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# Physical characteristics and Freundlich model of adsorption and desorption isotherm for fipronil in six types of Egyptian soil

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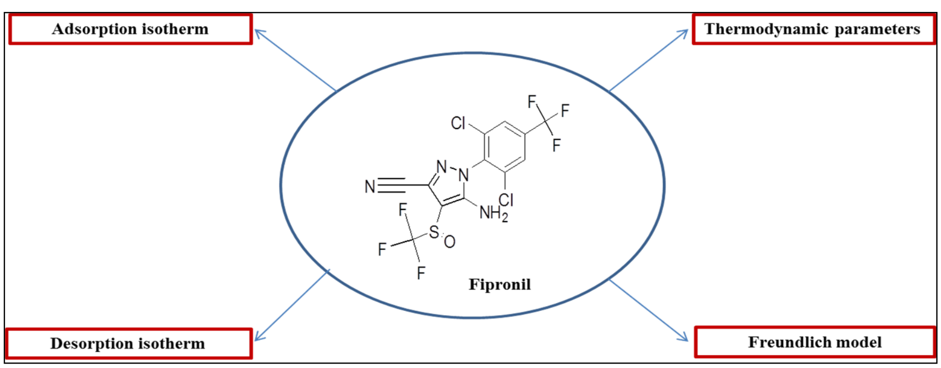
A B S T R A C T

The soil type and temperature are considered important parameters that can influence the rates and equilibria of different environmental processes. Therefore, the adsorption and desorption isotherms of fipronil in clay loam, clay, sandy loam, sandy clay loam, sand and loamy sand soils at 25 and 50˚C was studied. The amount of fipronil adsorbed and desorbed by different soils was significantly influenced by the temperature. Adsorption was higher in clay loam, clay, sandy clay loam and sandy soil at 25°C, while sand soil and loamy sand soil at 50°C. The non-desorbed amount was greater at 25°C in different types of soil except for clay loam soil. The negative ΔG˚ indicated that the adsorption/desorption in different types of soil was spontaneous at different temperatures. The value of standard enthalpy change (ΔH˚) was positive in clay soil, sandy loam soil, sandy clay loam soil and loamy sand soil for adsorption and sandy loam soil, sand soil and loamy sand soil for desorption. Moreover, the standard entropy change (ΔS˚) was negative in soils for adsorption and desorption isotherms except clay loam soil. Adsorption and desorption isotherms trends as well as the values of the correlation coefficients indicated that the adsorption and desorption isotherms of fipronil in tested soils were fitted to the Freundlich model because the correlation coefficient is very close to 0.999.






**Graphical Abstract**

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## 1. Introduction

Fipronil is a soil and foliar broad-spectrum insecticide developed between 1985 and 1987 and manufactured by RhônePoulenc. Fipronil was marketed in 1993 and is active against a wide range of insects such as rice skippers, rice grasshoppers, vine weevil, black ants and termites in agricultural, pastoral zones and forestry as well as in urban environments.[1] In a variety of processes, sorption at the liquid or gaseous phase/solid surface interface is crucial. Sorption refers to adsorption processes that take place at the solid/solution interface, as well as those in which a solute (molecule or ion) penetrates the bulk of a sorbent phase. The forces that act between the sorbent and the sorbate are what cause solute sorption by a solid phase. The three forms of interactions are Van der Waals, Coulomb, and Lewis acid–base interactions, and they cover multiple orders of magnitude.[2] Different adsorption mechanisms can be discovered by evaluating the parameters of the calculated adsorption isotherms and studying the dependence of adsorption on various variables (pH, temperature, solute concentration, type ionic strengths, and surface topology). Furthermore, thermodynamic characteristics of adsorption from solutions provide a wealth of information about the type and mechanism of adsorption.[2] Different parameters, such as soil type, clay content, and organic matter content, influence the adsorption and desorption isotherm in soil. Clay has a bigger active surface area than other soil elements, according to the reported research.[3] The solid state organic fraction is the most important component determining pesticide sorption, with clay mineral content also playing a role. As soil organic matter and clay content rise, pesticides become more adsorbent, probably due to increased adsorption. Sand content had a substantial negative association with adsorption, but clay content had a strong positive correlation with adsorption. Because they govern the quantity of pesticide that may reach the target organism and the amounts that can be volatilized, degraded, or leached, adsorption–desorption processes are critical in determining the fate and distribution of agrochemicals in the soil.[1] The adsorption coefficients of fipronil and its sulphide derivative to soils were shown to be better connected to the soil organic carbon (OC) than to the clay content in studies.[1] A vast number of adsorption literatures have been published, the majority of which have undertaken adsorption isotherm analysis and thermodynamic parameter calculations. The Gibbs free energy change ($\Delta G^o$), enthalpy change ($\Delta H^o$), and entropy change ($\Delta S^o$) of adsorption are the key thermodynamic parameters investigated.[4,5] Because Gibbs free energy, enthalpy, and entropy are state functions, $\Delta G^o$, $\Delta H^o$ and $\Delta S^o$ are dependent on the adsorption system's final and initial states. It was reported that Gibbs free energy, enthalpy, and entropy were dependent on the adsorption system's final and initial states.[4,5] Many works employ the term $\Delta G^o$ to assess the spontaneity of adsorption. However, because most reactions do not match the requirements of the standard state, the utility of $\Delta G^o$ as a basis for judging reaction spontaneity is limited. The $\Delta G^o$ in the first condition is the general practical basis of the assessment.[4, 5] Adsorption kinetics and equilibrium isotherms are commonly used to infer the properties of adsorption behaviour. They're also useful for deciphering the adsorption mechanism and calculating and interpreting thermodynamic parameters theoretically.[5] The results revealed that the adsorption-desorption isotherms of fipronil were well matched to the Freundlich model, and that the physical reaction was the most important factor in the adsorption-desorption process.[6] The present study was performed to investigate the adsorption-desorption isotherms of fipronil in six soil types at two temperatures (25 & 50ºC) of northern Egypt to investigate the possible mechanism of interaction.

