

Mathematical models of the adsorption-desorption kinetics of fenitrothion in clay soil and sandy clay loam soil

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CHRONICLE

Article history:

Received January 20, 2024

Received in revised form

March 21, 2024

Accepted June 10, 2024

Available online

June 10, 2024

Keywords:

Mathematical models

Sorption

Kinetics

Fenitrothion

Soil

ABSTRACT

Batch adsorption and desorption kinetic experiments of fenitrothion on clay soil and sandy clay loam soil indicated that the equilibration time was approximately 30 hours. The kinetics of adsorption and desorption exhibited two distinct stages: a rapid process in the initial stages followed by a slow process. The pseudo-first-order model followed by the Elovich kinetic model fit the experimental adsorption and desorption data quite well, with high values of R^2 and low values of $\Delta q_e\%$ and SSE. Accordingly, the pseudo-first-order model is most suitable for describing the adsorption and desorption kinetics of fenitrothion on clay soil and sandy clay soil. Pseudo-second-order model type-1 and type-2 models fit the experimental adsorption data; however, these models cannot be used to describe desorption kinetics. Moreover, the modified Freundlich model has limited applicability, and the intraparticle diffusion kinetic model cannot describe the kinetics of the adsorption and desorption of fenitrothion on clay and sandy clay loam soils.

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1. Introduction

In recent decades, many mathematical adsorption and desorption kinetic models have been proposed to describe these data.¹ There are two main types of the models: adsorption reactions and adsorption diffusion. Adsorption diffusion models are based on three methods: diffusion across the liquid film surrounding the particles, diffusion in the liquid contained in the pores or along its walls, called intraparticle diffusion, and adsorption-desorption between the adsorbate and active sites. Adsorption reaction models are based on the whole process of adsorption.² Adsorption can be modeled based on the equations of equilibrium and transport kinetics. However, the adsorption kinetics are always described by an empirical approach using different models.³⁻⁴ Kinetic modeling helps to determine the rate of adsorption. Adsorption might be fast at initial times (up to 10-15 min), which is due to the availability of vacant sites for adsorption. Subsequently, the adsorption slows down gradually until a maximum adsorption capacity is reached. Until that point, the duration of contact time is considered the equilibration time.⁵ Adsorption reaction models include Elovich, pseudo-first-order, pseudo-second-order, and second-order equations. Additionally, adsorption diffusion models, such as the intraparticle diffusion, liquid film diffusion, and double exponential models, were used.

The Elovich equation was proposed by Roginsky and Zeldovich.⁶ This model has been widely used for chemisorption kinetics and is suitable for heterogeneous surfaces.⁷⁻⁸ The Elovich model was used to describe the adsorption kinetics of gases on solid materials. This model assumes that the adsorption rate decreases exponentially as the adsorbed amount increases.⁹

The intraparticle diffusion model was presented by Weber and Morris in 1962.¹⁰⁻¹¹ Many articles have been surveyed.¹²⁻¹⁴ This model can be applied in three forms: (a) q_t (the adsorbed quantity at any time) versus $t^{1/2}$ to obtain a straight line that is forced to pass through the origin;¹³ (b) multi-linearity in the plot of q_t versus $t^{1/2}$ (which is; 2-3 steps involved in the process).¹⁴ In the first step, external surface adsorption occurs. In the second step, gradual adsorption occurs, intraparticle diffusion is controlled, and in the third step, final equilibrium is achieved, where the solute moves slowly from macropores

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to micropores.^{12,14} The literature indicates that the intercepts are positive; because rapid adsorption occurs within a short time period. The curve of this model includes four zones of adsorption according to the values of adsorption factors ranging from 0 to 1: completely, strongly, intermediately, and weakly initial adsorption.

