_e the equilibrium concentration of the solute in the bulk solution (mg L^{-1}), q_m the maximum adsorption capacity ($\mu\text{g g}^{-1}$) and b is the constant related to free energy of adsorption (L mg^{-1}). The equation can be linearized to five different linear forms as shown in Table (4). The adsorption data for tested pesticides in tested soils were analyzed by a regression analysis to fit the five linearized expressions of Langmuir isotherm model. The details of the different forms of linearized Langmuir equations and the methods to estimate the Langmuir constants q_m and b from these plots were explained in Table (3). Values of the Langmuir constant are presented in Table (4) for the adsorption of the tested pesticides in clay loam soil and sandy loam soil.

It was observed that the values of Langmuir parameters obtained from different linear expressions were different. The values of the coefficient of correlation obtained from different Langmuir expressions indicate that the soil type is the essential factor affecting on the suitable model expression. Low determination coefficient values of tested pesticides in different soils were obtained from all Langmuir expressions except the coefficient values of Langmuir 3 and 4 for MBZ in clay loam (Table 4). The Langmuir sorption isotherms of different pesticides in different studied soils are shown in Fig. (4).

Table (4) Parameters of Langmuir isotherm model of BPS and MBZ in clay loam and sandy loam soil.

Langmuir type	Clay loam soil		Sandy loam soil		
	BPS	MBZ	BPS	MBZ	
Expression 1	q_m	- 108.6957	- 19.8807	- 1000.0000	- 99.0099
	b	- 0.0856	- 0.0509	- 0.0083	- 0.0183
	R^2	0.8958	0.8461	0.9994	0.9910
	SE	0.0251	0.0110	0.0006	0.0001
Expression 2	q_m	- 285.7143	- 29.3255	- 1111.1111	- 119.0476
	b	- 0.0422	- 0.0420	- 0.0077	- 0.0138
	R^2	0.2675	0.6211	0.4948	0.3989
	SE	0.0939	0.0155	0.2490	0.1819
Expression 3	q_m	1.5160	- 34.2080	- 541.3900	- 49.2990
	b	- 0.1775	- 0.0409	- 0.0147	- 0.0281

Langmuir type	Clay loam soil		Sandy loam soil		
	BPS	MBZ	BPS	MBZ	
	R ²	0.2353	0.9347	0.5391	0.87011
	SE	0.1481	0.0016	0.2090	0.0000
Expression 4	q _m	- 314.8563	- 40.9555	- 1074.0253	- 64.2049
	b	- 0.0418	- 0.0382	- 0.0079	0.0244
	R ²	0.2353	0.9347	0.5391	0.8704
	SE	0.1482	0.0016	0.2090	0.0000
Expression 5	q _m	- 78.6780	- 14.3849	- 997.0824	- 93.8534
	b	- 0.1059	- 0.0595	- 0.0085	- 0.0191
	R ²	0.8958	0.8461	0.9994	0.9994
	SE	0.1651	0.0110	0.0006	0.0006