## 2. Experimental

### *2.1. Materials and Methods*

#### *2.1.1. Fipronil*

Common name: Fipronil, Trade name: Prince, Chemical class: phenylpyrazole, IUPAC name: (±)-5-amino-1-(2,6-dichloro-a,a,a-trifluoro-p-tolyl)-4-trifluoromethyl-sulfinylpyrazole-3-carbonitrile, Molecular formula: $C_{12}H_4Cl_2F_6N_4OS$, Molecular weight: 437.2, Activity: Systemic insecticide, Activation: Acts as a potent blocker of the GABA-regulated chloride channel, Solubility in water: 1.9 mg/L (20 °C), Kd: 25 (L/g), Vapor pressure: $4 \times 10^{-7}$ mpa (25 °C), Formulation: 5% FL, and Rate of application: 71.9 (g.ai/ha).

#### *2.1.2. Tested soils*

The soil samples were collected from the surface layer (0-20 cm) from different locations. Soils will be air-dried, ground and passed through a 2-mm sieve prior to use. The physical and chemical properties of the soil samples were determined (**Table 1**).

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

| Particle Size (%) | | | Texture class | pH | EC (ds/m) | Total soluble cations (meq/L) | Total soluble anions (meq/L) | Total carbonate (%) |
|---|---|---|---|---|---|---|---|---|
| Clay | Silt | Sand | | | | | | |
| 42 | 18 | 40 | Clay loam | 8.25 | 1.32 | 18.17 | 13.30 | 7.87 |
| 64 | 24 | 12 | Clay | 8.22 | 2.06 | 25.7 | 21.5 | 15.97 |
| 14 | 11 | 75 | Sandy loam | 8.20 | 2.33 | 33.50 | 23.30 | 40.09 |
| 20 | 13 | 67 | Sandy clay loam | 8.15 | 5.03 | 60.30 | 50.30 | 44.64 |
| 10 | 3 | 87 | Sand | 8.51 | 1.18 | 17.42 | 15.51 | 4.01 |
| 13 | 3 | 84 | Loamy Sand | 7.40 | 9.50 | 114.15 | 104.5 | 3.76 |

### 2.1.3. Laboratory experiments

*Adsorption isotherm*

Adsorption isotherms by six soils were quantified using the batch equilibration technique.[7] Experiments were carried out in duplicate with a sorbent mass to fipronil solution ratio of 1:5 for the soil. The Initial fipronil concentrations ranged from 0.5-50 µg $mL^{-1}$ and were prepared in 0.01 M $CaCl_2$. The fipronil solutions were equilibrated with soil in 20 mL polypropylene centrifuge tubes. The tubes were shaken mechanically at 150 rpm at two temperatures (25 & 50ºC) for a time period to achieve equilibrium (24 hours) based on its kinetics study and centrifuged at 4000 rpm for 15 min. The fipronil concentration in supernatants was determined by a spectrophotometer at 208 nm ($\lambda_{max}$). Control samples (no fipronil) 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 the reaction tube was insignificant. The amount of fipronil sorbed, $C_s$, by solid phase after equilibrium was calculated,

$$C_s = (C_i - C_e) \times \frac{V}{M_s} \tag{1}$$

where $C_s$ is the concentration or amount of fipronil sorbed per mass unit of adsorbent (µg $g^{-1}$), $C_i$ is the initial concentration of fipronil (µg $mL^{-1}$), $C_e$ is the equilibrium concentration of fipronil per mass unit of solution (µg $mL^{-1}$), $V$ is the volume of added solution (mL) and $M_s$ is the weight of the adsorbent sample (g).[8]