The modified Freundlich kinetic model was originally developed by Kuo and Lotse.¹⁵ It was used to investigate the mechanism of adsorption and rate of potential control of the processes of mass transport and chemical reactions. The modified Freundlich model yielded better R^2 values than did the Freundlich model.¹⁶

The treatment of polluted aqueous effluents containing heavy metals and dyes by various sorbents and biosorbents has been widely studied. More than 50% of the treatment systems that have been reported since 1984 are based on a pseudo-first-order kinetic mechanism.¹⁷ Both pseudo-first-order and pseudo-second-order models are commonly used to describe soil sorption kinetics.¹⁸ The pseudo-second-order equation was introduced in 1999 to describe the adsorption kinetics, and this model has been widely used in liquid-phase systems.¹⁴ Pan and Xing indicated that linearized pseudo-second-order data are more computable than adsorption kinetics data.¹⁸

2. Materials and methods

2.1 Fenitrothion

The O,O-dimethyl-O-(3-methyl-4-nitrophenyl) phosphorothioate (IUPAC) is a phosphorothioate (organophosphate) insecticide that is inexpensive and widely used worldwide. Trade names include fenthion and sumithion. The chemical structure is shown in Fig. 1.

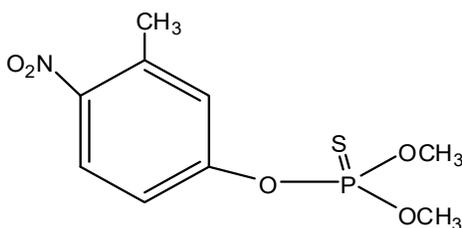


Fig. 1. Chemical structure of fenitrothion.

2.2 Soils

The soil samples were air-dried, ground and passed through a 2-mm sieve prior to use. The soil texture was determined by the hydrometer method.¹⁹⁻²⁰ The soil pH was measured using 0.01 M calcium chloride (CaCl_2) in a 1:2 w/w soil : solution slurry. The organic matter (OM) content was determined by dichromate oxidation according to the Walkley-Black method.²¹⁻²² The physiochemical 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 soils

Properties	Clay soil	Sandy clay loam soil
Particle size distribution (%)		
Clay	43	20
Silt	18	13
Sand	39	67
Water holding capacity (%)	46	38
Soil pH	8.3	8.2
EC (m mhos/cm) at 25°C	1.3	5.1
OM content (%)	3.3	1.6
Total carbonate (%)	7.9	44.7
Soluble cations conc. (meq/L)		
Ca^{++}	3.8	18.7
Mg^{++}	5.0	8.8
Na^+	9.4	22.5
K^+	0.5	0.3
Soluble anions conc. (meq/L)		
CO_3^{--}	1.6	0.8
HCO_3^-	2.6	4.6
Cl^-	8.5	21.0
SO_4^{--}	0.6	23.9

2.3 Adsorption kinetics

A kinetic study was carried out to determine the equilibration time for the sorption of fenitrothion on the tested soils. The batch sorption kinetics experiment was performed in duplicate. A known weight of soil (1g) was placed in a vial with a measured volume of 0.01M CaCl₂ solution containing a known concentration (30 µg/mL) of fenitrothion (1:5/soil : solution). Polypropylene centrifuge tubes (25 mL) containing the soil and the pesticide solution were mechanically shaken at 150 rpm in the dark at room temperature. After time intervals of 1, 2, 3, 6, 12, 24, 30, 36, and 48 h, the tubes were centrifuged at 4000 rpm for 15 min, and the supernatant was measured using a UV-visible spectrophotometer at 266 nm.²³⁻²⁴

2.4 Desorption kinetics

The desorption experiments were conducted immediately after the adsorption experiments for a concentration (of 30 µg/mL) using a parallel system. At the end of the sorption experiment, a decant refill technique was used, and 5 mL of fresh 0.01 M CaCl₂ background solution was added to each tube to measure the desorption equilibrium at various times (1, 2, 3, 6, 12, 24, 30, 36, and 48 h). The tubes were shaken mechanically at 150 rpm in the dark at room temperature. After centrifugation, the liquid phase containing the desorbed pesticide was analyzed by a UV-visible spectrophotometer. The quantity of desorbed pesticide was corrected for the amount in the solution left with the soil in the centrifuge sediment, considering the final concentration of the solution and the weight of the retained solution.²⁵