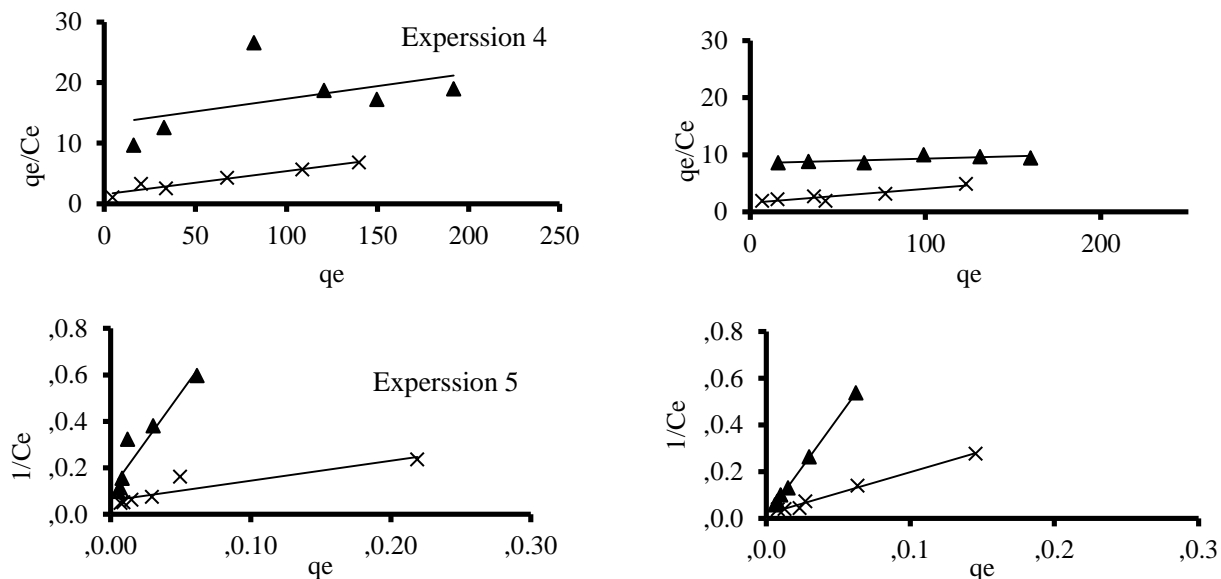


Fig. (4) Langmuir (five expressions) linear fitted adsorption isotherms of BPS and MBZ in clay loam and sandy loam soil.

Freundlich model:

The empirical formula of the Freundlich equation (Freundlich 1906) can be written as;

$$q_e = K_F C_e^{1/n}$$

Where K_F is a constant indicative of the adsorbent ($\text{mg}^{1-(1/n)} \text{L}^{-1/n} \text{g}^{-1}$) and $1/n$ is a constant indicative of the intensity of the adsorption. The maximum adsorption capacity ($q_m \text{ mg g}^{-1}$) could be theoretically determined, $K_F = \frac{q_m}{C_o^{1/n}}$, it is necessary to operate with constant initial concentration (C_o); thus $\log q_m$ is the extrapolated value of $\log q$ for $C = C_o$.

The Freundlich sorption isotherms of tested pesticides in clay loam soil and sandy loam soil are shown in Fig. (5). The parameters values of K_F , $1/n$ and R^2 were presented in Table (5). The Freundlich model has agreement with experimental data for MBZ and BPS in clay loam soil, for MBZ and BPS in sandy loam, as indicated by higher values of determination coefficient (R^2) with lower values of standard error (Asfaram et al., 2017; Liu et al., 2017).