*Desorption isotherm*

Desorption experiments were conducted immediately after the adsorption experiments for all concentrations using parallel system. Following the sorption experiment using a decant refill technique, 5 mL of fresh 0.01 M $CaCl_2$ background solution was added to each tube for desorption equilibrium step. Tubes were shaken mechanically at 150 rpm to establish a new desorption equilibrium. After centrifugation, the liquid phase containing desorbed fipronil was analyzed. The quantity of desorbed fipronil was corrected for the amount in the solution left with the soil in the centrifuge sediment, taking into account the final concentration of the solution and the weight of retained solution.[9]

## 2.2. Thermodynamic parameters

The tested fipronil adsorption-desorption enthalpy on six soils was determined using the batch experiments as described above. The adsorption process was performed at different temperatures (25 and 50°C). Thermodynamic parameters are calculated from the variation of the thermodynamic equilibrium constant $K_o$ with changes in temperature. $K_o$ can be calculated according to.[4, 10]

$$K_o = \frac{a_s}{a_e} = \frac{v_s}{v_e} \times \frac{C_s}{C_e}, \tag{2}$$

where $a_s$, the activity of the adsorbed solute, $a_e$, activity of the solute in the equilibrium solution, $C_s$, concentration of fipronil on solid phase (mmoles/g of soil), $C_e$, concentration of fipronil in equilibrium suspension (mmol $ml^{-1}$), $v_s$, activity coefficient of the adsorbed solute, $v_e$, activity coefficient of the solute in the equilibrium solution. Values of $K_o$ are obtained by plotting $\ln(C_s/C_e)$ versus $C_s$ and extrapolating to zero $C_s$ as described by.[11]

$$\lim_{Cs \to 0} \frac{C_s}{C_e} = K_o \tag{3}$$

The standard free energy change (ΔG°) for the interaction was calculated from the relationship;[12]

$$\Delta G^o = -RT \ln K_o \tag{4}$$

where R is the universal gas constant (8.314 J $mol^{-1}$ $K^{-1}$), T is temperature in Kelvin. The negative ΔG indicates that the adsorption of fipronil in soil is spontaneous at different temperatures. The standard enthalpy changes (ΔH°) will be calculated from the Van't Hoff isochore equation:

$$ln \left[\frac{K_{oT2}}{K_{oT1}}\right] = \left[\frac{-\Delta H^\circ}{R}\right]\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Negative values of the standard enthalpies changes (ΔH°) indicate that fipronil and soil interactions are exothermic and products are energetically stable with high binding of pesticide to soil sites.

## 2.3. Freundlich model

The empirical formula of the Freundlich equation can be written as;[13]

$$q_e = K_F {C_e}^{1/n} \tag{5}$$

where $K_F$ is a constant indicative of the adsorbent ($mg^{1-(1/n)}$ $L^{-1/n}$ $g^{-1}$) and 1/n is a constant indicative of the intensity of the adsorption. The maximum adsorption capacity ($q_m$ 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 $C = C_o$.

## 3. Results

### *3.1. Adsorption and desorption isotherms of fipronil on soils*

Temperature is an important parameter that can influence the rates and equilibria of different environmental processes. Therefore, the adsorption and desorption isotherms of fipronil in clay loam, clay, sandy loam, sandy clay loam, sand and loamy sand soils at 25 and 50˚C was studied. The amount of fipronil adsorbed and desorbed by different soils was significantly influenced by the temperature (**Fig. 1** and **2**).