2.5 Mathematical kinetic models

Elovich equation

The Elovich equation is represented in **Table 2**, where q_t = is the amount of adsorbed or released adsorbate at time t ; β = is a constant related to the extent of surface coverage (mg g⁻¹) and activation energy for chemisorption; and α is a constant related to the chemisorption rate (mg/g h). Thus, a plot of q versus $\ln t$ should have a linear relationship with the slope $\frac{1}{\beta}$ and intercept of $\frac{1}{\beta} \ln(\alpha\beta)$.^{4,26}

Intraparticle diffusion equation

The empirical and linearized forms of the equation are shown in **Table 2**, where q_t = is the amount of pesticide adsorbed or desorbed in time t , and K_d = is the apparent diffusion rate coefficient. Thus, a plot of q_t versus $t^{1/2}$ should provide a linear relationship if the reaction conforms to the parabolic diffusion law.²⁷

Modified Freundlich equation

The modified Freundlich equation is shown in **Table 2**, where q_t = is the adsorbed or desorbed pesticide (mg g⁻¹); C_0 = is the initial pesticide concentration (mg L⁻¹); t = is the reaction time (min); and K_d = is the desorption or sorption rate coefficient (min⁻¹) and $\frac{1}{m}$ = is a constant.^{15-16,28}

Pseudo-first-order rate equation

The nonlinear and linear forms of the pseudo-first-order equation are included in **Table (2)**, where q_t = is the amount of pesticide adsorbed or desorbed in time t ; q_e = is the amount of pesticide adsorbed or desorbed at equilibrium, and K_1 = is the apparent adsorption or desorption rate coefficient.^{1,28}

Pseudo-second-order rate equation

The pseudo-second-order equation is expressed in **Table 2**, where K_2 is the rate constant of second-order adsorption (g/mg min). For the boundary conditions $t = 0$ to $t = t$ and $q = 0$ to $q = q$, and rearranging, the linearized form can be obtained. If pseudo-second-order kinetics are applied, the plot of $\frac{t}{q}$ against t should have a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot.²⁹

Table 2. Adsorption and desorption kinetic models and their linear forms.

Models	Empirical formula	Linear form	Plot
Elovich	$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t)$	$q_t = \left(\frac{1}{\beta}\right) \ln(\alpha\beta) + \left(\frac{1}{\beta}\right) \ln t$	q_t vs. $\ln t$
Intraparticle diffusion	$q_t = K_d t^{1/2}$	$q_t = C_{id} + K_{id} t^{1/2}$	q_t vs. $t^{1/2}$
Modified Freundlich	$q_t = K_d C_0 t^{1/m}$	$\ln q_t = \ln(K_{mf} C_0) + \frac{1}{m} \ln t$	$\ln q_t$ vs. $\ln t$
Pseudo-first order	$q_t = q_e(1 - e^{-k_1 t})$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$\ln(q_e - q_t)$ vs. t
Pseudo-second order Type-1		$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}$ vs. t
Type-2	$\frac{dq}{dt} = K_2 (q_e - q_t)^2$	$\frac{1}{q_t} = \frac{1}{q_e} + \left(\frac{1}{k_2 q_e^2}\right) \frac{1}{t}$	$\frac{1}{q_t}$ vs. $\frac{1}{t}$

