# Modeling study of adsorption isotherms of chlorantraniliprole and dinotefuran on soil

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| CHRONICLE | ABSTRACT |
|---|---|
| | Knowledge of pesticide adsorption characteristics is essential to predict their behavior in soil. The adsorption equilibrium isotherms of two insecticides chlorantraniliprole (CAP) and dinotefuran (DNF) on two common Egyptian soil types, clay loam and sandy loam were studied and modeled. To predict the adsorption isotherms and to determine the adsorption parameters, ten isotherm models: Langmuir (five linear forms), Freundlich, Temkin, Dubinin-Radushkevich, Elovick, Fowler-Guggenheim, Kiselev, Jovanoic, Harkins-Jura, and Halsey were applied on experimental data. The results revealed that the adsorption isotherm models fitted the data in the order of Halsey > Freundlich > Jovanoic > Langmuir isotherme. The models of Harkins-Jura, Elovich, Temkin, and Fowler-Guggenheim are not applicable to predict the adsorption isotherms of the tested insecticides. In order to determine the best-fit isotherm, the correlation coefficient ($R^2$), comparing the experimental (exp) and calculated (cal) adsorption data, and a normalized standard deviation ($\Delta g\%$) were used to evaluate the data. Therefore, the isotherm models Halsey and Freundlich could be used to predict the adsorption characteristics of CAP and DNF in the common Egyptian soil types, clay loam and sandy loam. Consequently, the mathematical models Halsey, Freundlich, and Jovanoic can describe the fate of CAP and DNF and can be used to control Egyptian soil contamination. |
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## 1. Introduction

Understanding the behaviour of pesticides in soil is important for their regulation and application.[1-2] Pesticides reach directly or indirectly to the soil and around 30-90% of the pesticide reach the soil depending on the application technique.[3] Adsorption is one of the most important processes face pesticides in soil, controls all other processes such as their movement, persistence, and transformation.[4-7] The sorption composed of several linear and non-linear isotherms.[8] Adsorption-desorption characteristics of pesticides in soil are essential to predict their mobility and fate in soil.[9-10] A literature review of the behaviour of neonicotinoid insecticides indicates that the little information is currently available about the environmental fate of dinotefuran (DNF). Also, chlorantraniliprole (CAP) is a new insecticide belonging to the anthranilic diamide class. It has been characterized as persistent in soil and mobile in terrestrial environment.[11-14]

The behaviour of pesticide in the environment is evaluated by using computation models.[15] Depending on the application, the models could be classified either as; screening, research or management models which are necessarily very useful for agricultural and environmental management.[16-17] Modelling the fate of pesticides will promote the development of environmentally friendly pesticides. As mathematical models can describe the fate of pesticides and can be used to control the environmental pollution.[18] Models of pesticides persistence and leaching are sensitively related to the sorption parameters. Environmental pesticide simulation has been used increasingly for many years for research purposes, and in the

past decade, for pesticide regulation [19-20] Moreover, modelling of the pesticide's sorption isotherm is important for prediction and adsorption performance. Many isotherm models are available for modelling of the adsorption data.[21-22]

## 2. Materials and Methods

### 2. 1. Tested insecticides

*Chlorantraniliprole (CAP)*

3-Bromo-N-[4-chloro-2-methyl-6-(methylcarbamoyl)phenyl]-1-(3-chloro-2-pyridine-2-yl)-1H-pyrazole-5-carboxamide, Anthranilic diamide. The chemical structure is shown in **Fig. 1**. Technical 95.30%. was supplied by Kafr El Zayat Pesticide (KZ) Co., Egypt.

*Dinotefuran (DNF)*

(RS)-1-methyl-2-nitro-3-(tetrahydro-3-furylmethyl) guanidine, Neonicotinoid. The chemical structure is presented in **Fig. 1**. Technical 90.0% was obtained from Central Laboratory of Pesticides, Giza, Egypt.



Chlorantraniliprole                    Dinotefuran
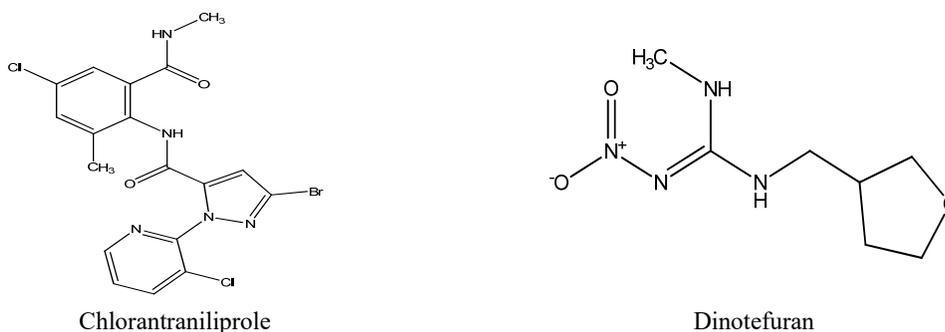
**Fig. 1.** Chemical structures of tested insecticides.