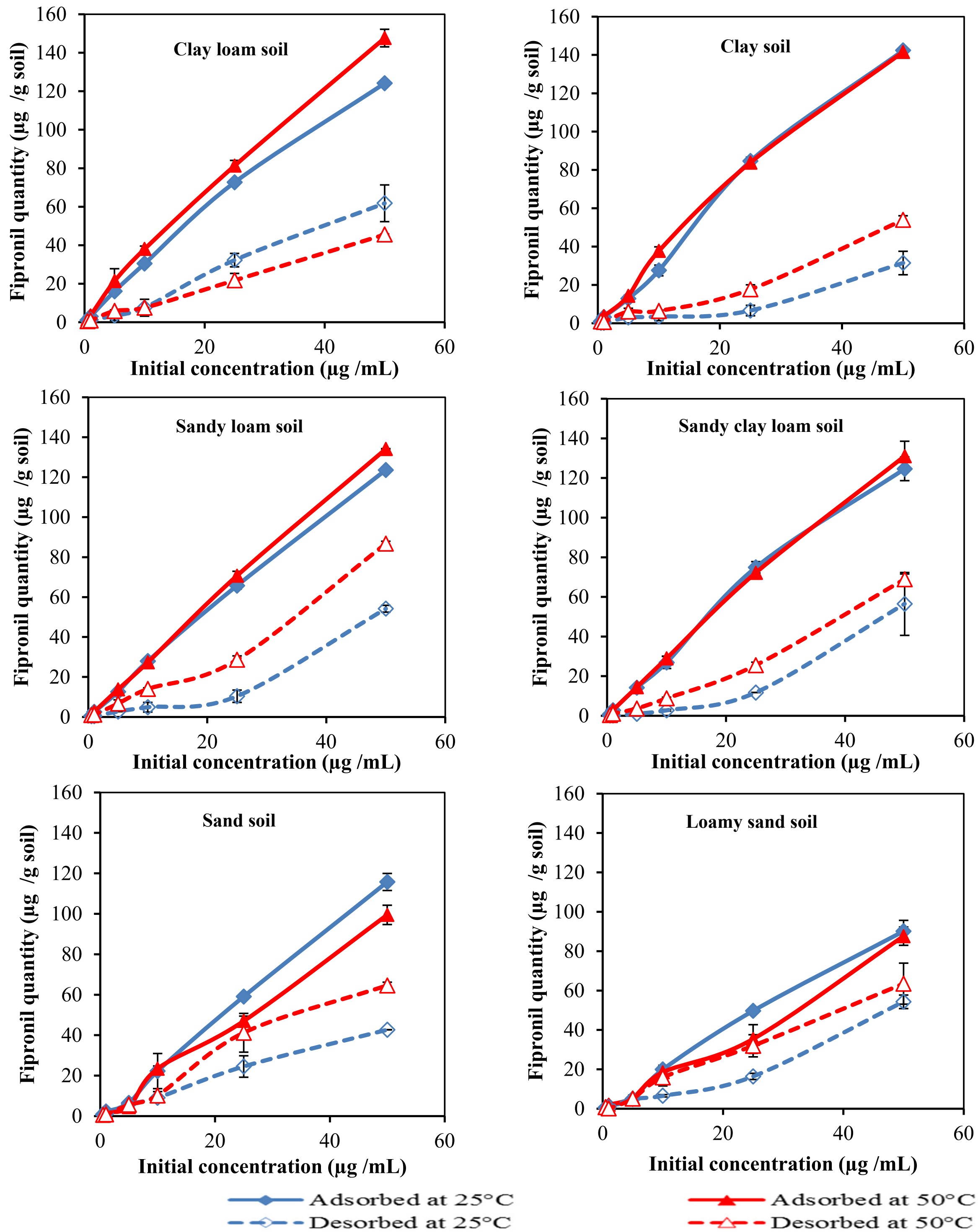



**Fig. 1.** Adsorption and desorption isotherm of fipronil in soils at 25 and 50°C

Under high temperature 50˚C, the average of the adsorbed and desorbed of fipronil by clay loam soil was 48.895 and 17.908 µg g soil$^{-1}$. However, the adsorbed and desorbed amount was reduced to 41.196 and 13.690 µg g soil$^{-1}$ as the temperature was decreased to 25˚C. No significant differences of adsorbed fipronil were detected between 25 and 50˚C in clay soil except at the concentration of 10 µg mL$^{-1}$. The adsorption of fipronil in sandy loam soil statistically increases with temperature while the opposite in desorption. The average of the adsorption was decreased from 41.528 to 38.827 µg g soil$^{-1}$ for fipronil at 50 and 25˚C, respectively. Temperature decrease from 50 to 25˚C was found to reduce the adsorption and desorption of insecticide in sandy clay loam soil. The average of the adsorption and desorption were decreased from 41.680 and 18.065 µg g soil$^{-1}$ to 40.703 and 12.053 µg g soil$^{-1}$ for fipronil, respectively. The mean of adsorption and desorption fate in loamy sand soil were 27.783, 13.861, 24.974 and 19.556 µg g soil$^{-1}$ for fipronil at 25 and 50ºC, respectively. The Kd values of adsorption and desorption isotherms were 6.226, 2.905, 9.034 and 3.194 of clay loam soil, 7.681, 3.129, 8.421 and 3.258 of clay soil, 5.900, 3.810, 6.652 and 3.715 of sandy loam soil, 6.297, 3.678, 6.721 and 3.780 of sandy clay loam soil, 3.996, 3.388, 3.031 and 3.722 in sand soil, 2.857, 3.876, 2.401 and 3.526 in loamy sand soil at 25 and 50 °C, respectively. In general, adsorption was higher in clay loam, clay, sandy clay loam and sandy soil at 25°C, while sand soil and loamy sand soil at 50°C. Adsorption order, clay soil > clay loam soil > sandy clay loam soil > sandy soil > sand soil> loamy sand soil at 25°C; clay loam soil > clay soil > sandy clay loam soil > sandy soil > sand soil > loamy sand soil at 50°C. The non-desorbed amount was greater at 25°C in different types of soil except for clay loam soil.