3. Results and discussion

3.1 Adsorption and desorption kinetics

Adsorption kinetics are studied by measuring the adsorption with respect to time at a constant concentration, which indicates the rate of solute adsorption. Thus, the equilibrium time is obtained from monitoring the kinetics. The adsorption and desorption of fenitrothion on clay and sandy clay loam soil versus time at a concentration of 30 $\mu\text{g/mL}$ at room temperature are illustrated in **Fig. (2)**. The kinetics of adsorption and its corresponding desorption exhibited two distinct stages: a rapid process in the initial stages followed by a slow process. The rapid stage could be due to the rapid filling of the surface vacant sites in the soil particles, followed by a slow migration and then diffusion of the compound into the soil OM matrix and soil mineral structure.³⁰⁻³¹ The data showed that the kinetic curves of fenitrothion the two soils tested were almost identical, particularly for adsorption. The adsorption of fenitrothion onto clay soil and sandy clay loam soil increased during the first 6 h. The sorption rate then slightly increased at 12 h and reached a plateau after up to 48 h of shaking. Thus, 30 hours was used as the equilibrium time for the subsequent adsorption-desorption experiments in this study. A similar result was achieved by Sundaram *et al.*³² They found that the adsorption equilibration time of fenitrothion in both soil types (organic soil and a silty clay loam soil) was within 30 hours. In general, the rate at which adsorption occurs is the most important factor in the adsorption process.³³⁻³⁴ Moreover, fenitrothion had a stronger affinity for clay soil than for sandy clay loam soil, which may be due to the higher clay content and OM in clay soil than in sandy clay loam soil. The adsorption of pesticides is reportedly enhanced with high soil clay and soil OM contents.³⁵ In general, the adsorption of pesticides was observed to be positively correlated with the soil clay and OM contents.³⁶ The adsorption kinetics of pesticides on soil are affected by soil properties such as carbonate content and OM content.³⁷

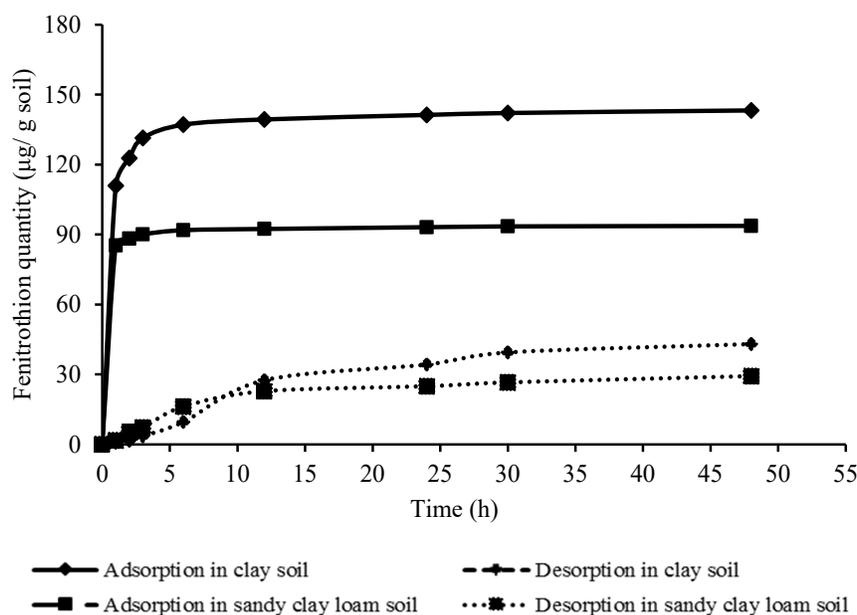


Fig. 2. Adsorption and desorption kinetics of fenitrothion in clay and sandy clay loam soils.

3.2 Modeling of adsorption and desorption kinetics

Elovich model

Elovich equation plots of the adsorption and desorption kinetics of fenitrothion in soil showing that linear relationships exist between “qt” and “ln t” for each soil type; are shown in **Fig. 3** and **Fig. 4**. The Elovich equation parameters, α and β , were calculated from the slope and intercept of the linear plots and are reported in **Table 3**. The amount of fenitrothion adsorbed and desorbed in clay soil is greater than that in sandy clay loam soil. According to Teng and Hsieh,³⁸ α represents the chemisorption rate at zero coverage, and β is based on the extent of surface coverage and chemisorption activation energy. When comparing the parameters α ($\mu\text{g/g h}$) and β ($\mu\text{g/g}$) for the two soils, it was observed that the α and β values for adsorption were greater (4.720×10^7 and 1.180×10^{19}) for α and (0.133 and 0.497) for β than those for desorption (7.749 and 8.721) for α and (0.081 and 0.132) for β in the clay soil and sandy clay loam soil, respectively. In addition, the Elovich parameters α and β of fenitrothion were greater in the sandy clay loam soil than in the clay soil. The values of α in the Elovich equation; are considered to be inversely proportional to the ambient rate of desorption.³⁹