### 2.2. Tested soils

Two types of the common Egyptian soils, clay loam soil (alluvial) from Agricultural Research Station, Abis, Alexandria, Egypt and sandy loam soil (calcareous) from Bangar Elsokar region were tested in the present study. The samples were collected from the top (0-30 cm) layers of the soil profiles from different locations.[23-25] The physical and chemical properties were determined at the Department of Soil and Water Sciences, Faculty of Agriculture, University of Alexandria and the data are presented in **Table 1**.

**Table 1.** Physical and chemical properties of the tested soils.

| Properties | Alluvial soil | Calcareous soil |
|---|---|---|
| Texture class | Clay loam | Sandy loam |
| 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 |

### 2.3. Insecticide measurements

*Determination of tested insecticides*

Each insecticide standard solutions (0.1-100 $\mu g\ mL^{-1}$) were prepared by the stepwise dilution of the insecticide stock solution (500 $\mu g\ mL^{-1}$) dissolved in aqueous dimethyl formamide solution. All concentration measurements in the experiments were performed by a UV-Vis Spectrophotometer (Thermo Corporation, Nicolet, evolution 100). To determine the optimum wavelength ($\lambda_{max}$) that is specific for each compound with a minimum interference, a scanning range of 200-400 nm was used to generate for 5 $\mu g/mL$ insecticide solution. It was showed that $\lambda_{max}$ values are 273 nm and 280 nm, also the standard calibration curves which obtained by plotting triplicates (n = 3) of known concentrations (0.1-100 $\mu g\ mL^{-1}$) indicated that k values are 0.0263 and 0.0231 $\mu g\ mL^{-1}$ for chlorantraniliprole and dinotefuran, respectively. For quality assurance and control, triplicate samples including controls and blanks were used.

*Pesticide detection and quantification limits*

The spectrophotometric method specificity for pesticide determination was verified through a spectral density curve (S-D curve). Limit of blank (LOB), limit of detection (LOD) and limit of quantitation (LOQ) are important terms to describe the smallest pesticide concentration that can be reliably determined under experimental conditions. To test the validity of this spectrophotometer method, guidelines for LOB, LOD and LOQ was calculated by the equations (1-3).

$$LoB = Mean_{blank} + 1.645\ SD_{blank} \qquad (1)$$

$$LoD = LoB + 1.645\ SD_{low\ concentration\ samples} \qquad (2)$$

$$LoQ \geq LoD \qquad (3)$$

*2. 4. Adsorption experiments of tested insecticides*

*Adsorption isotherm*

Adsorption isotherm by soil was quantified using the batch equilibration technique. The experiments were carried out in triplicate with an insecticide solution to sorbent mass ratio of 1:5. Initial insecticide concentrations in 1.0-100 mg $L^{-1}$ range were equilibrated with soil in 25-mL polypropylene centrifuge tubes. The tubes were shaken mechanically at 150 rpm at room temperature for a time to achieve equilibrium based on its kinetics study (24 h) and centrifuged at 4000 rpm for 15 min. To determine the insecticide concentration, the supernatants were measured by spectrophotometer at the proper wavelength. Control samples (no insecticide) containing only adsorbent substances and 0.01 M $CaCl_2$ were included. Blanks containing insecticide solution only without adsorbents indicated that sorption on the tube was insignificant. At equilibrium, the sorbed amount of insecticide, Cs, by solid phase was calculated by Eq. (4):

$$C_s = (C_i - C_e) \times \frac{V}{M_s} \qquad (4)$$

where, $C_s$ is the sorbed amount of insecticide per mass unit of adsorbent ($\mu g\ g^{-1}$), $C_i$ is the initial concentration of insecticide ($\mu g\ mL^{-1}$), $C_e$ is the equilibrium concentration of the insecticide per mass unit of solution ($\mu g\ mL^{-1}$), $V$ is the volume of added solution and $M_s$ is the weight of the adsorbent sample (g).[26]

*Modeling sorption isotherm*

To find a model that can accurately describe, the experimental adsorption isotherm results 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, Freundlich, Temkin, Dubinin-Radushkevich, Elovick, Fowler-Guggenheim, Kiselev, Jovanoic, Harkins-Jura and Halsey.[27] The validity of adsorption models was tested by correlation coefficient ($R^2$), comparing the experimental (exp) and calculated (cal) data and a normalized standard deviation ($\Delta g\%$) which is calculated as follows

$$\Delta g(\%) = 100 \times \sqrt{\frac{\Sigma[(q_e^{exp} - q_e^{cal})/q_e^{exp}]^2}{N-1}} \qquad (5)$$

where $N$ is the number of measurements.

*2. 5. Statistical analysis*

Experimental data are presented as mean ± standard error and the statistical analysis was performed by the SPSS program.