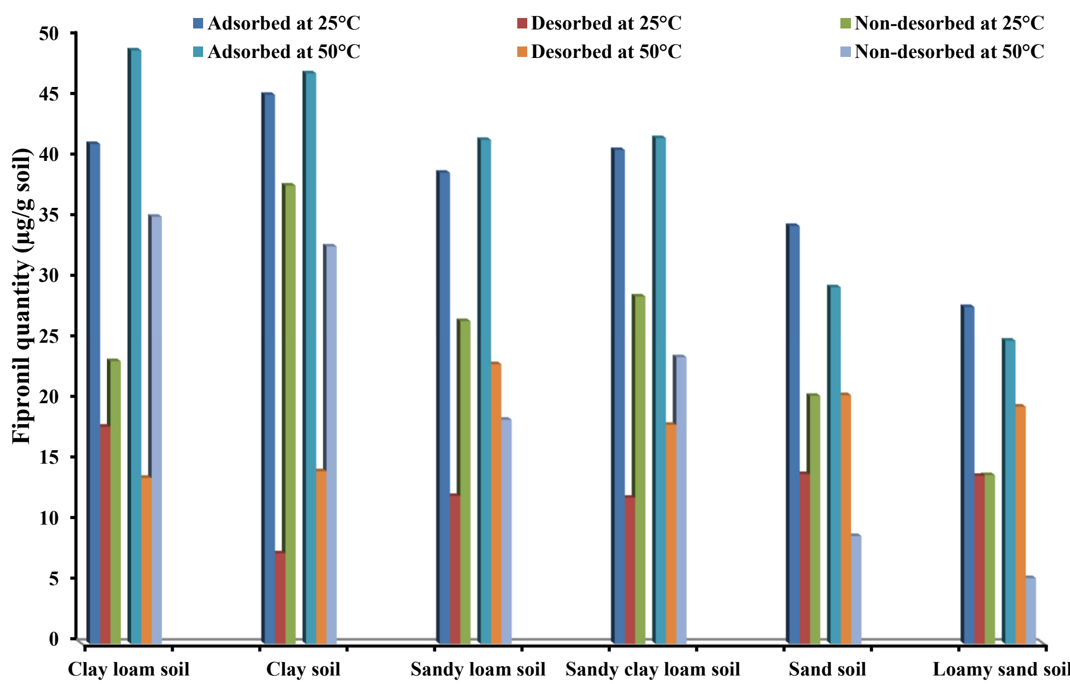



**Fig. 2.** Average of adsorbed, desorbed and non-desorbed tested fipronil (µg/g sorbent) at 25 and 50ºC in Egyptian soils.

*3.2. Thermodynamic parameters of fipronil*

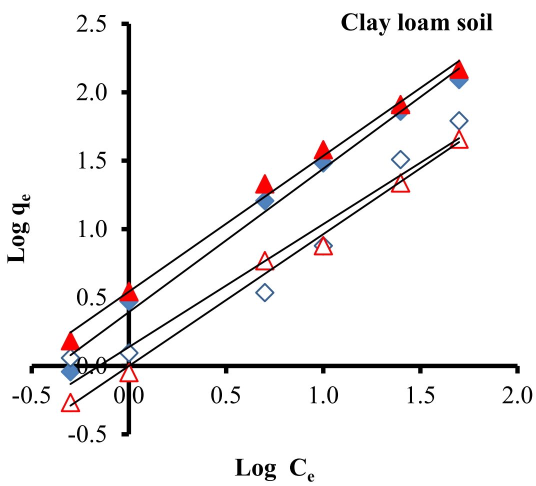
The thermodynamic parameters for adsorption and desorption isotherm of fipronil on different types soil summarized in **Table (2)**. The negative ΔG˚ indicated that the adsorption and desorption of tested insecticide in different types soil was spontaneous at different temperatures. The value of standard enthalpy change (ΔH˚) was positive in clay soil, sandy loam soil, sandy clay loam soil and loamy sand soil for adsorption and sandy loam soil, sand soil and loamy sand soil for desorption, indicating the endothermic nature of the adsorption and desorption process of fipronil. The negative values of the standard enthalpy change (ΔH˚) show that pesticide interaction with soil is exothermic and the products are energetically stable with a high binding of the insecticides to the soil sites. The influence of temperature on the mass transfer of solutes is particularly complete, where solubility of compounds in water, transport to the binding sites via diffusion and chemical sorption reactions are enhanced at higher temperature. Moreover, the standard entropy change (ΔS˚) was negative value in soils for adsorption and desorption isotherms except clay loam soil.