To compare the fitness of the models, the correlation coefficient (R^2), Δqe (%) and summed squared error (SSE) were calculated and are listed in **Table 3**. The Elovich equation better fit the experimental desorption data than the adsorption

data for the two soils, as indicated by the higher determination coefficients ($R^2 = 0.946$ and 0.977) than ($R^2 = 0.854$ and 0.893) for the clay soil and sandy clay loam soil, respectively.

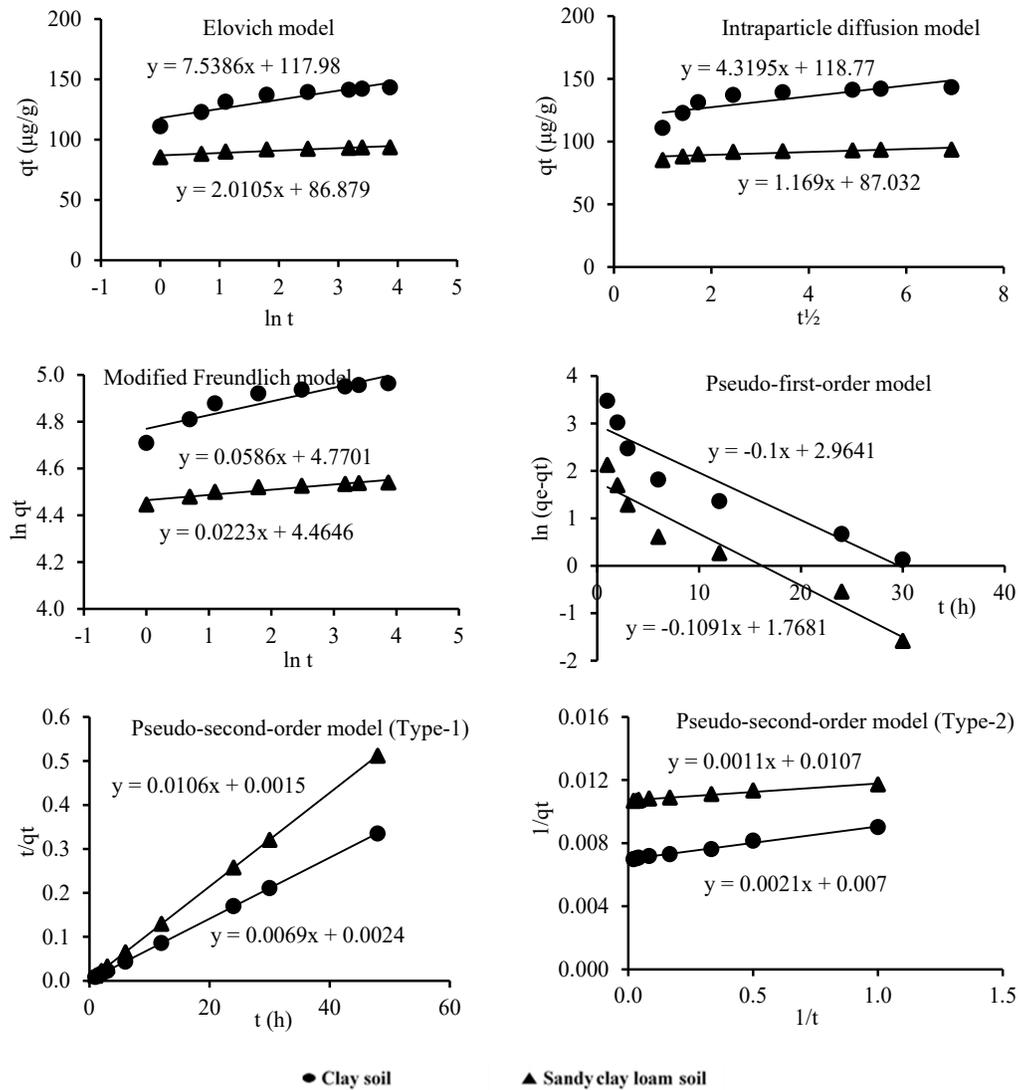
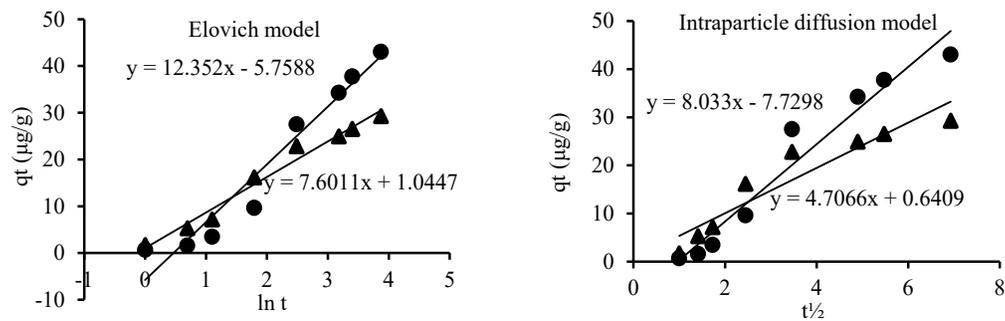