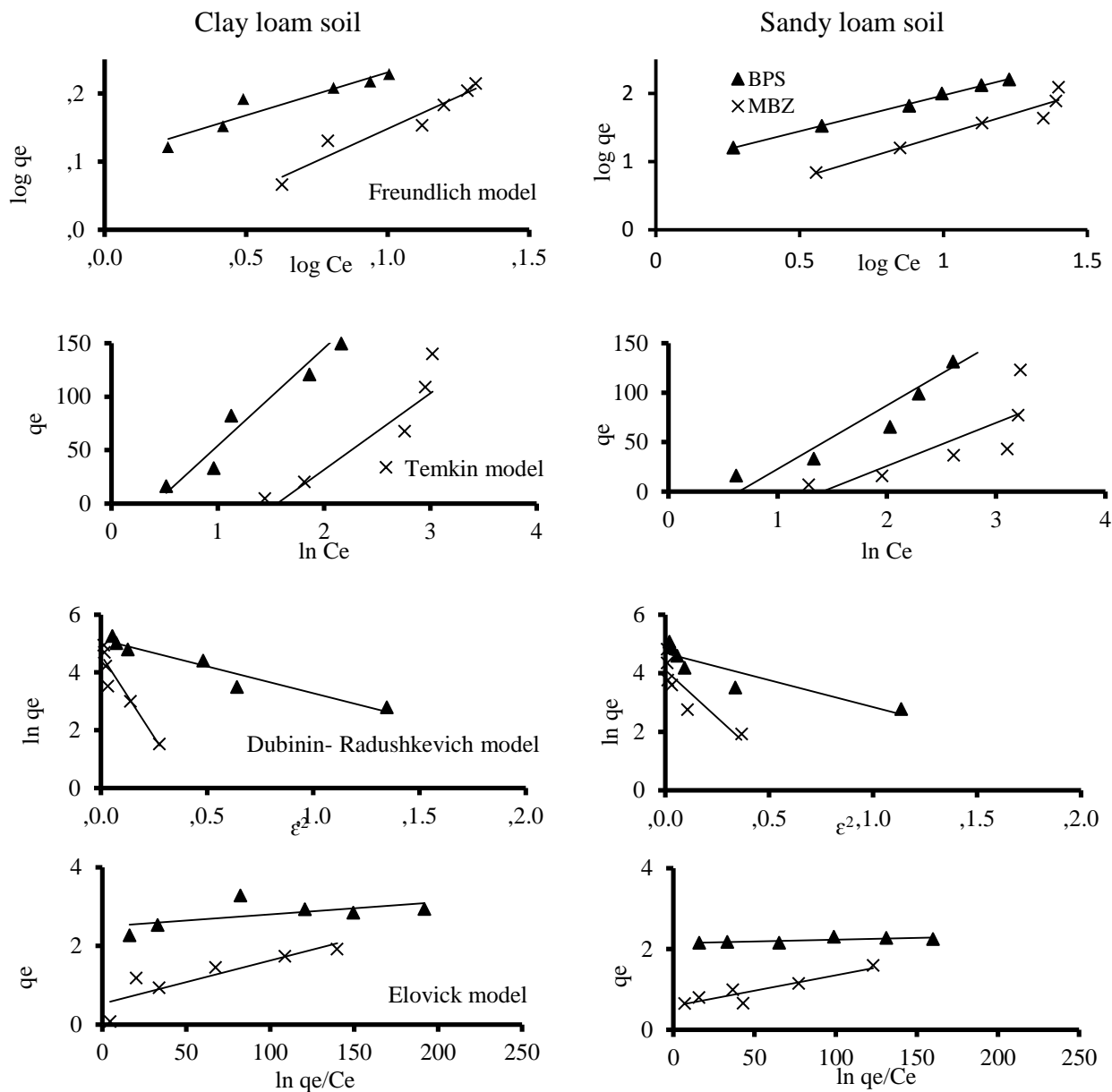


Fig. (5) Freundlich, Temkin, Dubinin- Radushkevich and Elovick linear fitted adsorption isotherms of BPS and MBZ in clay loam and sandy loam soil.

Table (5) Parameters of Freundlich, Temkin, Dubinin- Radushkevich and Elovick isotherm models of BPS and MBZ in clay loam and sandy loam soil.

Isotherm models	Clay loam soil		Sandy loam soil		
	BPS	MBZ	BPS	MBZ	
Freundlich	K_F	11.1864	0.3914	8.2244	1.2987
	$1/n$	1.2585	1.8879	1.0560	1.2768

Isotherm models		Clay loam soil		Sandy loam soil	
		BPS	MBZ	BPS	MBZ
	R ²	0.9031	0.9320	0.9973	0.9272
	SE	0.0025	0.0085	0.0025	0.0330
Temkin	β _T	91.3590	71.4380	64.2020	43.6380
	A _T	0.6647	0.2113	0.5270	0.2447
	B	0.0271	0.0347	0.0386	0.0568
	R ²	0.9479	0.7595	0.9086	0.6413
	SE	0.0118	0.0236	0.0008	0.0504
Dubinin- Radushkevich	β	1.8585	11.3600	1.8328	6.4963
	X _m	169.9323	99.0773	107.7270	61.2828
	R ²	0.9317	0.8952	0.8203	0.7620
	SE	0.1739	0.0098	0.2163	0.0291
Elovich	q _m	- 322.580	- 90.909	- 1111.11	- 129.87
	K _E	- 0.0375	- 0.0187	- 0.0077	- 0.0138
	R ²	0.3578	0.7734	0.5506	0.8536
	SE	0.0319	0.0071	0.0063	0.0558

Temkin model:

The Temkin model (Temkin 1941) assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent- adsorbate interactions, and that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. The model is given by

$$q_e = \beta_T \ln C_e + \beta_T \ln A_T$$

Where β_T and A_T are the Temkin equilibrium constants, $\beta_T = \frac{RT}{b}$, R the universal gas constant (kJ mol⁻¹ K⁻¹), T the temperature (K), b is a constant.