## 3. Results and discussion

*3. 1. Adsorption isotherm*

The experimental adsorption isotherms of tested insecticides CAP and DNF from aqueous solutions on clay loam soil and sandy loam soil are presented in **Fig. 2**. The obtained results showed that DNF was adsorbed more than CAP on the two tested soil types; clay loam soil and sandy loam soil.
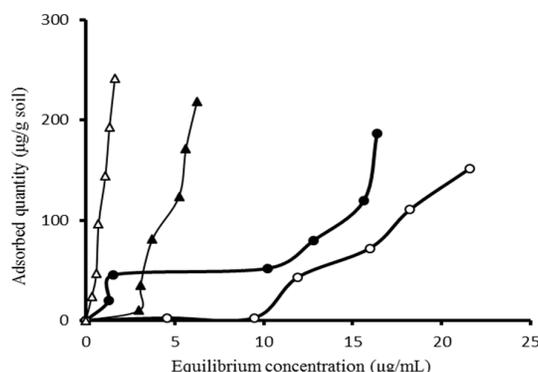


**Fig. 2.** Adsorption isotherm of chlorantraniliprole and dinotefuran in clay loam and sandy loam soil. Chlorantraniliprole in clay loam soil ● and in sandy loam soil ○; dinotefuran in clay loam soil ▲ and in sandy loam soil ∆.

*3.2. Mathematical models*

Many mathematical models were evaluated to describe the experimental adsorption isotherm data. To find the fit model and to determine the parameters of the pesticide adsorption process, ten isotherm models Langmuir (five linear forms), Freundlich, Temkin, Dubinin-Radushkevich (D-R), Elovich, Fowler-Guggenhiem, Kiselev, Jovanovic, Harkins-Jura, and Halsey were applied to experimental data of tested insecticides CAP and DNF in clay loam soil and sandy loam soil. The experimental values of $q_e$ (the amount of adsorbed solute) and $C_e$ (the equilibrium concentration) for each compound in each soil type are initially treated with the linearized equations to determine the parameters of the model that used to reconstitute the isotherms. The isotherm curves have shown the identical to the experimental data (points) with the theoretical points (lines). Linear correlation coefficients ($R^2$) presented the fit between experimental data of the sorption and linearized forms of model equations. Its value may vary from 0 to 1.[28] The adsorption isotherm models, and their empirical and linear forms are presented in **Table 2**.

**Table 2.** Adsorption isotherm models and their linear forms.

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

*Langmuir model*

It assumes energies of the adsorption sites. The Langmuir model is given by Eq. (6):

$$q_e = \frac{q_m\,b\,C_e}{1 + b\,C_e} \tag{6}$$

where $q_e$ is the amount of solute adsorbed per weight unit of adsorbent at equilibrium (µg g$^{-1}$), $C_e$ the equilibrium concentration of the solute in solution (mg L$^{-1}$), $q_m$ the maximum adsorption capacity (µg g$^{-1}$) and b is constant that depends on the free energy of adsorption (L mg$^{-1}$). The adsorption data for tested insecticides in tested soils were analysed by a regression analysis to fit the five linearized expressions of Langmuir isotherm model. The details of the different expressions of linearized equations and the methods to estimate the Langmuir constants $q_m$ and b from these plots were presented in **Table 2**. Values of the Langmuir constants are summarized in **Table 3** for the adsorption of the tested insecticides in clay loam and sandy loam soil.

**Table 3.** Parameters of Langmuir isotherm model for chlorantraniliprole and dinotefuran in clay loam and sandy loam soil.

| Langmuir type | | Clay loam soil | | Sandy loam soil | |
|---|---|---|---|---|---|
| | | CAP | DNF | CAP | DNF |
| Expression 1 | $q_m$ | 133.33 | -16.37 | -7.82 | -129.87 |
| | B | 0.176 | -0.169 | -0.043 | -0.478 |
| | $R^2$ | 0.728 | 0.562 | 0.731 | 0.976 |
| | SE | 0.308 | 0.008 | 0.216 | 0.043 |
| | $\Delta g$ (%) | 9.04 | 65.17 | 95.59 | 20.58 |
| Expression 2 | $q_m$ | 192.31 | -40.00 | -5.61 | -185.19 |
| | B | 0.083 | -0.080 | -0.050 | -0.378 |
| | $R^2$ | 0.323 | 0.442 | 0.485 | 0.704 |
| | SE | 0.034 | 0.005 | 0.159 | 0.078 |
| | $\Delta g$ (%) | 9.95 | 69.67 | 82.48 | 14.89 |
| Expression 3 | $q_m$ | 109.28 | -31.27 | -12.08 | -143.01 |
| | B | 0.492 | -0.152 | -0.048 | -0.446 |
| | $R^2$ | 0.094 | 0.941 | 0.949 | 0.810 |
| | SE | 0.021 | 0.001 | 0.013 | 0.060 |
| | $\Delta g$ (%) | 93.94 | 94.08 | 97.98 | 71.58 |
| Expression 4 | $q_m$ | 355.40 | -39.14 | -16.12 | -205.93 |
| | B | 0.046 | -0.143 | 0.046 | -0.361 |
| | $R^2$ | 0.094 | 0.941 | 0.949 | 0.810 |
| | SE | 0.021 | 0.001 | 0.013 | 0.060 |
| | $\Delta g$ (%) | 9.44 | 38.90 | 91.98 | 15.51 |
| Expression 5 | $q_m$ | 344.65 | -7.73 | -4.29 | -121.15 |
| | B | 0.050 | -0.201 | 0.057 | -0.499 |
| | $R^2$ | 0.728 | 0.562 | 0.731 | 0.976 |
| | SE | 0.308 | 0.008 | 0.216 | 0.043 |
| | $\Delta g$ (%) | 9.02 | 79.19 | 95.36 | 24.03 |

CAP: chlorantraniliprole; DNF: dinotefuran; $q_m$: the maximum adsorption capacity ($\mu g\ g^{-1}$); $b$: the Langmuir constant (L $mg^{-1}$); $R^2$: linear correlation coefficient; SE: standard error; $\Delta g$% normalized standard division.