Fig. 3. Model plots of fenitrothion adsorption kinetics in soils.



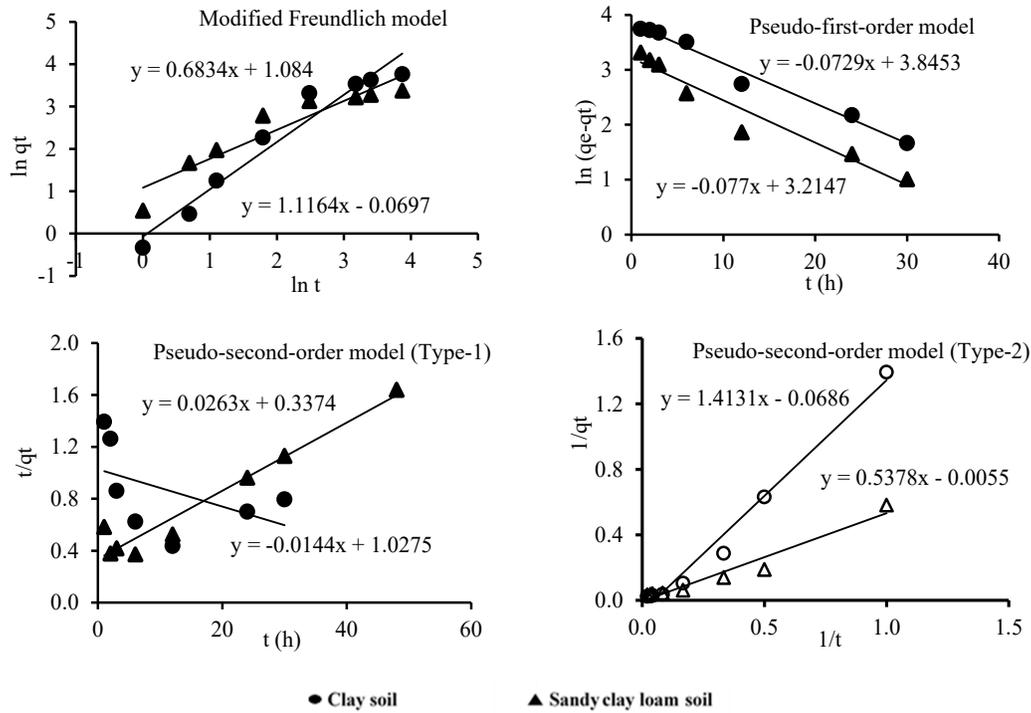


Fig. 4. Model plots of fenitrothion desorption kinetics in soils.