The Temkin sorption isotherm of tested pesticides in studied soils is shown in Fig. (5). The Temkin equilibrium constants can be calculated from the linear plotting of q_e versus $\ln C_e$, β_T is the slope and $\beta_T \ln A_T$ is the intercept (Table 5). The adsorption data for tested pesticides in soils were analyzed by a regression analysis to test their fit with Temkin isotherm model. This model perfectly describes the adsorption

isotherms of BPS in clay loam soil and sandy loam soil because of the higher coefficients of correlations and lower standard error values while it is invalid to describe the adsorption isotherm of MBZ in different tested soils (Rigi et al., 2018).

Dubinin- Radushkevich (D- R) isotherm model:

D- R isotherm (Dubinin and Radushkevich 1947) is an empirical model initially conceived for the adsorption of subcritical vapors onto micropore solids following a pore filling mechanism. It was usually applied to distinguish the physical and chemical adsorption of metal ions. The model is;

$$q_e = X_m \exp(-\beta \epsilon^2)$$

The linear form is presented in Table (5). The β is the isotherm constant and the parameter ϵ can be correlated as:

$$\epsilon = RT \ln\left[1 + \frac{1}{C_e}\right]$$

Where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is absolute temperature (K) and C_e is adsorbate equilibrium concentration (mg L^{-1}). The equilibrium data were analyzed using the linearized form of D- R equation using the same set experimental data, by plotting $\ln q_e$ versus ϵ^2 (Fig. 5). The isotherm constants and the corresponding coefficient of correlation values were shown in Table (5). It was observed that the coefficient of correlation values were low, therefore, this model does not suitable to describe the equilibrium data for tested pesticides in different soils (Parolo et al., 2017; Dowling et al., 2018).

Elovich model:

The Elovich model equation (Elovich and Larinov 1962) which implies a multilayer adsorption can be expressed as follow;

$$\frac{q_e}{q_m} = K_E C_e \exp\left(-\frac{q_e}{q_m}\right)$$

Where K_E is the Elovich equilibrium constant (L mg^{-1}) and q_m is the Elovich maximum adsorption capacity (mg g^{-1}). The parameters can be calculated from the slope and the intercept of the plot $\ln\left(\frac{q_e}{C_e}\right)$ versus q_e using the linear form of the equation; $\ln\left(\frac{q_e}{C_e}\right) = \ln K_E q_m - \frac{q_e}{q_m}$ (Table 3).

The simulated isotherm curves determined using the Elovich model is given in Fig. (5). The Elovich isotherm constants K_E and q_m , as well as the correlation coefficient (R^2) for the adsorption of tested pesticides in soils are presented in Table (5). It was observed that the coefficients of correlation are low (< 0.86) for tested pesticides in tested soils indicating a bad linearity.

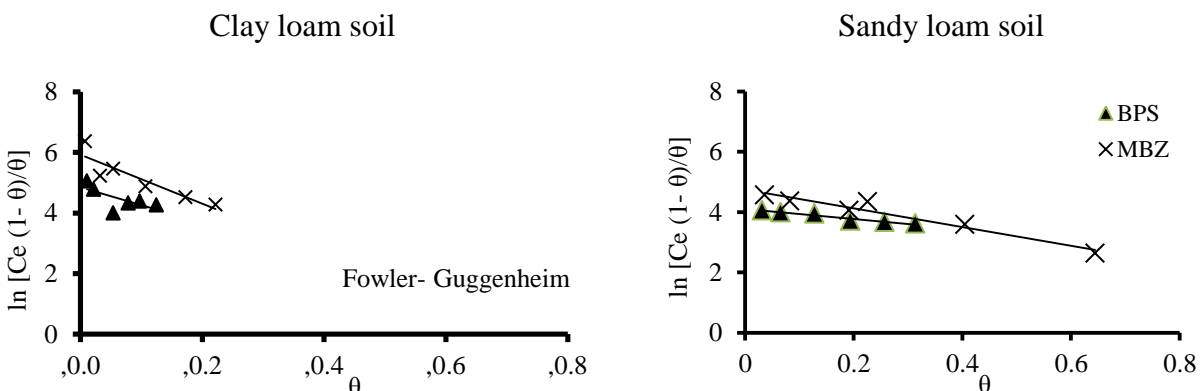
Fowler- Guggenheim model:

Fowler- Guggenheim (Fowler and Guggenheim 1939) derived an isotherm equation which takes the lateral interaction of the adsorbed molecules into account. This model is expressed by

$$K_{FG} C_e = \frac{\theta}{1 - \theta} \exp \left(\frac{2\theta W}{RT} \right)$$

Where K_{FG} is the Fowler- Guggenheim equilibrium constant ($L\ mg^{-1}$), θ is the fractional coverage, R the universal gas constant ($kJ\ mol^{-1}\ K^{-1}$), T the temperature (K), and W is the interaction energy between adsorbed molecules ($kJ\ mol^{-1}$). Fowler- Guggenheim equation is one of the simplest equations allowing for the lateral interaction. When there is no interaction between adsorbed molecules (that is $W = 0$), this equation will reduce to the Langmuir equation. It is very important to state that the value of q_m that can be used to calculate the surface coverage, θ could be obtained from the Freundlich, Langmuir and Elovich equation (Hamdaoui and Naffrechoux 2007).

The adsorption data for the tested pesticides in different soils were analyzed by a regression analysis to fit the Fowler- Guggenheim isotherm. The Fowler- Guggenheim equation is carried out by calculating the surface coverage using the value q_m obtained from Freundlich model. Hamdaoui and Naffrechoux (2007) reported that the Fowler- Guggenheim isotherm is only valid for $\theta < 0.6$ when the Langmuir and Freundlich maximum adsorption capacities are used. The calculated values of θ depend on the Freundlich model are lower than 0.6. Therefore, the Fowler- Guggenheim model could be used to describe the adsorption of the tested pesticides. The plots of the Fowler- Guggenheim model were shown in Fig. (6). Also, the coefficient of correlation and the parameters of the Fowler- Guggenheim isotherm model are summarized in Table (6). However, the correlation coefficient values are low in the case of all tested pesticides in different soils. Accordingly, the Fowler- Guggenheim model is unable to simulate the experimental results of the tested pesticides adsorption isotherms when the surface coverage is calculated using Freundlich maximum adsorption capacity. The interaction energy, W , is negative, for all tested pesticides, which indicates that there is no repulsion between the adsorption molecules (Lin et al., 2017; Pye et al., 2017).