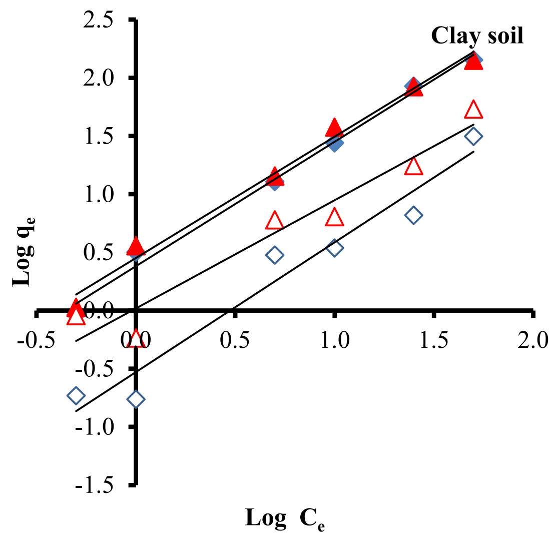
*3.3. Freundlich parameters of fipronil*

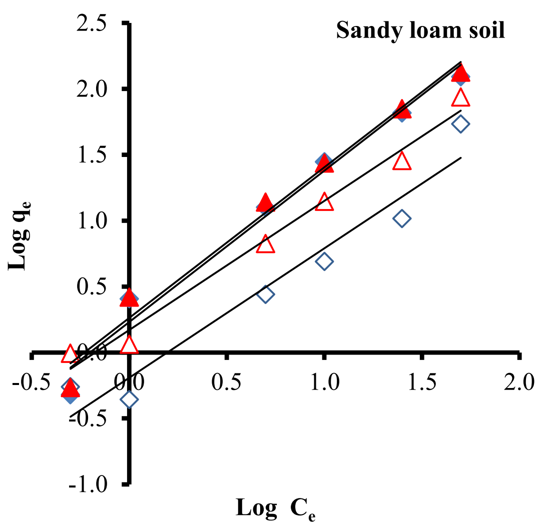
The data from the adsorption and desorption behaviour of fipronil on six soils at different temperatures corresponded will with the Freundlich isotherm (**Fig. 3**). The values of Freundlich adsorption coefficient (KF), the Freundlich adsorption exponent (1/n) and correlation coefficient ($R^2$) for adsorption and desorption of fipronil in clay loam, clay, sandy loam, sandy clay loam, sand and loamy sand soil are presented in **Table (3)**. Adsorption and desorption isotherms trends as well as the values of the correlation coefficients indicated that the adsorption and desorption isotherms of fipronil in tested soils were fitted to the Freundlich equation. The value of $KF_{ads}$ for insecticide is higher at 50˚C in clay loam soil, clay soil, sandy loam soil and loamy sand soil than that at 25˚C. Temperature increase was found to increase the adsorption of tested pesticide in soil through its effect on solubility and vapor pressure. The Kd values were reduced with temperature increases of adsorption and desorption in sand soil. The 1/n values in the case of sorption fipronil were low than unity (1/n < 1.0), are indicative of adsorption by heterogeneous media where high energy sites are occupied first, followed by adsorption at lower energy sites. Whereas the 1/n values were more than unity (> 1.0), indicating relative increased adsorption of insecticide with increasing initial concentration.

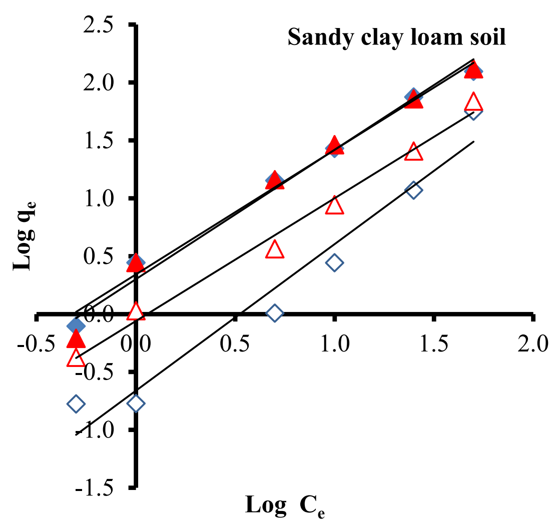
**Table 2.** Thermodynamic parameters for adsorption and desorption isotherm of fipronil in soils