It was observed that different values of Langmuir parameters were obtained from different linear expressions. The values of the correlation coefficient obtained from different Langmuir expressions indicated that the soil type was the essential factor affecting 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 DNF in clay loam soil and for CAP in sandy loam soil (**Table 3**).
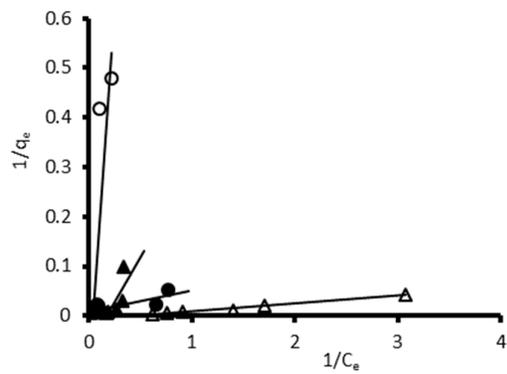


Expression 1
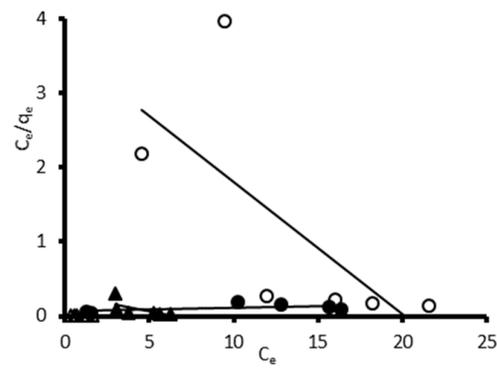


Expression 2
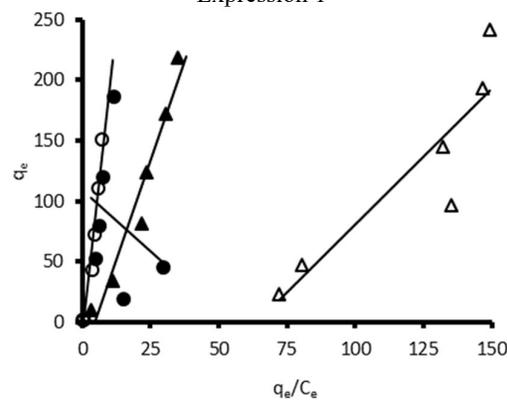


Expression 3
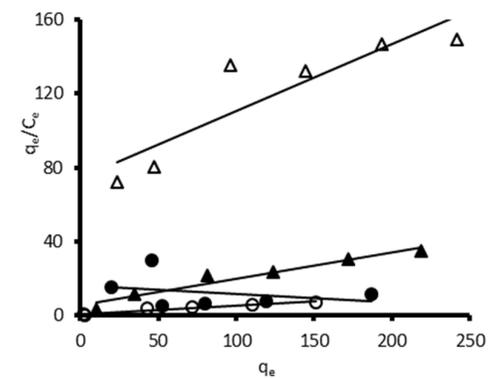


Expression 4
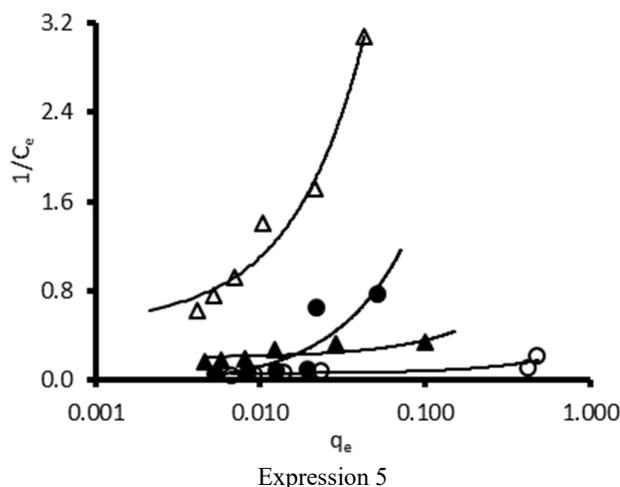
Expression 5

**Fig. 3.** Adsorption isotherm of chlorantraniliprole and dinotefuran in clay loam and sandy loam soil fitted in different expressions of Langmuir model. Chlorantraniliprole in clay loam soil ● and in sandy loam soil ○; dinotefuran in clay loam soil ▲ and in sandy loam soil ∆.