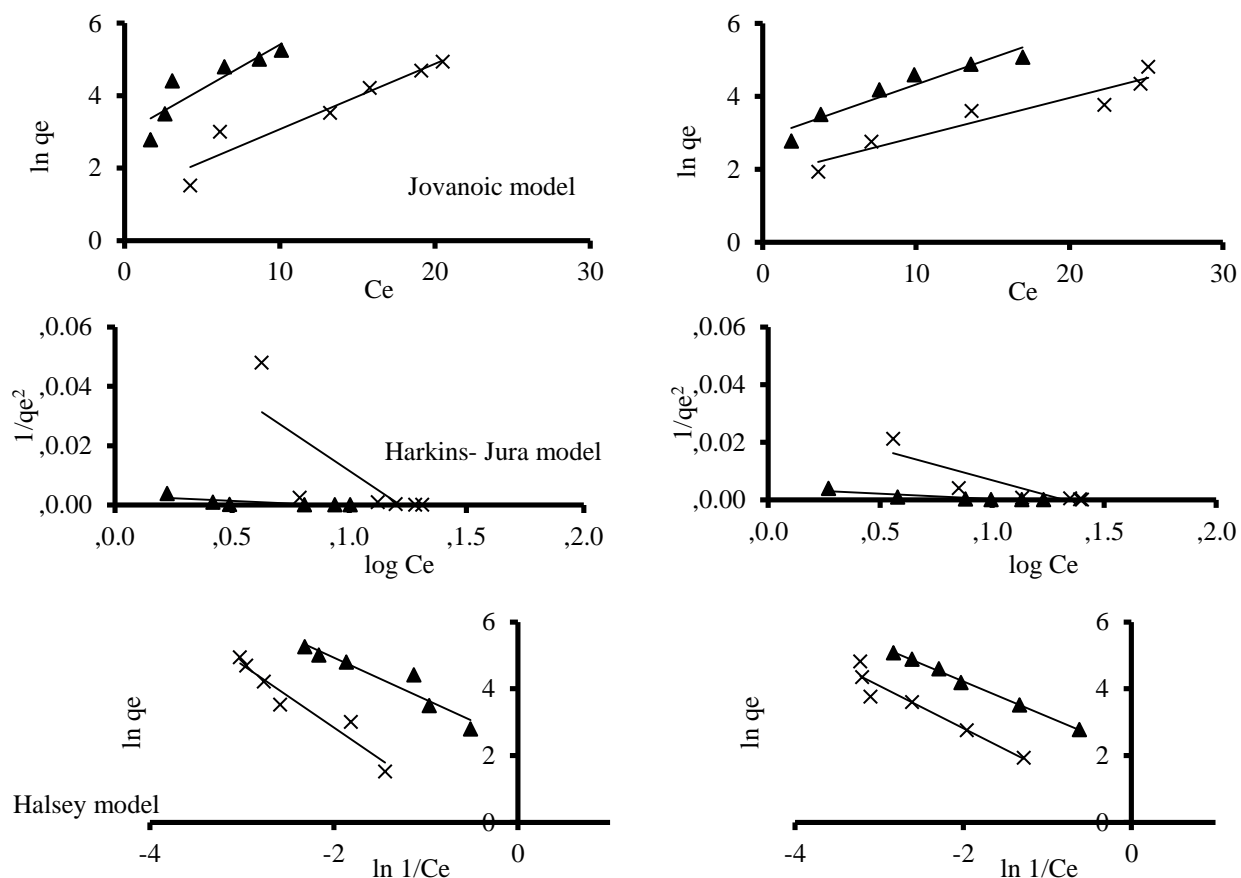


Fig. (6) Fowler- Guggenheim, Jovanoic, Harkins- Jura and Halsey linear fitted adsorption isotherms of BPS and MBZ in clay loam and sandy loam soil.

Table (6) Parameters of Fowler- Guggenheim, Jovanoic, Harkins- Jura and Halsey isotherm models of BPS and MBZ in clay loam and sandy loam soil.

Isotherm models		Clay loam soil		Sandy loam soil	
		BPS	MBZ	BPS	MBZ
Fowler- Guggenheim	W	- 7.2298	- 9.9909	- 2.0538	- 3.8305
	K_{FG}	0.0079	0.0027	0.0163	0.0087
	R^2	0.4564	0.8236	0.95.3	0.9467
	SE	0.1261	0.0077	0.0410	0.0081
Jovanoic	K_j	- 0.0829	- 0.1428	- 0.0315	- 0.0592
	q_m	19.2440	3.5477	17.3605	6.1184
	R^2	0.7971	0.9130	0.9144	0.9077

Isotherm models	Clay loam soil		Sandy loam soil		
	BPS	MBZ	BPS	MBZ	
	SE	0.0096	0.0046	0.0131	0.0143
Harkins- Jura	A _{HJ}	270.2703	18.8324	270.2703	47.1698
	B _{HJ}	0.8649	1.2166	1.0811	1.3255
	R ²	0.5942	0.6008	0.7885	0.7763
	SE	0.0453	0.2740	0.0220	0.0405
Halsey	K _H	6.8122	0.6084	7.3548	1.2272
	n _H	0.7946	0.3297	0.9470	0.7882
	R ²	0.9031	0.9320	0.9973	0.9272
	SE	0.0024	0.0085	0.0027	0.0329

Kiselev model:

The equation of Kiselev (Kiselev 1958) known as the adsorption isotherm in localized monomolecular layer is expressed by

$$K_1 C_e = \frac{\theta}{(1 - \theta)(1 + K_n \theta)}$$

Where K_1 is the kiselev equilibrium constant (L mg⁻¹), θ the fractional coverage and K_n is the constant of complex formation between adsorbed molecules. The linear form of the isotherm is shown in Table (3). The plotting of the Kiselev model $\frac{1}{[C_e(1-\theta)]}$ versus $\frac{1}{\theta}$. The values of surface coverage (θ) was calculated using the maximum adsorption capacity q_m determined from the Freundlich model. Because the Kiselev isotherm is only applicable for $\theta > 0.68$, but in fact in this study the calculated θ values are lower than 0.68. Therefore, the use of the Kiselev model to describe the adsorption of tested pesticides in soils is impossible. Even it was used, the linearization is very bad.