| Thermodynamic parameters | Clay loam soil | | Clay loam soil | | Sandy loam soil | | Sandy clay loam soil | | Sand soil | | Loamy sand soil | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 25°C | 50°C | 25°C | 50°C | 25°C | 50°C | 25°C | 50°C | 25°C | 50°C | 25°C | 50°C |
| | | | | | | Adsorption | | | | | | |
| $K_o$ | 1822.7 | 6409.1 | 1544 | 101.47 | 1522.1 | 1274.5 | 17086 | 5899.4 | 1334.2 | 42404 | 2504.8 | 508.69 |
| ΔG° | -18601.8 | -23539 | -18190.7 | -12406.2 | -18155.7 | -19201.6 | -24146.5 | -23316.5 | -17828.8 | -28613.2 | -19389.4 | -16735.2 |
| ΔH° | -40249.661 | | 87143.644 | | 5683.001 | | 1119.651 | | -110720.532 | | 4712.439 | |
| ΔS° | 72.644 | | -353.471 | | -79.994 | | -84.786 | | -311.717 | | -80.879 | |
| | | | | | | Desorption | | | | | | |
| $K_o$ | 25.418 | 7867.9 | 520.08 | 8958.6 | 631.39 | 69.712 | 724.12 | 842.7 | 11785 | 18.341 | 485.94 | 454.3 |
| ΔG° | -8016.08 | -24089.7 | -15494.7 | -24438.4 | -15975.2 | -11397.9 | -16314.8 | -18090.9 | -23226.2 | -7812.3 | -15326.5 | -16431.5 |
| ΔH° | -183581.516 | | -91113.490 | | 70536.183 | | -3308.060 | | 206960.345 | | 2228.408 | |
| ΔS° | 51.736 | | -308.203 | | -77.042 | | -75.654 | | -254.202 | | -66.401 | |