Also, Langmuir expression 1 and 5 produced high values of ($R^2$) for DNF in sandy loam soil. In addition, high $\Delta g\%$ values of CAP and DNF in both soil types were recorded indicating that all Langmuir expressions are invalid to describe the adsorption of these compounds. The Langmuir sorption isotherms of different pesticides in different studied soils are shown in **Fig. 3**. In general, the low coefficient, high standard error values and high normalized standard division of the most cases of the Langmuir expressions, suggesting that it is not applicable to use this type of linearization.

*Freundlich model*

The empirical formula of the Freundlich equation can be written as Eq. (7):

$$q_e = K_F C_e^{1/n} \tag{7}$$

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

The Freundilch sorption isotherms of CAP and DND in both soil types; clay loam and sandy loam are shown in **Fig. 4**. The parameters values of $K_F$, 1/n and $R^2$ are presented in **Table 4**. The Freundilch model agrees with experimental data for DNF more than that for CAP as indicated by higher values of determination coefficient ($R^2$) with lower values of standard error. However, the low $\Delta g\%$ values were obtained, and the lowest value was obtained from the adsorption of CAP in clay loam soil.

The shape of the isotherms is necessary to identify the nature of a specific adsorption phenomenon. The sorption isotherms have been classified into four main groups; S, L, H and C according to Giles.[29] Table 4 indicates that the isotherms displayed an S-type isotherm (1/n > 1) except the isotherm of CAP in clay loam soil that is L-type isotherm (1/n < 1). 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 concentration. In the case of the L-type isotherm, there was no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites.[27] It was characterized by a decrease in the absorption of pesticides at higher concentrations. This indicates that as the dissolved concentration increased in solution, competition for adsorption sites increased.[30]

*Temkin model*

The Temkin model[31] assumes that the adsorption heat of molecules in the layer reduces linearly with the surface coverage with the adsorbent-adsorbate interactions. The model can be written as Eq. (8):

$$q_e = \beta_T \ln C_e + \beta_T \ln A_T \tag{8}$$

where $\beta_T$ and $A_T$ are the Temkin equilibrium constants, $\beta_T = RT/b$, R the Universal gas constant (kJ $mol^{-1}$ $K^{-1}$), T the temperature (K), b is a constant.
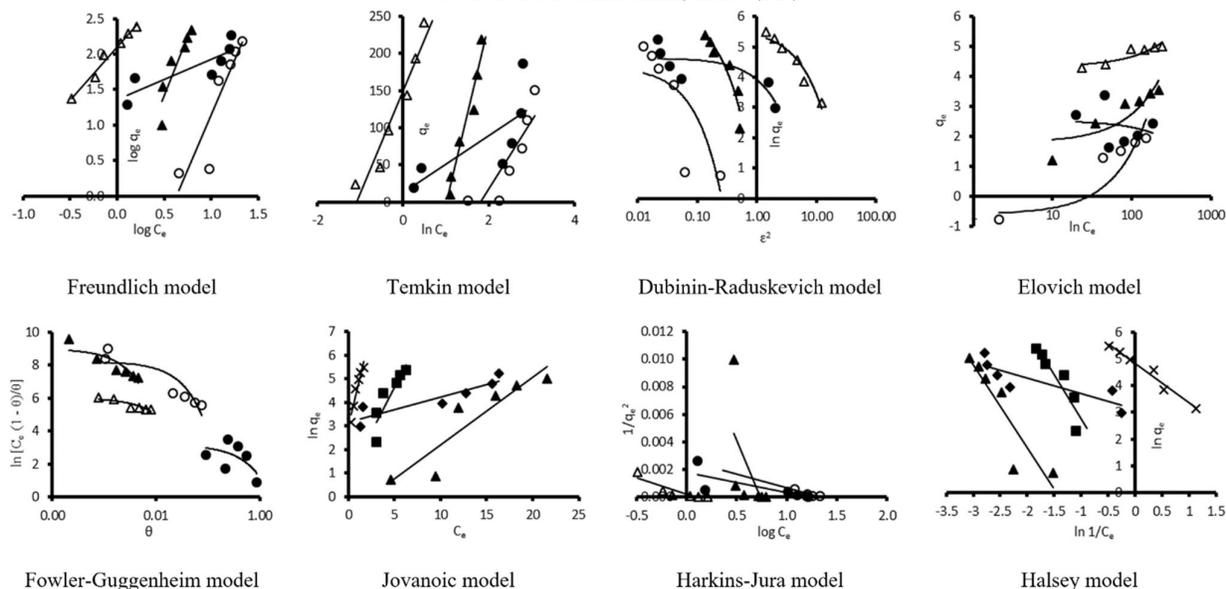
**Fig. 4.** Adsorption isotherm of tested insecticides in clay loam and sandy loam soil fitted in different adsorption mathematical models. Chlorantraniliprole in clay loam soil ● and in sandy loam soil ○; dinotefuran in clay loam soil ▲ and in sandy loam soil Δ.