Jovanovic model:

In addition the some assumptions contained within the Langmuir model, the Jovanovic model considers the possibility of some mechanical contacts between the adsorbed and desorbed molecules.

The model of an adsorption surface considered by Jovanovic (Jovanovic 1969) is two- parameter isotherm model. It is the some kind of approximation leads to the result that monolayer adsorption. The Jovanovic model can be shown using the following nonlinear relationship:

$$q_e = q_m (1 - e^{K_J C_e})$$

It can be written in the following form:

$$q_e = q_m (1 - \exp(-K_J C_e))$$

The linear form is;

$$\ln q_e = \ln q_m - K_J \ln q_m C_e$$

The isotherms were obtained from the plotting of $\ln q_e$ versus $\ln C_e$ are shown in Fig. (6). The coefficient values of the tested pesticides BPS and MBZ were 0.7971, and 0.9130 in clay loam soil, 0.9144 and 0.9077 in sandy loam soil. The isotherm constant values of this model K_J and q_m are shown in Table (6).

Harkins- Jura model:

The adsorption equation proposed by Harkins and Jura (Harkins and Jura 1943) derived for the adsorption of solutes from solutions on solid surface is given by either equation (1) or (2).

Equation (1) as follows,

$$\log C_e = \alpha + \frac{\beta}{a^2}$$

Where C_e is the equilibrium concentration, a is the specific adsorption and α and β are constants. A plot of $\log C_e$ against $\frac{1}{a^2}$ should give a straight line having a slope β , which related to the specific surface area of the adsorbent.

Equation (2) as the follow;

$$\frac{1}{q_e^2} = \left(\frac{B_{HJ}}{A_{HJ}} \right) - \left(\frac{1}{A_{HJ}} \right) \log C_e$$

A plot of $\frac{1}{q_e^2}$ against $\log C_e$ should give a straight line, its slope is $-\frac{1}{A_{HJ}}$ and its intercept is $\frac{B_{HJ}}{A_{HJ}}$.

The adsorption data for the tested pesticides in different tested soils were analyzed by a regression analysis to fit the equation of Harkin- Jura isotherms (Fig. 6). The coefficient of correlation and the parameters of the Harkins- Jura model are presented in Table (6).

Halsey model:

Halsey equation (Halsey 1948) is described the relationship of various types of material in a broad range of relative humidies and temperatures. The empirical equation as follow;

$$q_e = \exp \left[\frac{(\ln K_H - \ln C_e)}{n_H} \right]$$

Where K_H is Halsey constant, n_H is exponent. The Halsey isotherms of the tested pesticides in different soils are shown in Fig. (6). The Halsey isotherm constants K_H and n_H , as well as the coefficient of

correlation (R^2), are obtained using the linear form of the equation (Table 3). The two parameters can be calculated from the linear form were presented in (Table 6). Halsey isotherm is suitable for the experimental results because of the higher coefficients of correlation were obtained for tested pesticides in most cases.

Conclusion

Linear correlation coefficients (R^2) presented the fit between experimental data and linearized forms of model equations. The lower coefficient of different Langmuir expressions and high standard error values for two tested pesticides, are suggesting that it is not appropriate to use this type of linearization. The Freundlich and Halsey models have agreement with experimental data as indicated by higher values of determination coefficient with lower values of standard error. Temkin isotherm model perfectly describes the adsorption isotherms of BPS in two soils while it is invalid to describe the adsorption isotherm of MBZ in different tested soils. The Dubinin- Radushkevich (D- R) and Elovich models are unable to describe the adsorption isotherms of the tested pesticides. The calculated values of the surface coverage θ depend on the Freundlich model are lower than 0.6. Although, the Fowler- Guggenheim model is unable to simulate the experimental results of the tested pesticides adsorption isotherms. Also, the use of the Kiselev model to describe the adsorption of tested pesticides in soils is impossible because this model is only applicable for $\theta > 0.68$. In general, the Freundlich model was the best fit for sorption of different pesticides, therefore the Freundlich isotherm model was used to be consistent with the different tested pesticides BPS and MBZ in different soils studied.

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