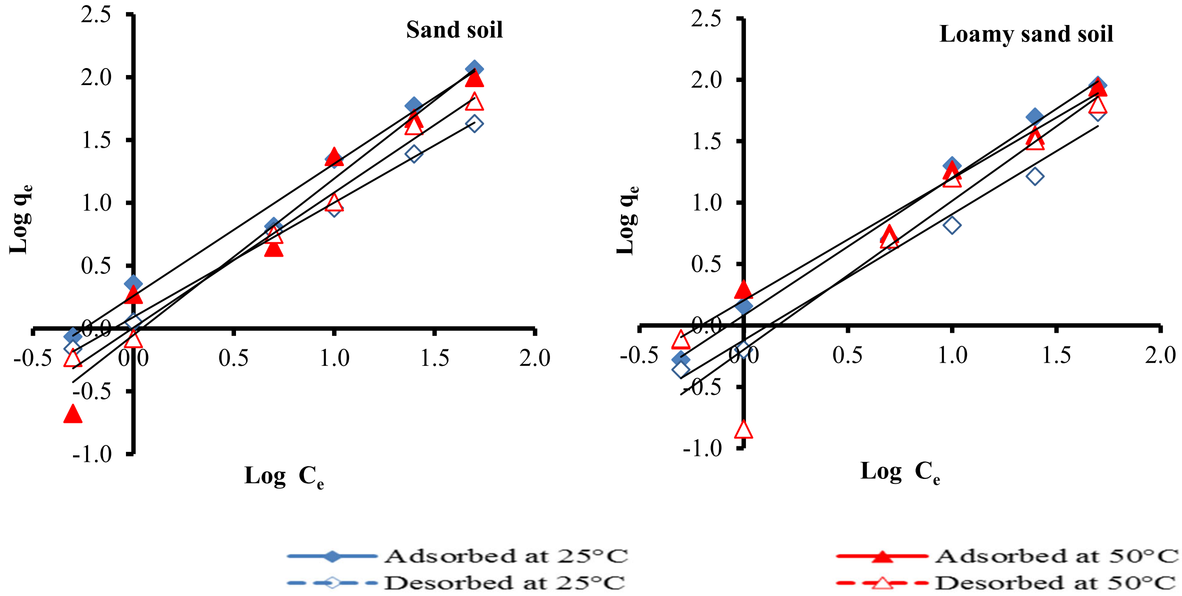



**Fig. 2.** Adsorption and desorption isotherm of fipronil in soils at 25 and 50°C fitted in Freundlich mod

**Table 3.** Freundlich parameters of adsorption and desorption isotherm of fipronil in soils at 25 and 50°C

| Parameters | $K_f$ | | 1/n | | $R^2$ | |
|---|---|---|---|---|---|---|
| | 25°C | 50°C | 25°C | 50°C | 25°C | 50°C |
| **Soil** | | | **Adsorption** | | | |
| **Clay loam** | 2.478 | 3.491 | 1.048 | 0.992 | 0.990 | 0.994 |
| **Clay** | 2.405 | 2.825 | 1.069 | 1.042 | 0.992 | 0.989 |
| **Sandy loam** | 1.704 | 1.830 | 1.148 | 1.143 | 0.978 | 0.982 |
| **Sandy clay loam** | 2.202 | 2.004 | 1.076 | 1.118 | 0.990 | 0.983 |
| **Sand** | 1.816 | 0.887 | 1.052 | 1.245 | 0.987 | 0.953 |
| **Loamy sand** | 1.208 | 1.598 | 1.121 | 0.993 | 0.988 | 0.987 |
| **Soil** | | | **Desorption** | | | |
| **Clay loam** | 1.375 | 0.999 | 0.898 | 0.963 | 0.944 | 0.993 |
| **Clay** | 0.296 | 1.041 | 1.115 | 0.930 | 0.953 | 0.940 |
| **Sandy loam** | 0.644 | 1.482 | 0.982 | 0.980 | 0.941 | 0.985 |
| **Sandy clay loam** | 0.218 | 0.871 | 1.265 | 1.061 | 0.956 | 0.990 |
| **Sand** | 1.231 | 1.014 | 0.912 | 1.076 | 0.997 | 0.991 |
| **Loamy sand** | 0.760 | 0.635 | 1.026 | 1.212 | 0.985 | 0.871 |

## 4. Discussions

Pesticide qualities, soil features, and environmental conditions all have an impact on how pesticides and soil interact. Several physico-chemical reactions take place after the pesticide application. The majority of procedures involve their adhering to soil particles. Molecules are continuously dispersed between the soil solution and the soil particle surfaces during the dynamic process of sorption. Different pesticides adsorb differently in the same type of soil due to different physical and chemical properties.[14] The adsorption-desorption processes of Fipronil have been performed by using batch equilibrium experiments on eight agricultural soils samples from different locations in south of Iraq. The kinetics study for adsorption-desorption processes proved that first order rate law is ogled.[15] There is a general consensus that the magnitude of Kd values usually indicates the affinity of the compound to the adsorbent matrix.[16]

Thermodynamic parameters are calculated from the variation of the thermodynamic equilibrium constant Ko with changes in temperature. The Ko values were calculated according to.[11] The standard free energy changes ($\Delta G^{\circ}$) was calculated depend on.[4, 12] The standard enthalpy changes ($\Delta H^{\circ}$) were calculated from the Van't Hoff isochore equation. Also, the standard entropy changes ($\Delta S^{\circ}$) are obtained according to.[11] Thermodynamic parameters ($\Delta G0$, $\Delta H0$ and $\Delta S0$) were also calculated for adsorption process of Fipronil at 288.15, 298.15, and 308.15 K.[15] A net sorption occurs when the free energy of the sportive exchange is negative.[17] The small negative values of free energy change indicate the adsorption is physical in nature involving weak forces of attraction.[18] A thermodynamic approach was used to study the effect of temperature on the pesticide adsorption processes on different adsorbents. It also suggests a high persistence and resistance to degradation of fipronil. The same comment was reported by *Singh et al.*, who stated that the negative value of $\Delta G^{\circ}$ indicated the pesticides-soil interaction is spontaneous; it is high resistance to degradation in soil.[19] Reported that the Freundlich isotherm equation properly represents the experimental data when the correlation coefficient ($R^2$) is very close to 1.[20] This work confirms the previous data that clarify the importance of scientific research in nature.[21-49]

## 5. Conclusion

Fipronil is a soil and broad-spectrum insecticide and active against a wide range of insects. Different sorption mechanisms can be discovered by evaluating the parameters of the calculated sorption isotherms and studying the dependence of adsorption on various variables (temperature and soil type). Furthermore, thermodynamic characteristics and Freundlich model of adsorption from solutions provide a wealth of information about the type and mechanism of sorption fipronil. Generally, the adsorption is higher in all tested soils at 50ºC except for the sand soil and loamy sand soil. Likewise, desorption was high in all soils 50ºC, except for the clay loam soil. As for the non-desorped amount, it was greater in tested soils at 25ºC except for clay soil. The clay and clay loam soil are high in adsorption, sandy clay loam and sandy loam soil are medium of adsorption, and sand and loamy sand soil are low in adsorption. The negative ΔG° indicated that the adsorption and desorption of fipronil in different types of soil was spontaneous at different temperatures. The Freundlich equation is excellent for describing the experimental results of adsorption and desorption isotherms of fipronil in the tested soils.

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