The Temkin sorption isotherm of tested insecticides in studied soils is shown in **Fig. 4**. The Temkin equilibrium constants can be calculated from the linear plotting of $q_e$ versus $lnC_e$, $\beta_T$ is the slope and $\beta_T \ln A_T$ is the intercept **(Table 2)**. The adsorption data for tested insecticides in soils were analysed by a regression analysis to test their fit with Temkin isotherm model. This model perfectly describes the adsorption isotherms of DNF in clay loam soil and sandy loam soil because of the higher coefficients of correlations and lower standard error values while it was invalid to describe the adsorption isotherm of CAP in clay loam soil.

*Dubinin-Radushkevich (D-R) isotherm model*

D-R isotherm is an empirical model usually used to distinguish the chemical and physical adsorption of metal ions.[32] The model equation is presented in Eq. (9):

$$q_e = X_m \, exp(-\, \beta \varepsilon^2) \tag{9}$$

The linear form is presented in **Table 2**. The β is the isotherm constant and the parameter ε can be correlated as Eq. (10):

$$\varepsilon = RT \, ln[1 + \frac{1}{C_e}] \tag{10}$$

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is absolute temperature (K) and $C_e$ is adsorbate equilibrium concentration (mg L$^{-1}$). The data of the adsorption equilibrium were analysed by the linearized form of D-R equation, using plotting $ln \, q_e$ versus $\varepsilon^2$ **(Fig. 4)**. The isotherm constants and the corresponding values of correlation coefficient are shown in Table 4. It was observed that the correlation coefficient values of CAP in both soil types; clay loam and sandy loam were low and the Δg% values were high, therefore, this model does not suitable to describe the equilibrium data for this insecticide.

*Elovich model*

The Elovich model equation[33] which implies a multilayer adsorption can be expressed as follow in Eq. (11):

$$\frac{q_e}{q_m} = K_E C_e \, exp \left(-\frac{q_e}{q_m}\right) \tag{11}$$

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 obtained from the slope and the intercept values of the plot $ln \, q_e/q_m$ versus $q_e$ using the Elovich equation in linear form **(Table 2)**.

**Table 4.** Parameters of different mathematical adsorption isotherm models for chlorantraniliprole and dinotefuran in clay loam and sandy loam soil.

| Soil type / Insecticide | | Freundlich | | | | | Temkin | | | | | Dubinin-Radushkevich | | | | | Elovich | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $K_F$ | $1/n$ | $R^2$ | SE | Δg% | $A_T$ | b | $R^2$ | SE | Δg% | β | $X_m$ | $R^2$ | SE | Δg% | $q_m$ | $K_E$ | $R^2$ | SE | Δg% |
| Clay loam soil | CAP | 22.82 | 0.575 | 0.731 | 0.095 | 9.97 | 1.39 | 0.064 | 0.555 | 0.023 | 21.01 | 0.72 | 102.50 | 0.683 | 0.028 | 32.65 | 454.55 | 0.028 | 0.043 | 0.201 | 18.52 |
| | DNF | 0.57 | 3.310 | 0.835 | 0.009 | 18.06 | 0.36 | 0.010 | 0.949 | 0.001 | 58.79 | 6.54 | 521.03 | 0.789 | 0.003 | 85.91 | -105.26 | -0.057 | 0.752 | 0.001 | 86.29 |
| Sandy loam soil | CAP | 0.01 | 3.098 | 0.824 | 0.061 | 19.52 | -1.81 | 0.027 | 0.763 | 0.029 | 32.45 | 16.98 | 77.17 | 0.598 | 0.011 | 79.89 | -47.85 | -0.012 | 0.761 | 0.083 | 70.21 |
| | DNF | 125.83 | 1.499 | 0.977 | 0.036 | 15.09 | 3.00 | 0.018 | 0.926 | 0.033 | 61.22 | 0.22 | 268.89 | 0.935 | 0.017 | 98.65 | -303.03 | -0.249 | 0.779 | 0.050 | 91.98 |

| Soil type / Insecticide | | Fowler-Guggenheim | | | | | Jovanoic | | | | | Harkins-Jura | | | | | Halsey | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | W | $K_{FG}$ | $R^2$ | SE | Δg% | $K_J$ | $q_m$ | $R^2$ | SE | Δg% | $A_{HJ}$ | $B_{HJ}$ | $R^2$ | SE | Δg% | $K_H$ | $n_H$ | $R^2$ | SE | Δg% |
| Clay loam soil | CAP | -2.46 | 0.043 | 0.364 | 0.004 | 63.83 | -0.03 | 23.639 | 0.820 | 0.028 | 34.57 | 666.67 | 1.20 | 0.585 | 0.175 | 35.05 | 233.66 | 1.745 | 0.731 | 0.095 | 9.97 |
| | DNF | -566.37 | 0.001 | 0.753 | 0.001 | 74.87 | -0.46 | 2.524 | 0.801 | 0.010 | 29.71 | 574.71 | 7.41 | 0.368 | 0.005 | 59.41 | 0.843 | 0.302 | 0.835 | 0.009 | 18.06 |
| Sandy loam soil | CAP | -53.54 | 0.001 | 0.770 | 0.047 | 98.95 | 0.43 | 0.513 | 0.848 | 0.025 | 57.41 | 2.58 | 1.26 | 0.811 | 0.222 | 78.63 | 0.233 | 0.323 | 0.824 | 0.061 | 19.52 |
| | DNF | -127.26 | 0.003 | 0.782 | 0.050 | 67.99 | -0.60 | 18.181 | 0.907 | 0.001 | 19.82 | 416.67 | 0.08 | 0.755 | 0.042 | 38.47 | 25.66 | 0.671 | 0.977 | 0.036 | 15.09 |

CAP: chlorantraniliprole; DNF: dinotefuran; $K_F$: the Freundlich constant; $1/n$: the Freundlich exponent; $A_T$: the Temkin equilibrium constant; b: constant; β and $X_m$: the isotherm constants; $K_E$: the Elovich equilibrium constant; $W$: the interaction energy among adsorbed molecules; $K_{FG}$: the Fowler-Guggenheim equilibrium constant; $K_J$: the Jovanoic constant; $A_{HJ}$ and $B_{HJ}$: the Harkins-Jura constants; $K_H$: the Halsey constant; $n_H$: the Halsey exponent; $R^2$: linear correlation coefficient; $SE$: standard error; Δg% normalized standard deviation

The isotherm curves determined from the Elovich model is given in **Fig. 4**. The Elovich isotherm constants $K_E$ and $q_m$, as well as the correlation coefficient ($R^2$) for the adsorption of tested insecticides in soils are presented in Table 4. It was observed that the coefficients of correlation are low (< 0.8) for both tested compounds CAP and DNF indicating a bad linearity. Thus, the Elovich model was unable to describe the adsorption isotherms of CAP and DNF in clay loam and sandy loam soil.

*Fowler-Guggenheim model*

Fowler-Guggenheim derived an isotherm equation which takes the lateral interaction of the adsorbed molecules into account.[34] This model can be expressed as follow in Eq. (12):

$$K_{FG} C_e \; = \; \frac{\theta}{1-\theta} \; exp \left( \frac{2\theta W}{RT} \right) \tag{12}$$

where $K_{FG}$ is the Fowler-Guggenheim equilibrium constant (L mg$^{-1}$), $\theta$ is the fractional coverage, R the universal gas constant (kJ mol$^{-1}$ K$^{-1}$), T the temperature (K), and W is the interaction energy among adsorbed molecules (kJ mol$^{-1}$). Fowler-Guggenheim model is one of the simplest models. When there is no lateral interaction among adsorbed molecules (that is W = 0), the equation will be reduced 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, $\theta$ could be obtained from the Freundlich, Langmuir and Elovich equation.[27]

The adsorption data for CAP and DNF in different soils were analysed by a regression analysis to fit the Fowler-Guggenheim isotherm. It was reported that the Fowler-Guggenheim isotherm was only valid for $\theta < 0.6$ when the Langmuir and Freundlich maximum adsorption capacities are used.[27] The calculated values of $\theta$ depend on the Freundlich model were lower than 0.6. Therefore, the Fowler-Guggenheim model could be tested to describe the adsorption of the tested pesticides. The plots of the Fowler-Guggenheim model are shown in **Fig. 4**. Also, the coefficient of correlation and the parameters of the Fowler-Guggenheim isotherm model are summarized in **Table 4**. However, the correlation coefficient values were low particularly that of CAP in clay loam soil. Accordingly, the Fowler-Guggenheim model was unsuitable to simulate the experimental results of the tested pesticides adsorption isotherms.

*Kiselev model*

The equation of Kiselev[35] that is the adsorption isotherm in localized monomolecular layer is given by Eq. (13):

$$K_1 C_e = \frac{\theta}{(1-\theta)(1+K_n \theta)} \tag{13}$$

where $K_1$ is the Kiselev equilibrium constant (L mg$^{-1}$), $\theta$ the fractional coverage and $K_n$ is the constant of complex formation among adsorbed molecules. The isotherm in the linear form is shown in **Table 2**. The surface coverage $\theta$ values were calculated using the maximum adsorption capacity $q_m$ obtained from the Freundlich model. Because the Kiselev isotherm was only applicable for $\theta > 0.68$, but in fact in this study the calculated $\theta$ values were lower than 0.68. Therefore, the use of the Kiselev model to describe the adsorption of tested insecticides in soils was impossible. Even when it was used, the linearization was very bad.

*Jovanovic model*

The model of Jovanovic considers the possibility of some mechanical contacts between the adsorbed and desorbed molecules.[36] It is a kind of approximation due to that the monolayer adsorption. The Jovanovic model can be shown using the following nonlinear relationship in Eq. (14):

$$q_e = q_m \left( 1 - e^{K_J C_e} \right) \tag{14}$$

It can be written in the form as follow in Eq. (15):

$$q_e = q_m \left( 1 - exp(-K_J \, C_e) \right) \tag{15}$$

The linear form is presented in Eq. (16):

$$ln \; q_e \; = \; ln \; q_m \; - \; K_J \; ln \; q_m \; C_e \tag{16}$$

The isotherms were obtained from the plotting of $ln \; q_e$ versus $C_e$ are shown in **Fig. 4**. The coefficient values of the tested pesticides CAP and DNF were 0.8196 and 0.8005 in clay loam soil and 0.8479 and 0.9070 in sandy loam soil, respectively. The isotherm constant values of this model $K_f$ and $q_m$ are shown in **Table 4**.

*Harkins-Jura model*

The adsorption equation proposed by Harkins and Jura derived for the adsorption of solutes from solutions on solid surface is given by either equation (16) or (17).[37]
Eq. (17) as follows,

$$log\ C_e = \alpha + \frac{\beta}{a^2} \tag{17}$$

where $C_e$ is the equilibrium concentration, a is the specific adsorption and $\alpha$ and $\beta$ are constants. A plot of log $C_e$ against $1/\alpha^2$ should give a straight line laving a slope $\beta$, which related to the specific surface area of the adsorbent. Eq. (18) is presented in **Table 2**, as the follow;

$$\frac{1}{q_e^2} = \left(\frac{B_{HJ}}{A_{HJ}}\right) - \left(\frac{1}{A_{HJ}}\right) log\ C_e \tag{18}$$

The straight line obtained from a plot of *1/q_e²* against *log C_e* has a slope equal -*1/A_HJ* and intercept equal *B_HJ/A_HJ*.

The adsorption data for CAP and DNF in different tested soils were analysed by a regression analysis to fit the equation of Harkins-Jura isotherms **(Fig. 4)**. The coefficient of correlation and the parameters of the Harkins-Jura model are presented in **Table 4**. According to the correlation coefficients and $\Delta g\%$ values, the linearization was bad for the two tested compounds in clay loam soil.

*Halsey model*

Halsey equation is described the relationship of various types of material in a broad range of relative humidity and temperatures.[38] The empirical equation as follow in Eq. (19):

$$q_e = exp\left[\frac{(ln\ K_H - ln\ C_e)}{n_H}\right] \tag{19}$$

where $K_H$ is Halsey constant, $n_H$ is exponent. The Halsey isotherms of the tested pesticides in different soils are shown in **Fig. 4**. The Halsey isotherm constants $K_H$ and $n_H$, as well as the coefficient of correlation ($R^2$), were obtained using the linear equation form were presented in **Table 4**. Halsey isotherm was valid for the experimental results of CAP and DNF because of the high correlation coefficients, high $\Delta g\%$ values and the low standard error were obtained.

*Comparison of the tested adsorption isotherm models*

The sorption equilibrium data are generally presented in the form of different isotherm models. The existing models of the sorption isotherm were empirical and linear form and consisted of different constants.
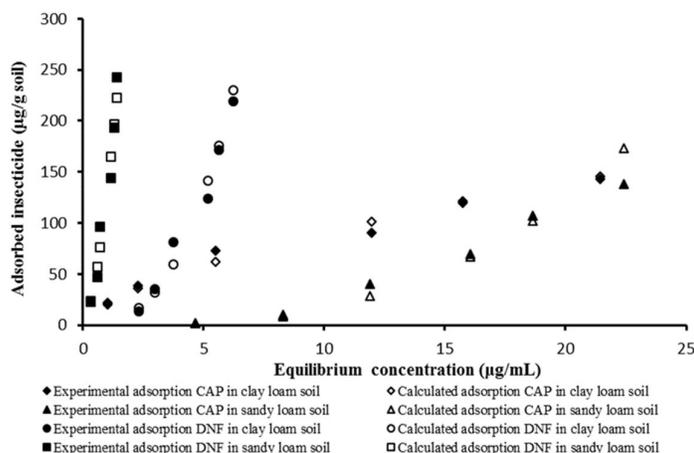


**Fig. 5.** Comparison of the experimental and calculated adsorption Freundlich data of CAP and DNF on clay loam and sandy loam soil.

The correlation coefficient of determination ($R^2$), comparing the experimental and calculated adsorption data and a normalized standard deviation ($\Delta g\%$) were used to gauge the goodness-of-fit. The models that produced relatively high $R^2$ for CAP in clay loam soil and sandy loam soil are Jovanoic, Freundlich, Halsey and Langmuir isotherm models (expression

1 and 5). All tested models were appropriated to describe the adsorption isotherm of DNF in clay loam soil and sandy loam soil except the models of Harkins-Jura and Langmuir (expression 1, 2 and 5). The Langmuir isotherm has only limited applicability.[39] The model of Harkins-Jura, Elovich, Temkin and Fowler-Guggenheim does not apply easily to the experimental results. The experimental and calculated data of Freundlich adsorption are almost identical **(Fig. 5)**. In addition, Freundlich model was the best fit for sorption of different pesticides as reported in other previous studies such as; CAP,[40, 41] DNF,[42] and other pesticides atrazine, phenyl urea, bentazone, 2,4-D, methamidophos, aldicarb, imidacloprid, endosulfan, bispyribac-sodium, and metribuzin. [7, 43-53]

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