Table 3. Kinetic parameters for the adsorption and desorption of fenitrothion in soils.

Models	Parameters	Adsorption		Desorption	
		Clay soil	Sandy clay loam soil	Clay soil	Sandy clay loam soil
Elovich	α ($\mu\text{g g}^{-1} \text{h}^{-1}$)	4.721×10^7	1.176×10^{19}	7.749	8.721
	β ($\mu\text{g g}^{-1}$)	0.133	0.497	0.081	0.132
	R^2	0.854	0.893	0.946	0.977
	Δq_e (%)	3.483	1.088	66.230	16.311
	SSE	1.056	0.074	11.359	1.449
Intraparticle diffusion	K_{id}	4.320	1.169	8.033	4.707
	C_{id}	118.770	87.032	-7.730	0.641
	R^2	0.667	0.718	0.952	0.891
	Δq_e (%)	5.372	1.777	62.706	82.837
	SSE	2.456	0.196	8.345	11.897
Modified Freundlich	K_{mf}	2.359	1.738	0.019	0.059
	$1/m$	0.059	0.022	1.116	0.683
	R^2	0.832	0.886	0.951	0.887
	Δq_e (%)	3.688	1.121	35.396	37.311
	SSE	1.200	0.079	24.444	11.125
Pseudo-first-order	K_i (h^{-1})	0.100	0.109	0.073	0.080
	q_e ($\mu\text{g g}^{-1}$)	19.377	5.860	46.773	24.799
	R^2	0.891	0.936	0.983	0.945
	Δq_e (%)	5.455	1.538	37.981	27.491
	SSE	2.369	0.143	3.462	3.207
Pseudo-second-order (Type 1)	K_2 ($\text{g } \mu\text{g}^{-1} \text{h}^{-1}$)	0.020	0.075	0.350×10^{-5}	0.002
	q_e ($\mu\text{g g}^{-1}$)	144.928	94.340	-555.556	38.023
	R^2	1.000	1.000	0.008	0.944
	Δq_e (%)	1.429	1.284	36.381	25.710
	SSE	0.171	0.100	15.179	2.529
Pseudo-second-order (Type 2)	K_2 ($\text{g } \mu\text{g}^{-1} \text{h}^{-1}$)	0.023	0.104	0.003	0.0001
	q_e ($\mu\text{g g}^{-1}$)	142.857	93.458	-14.577	-181.818
	R^2	0.993	0.980	0.983	0.952
	Δq_e (%)	0.873	0.470	27.156	22.971
	SSE	0.069	0.014	3.539	2.151

The kinetic curves of the q_e experimental data and q_e calculated from the Elovich equation for fenitrothion in clay and sandy clay loam soil are shown in Fig. 5 and Fig. 6. The curves indicate the compliance between the experimental and

calculated data. In general, the Elovich model was used to describe five organophosphorus pesticides (malathion, monocrotophos, methyl parathion, phosphamidon and dimethoate).⁷

Intraparticle diffusion model

The linearized plots of q_t versus $t^{1/2}$ according to the intraparticle diffusion model for the adsorption and desorption of fenitrothion on two kinds of soil are shown in **Fig. 3** and **Fig. 4**. The model parameter values of K_{id} and C_{id} ; and the statistical parameters R^2 , Δq_e (%) and SSE are presented in **Table 3**. The slope (K_{id}) for the desorption of fenitrothion in the two soils was greater than that for the adsorption. In addition, the K_{id} values for the adsorption and desorption of the tested compounds were greater in the sandy clay loam soil than in the clay soil, revealing that the desorption rates of fenitrothion were faster than the adsorption rates in the two soils and that the rates of adsorption and desorption were faster in the sandy clay loam soil than in the clay soil. Larger K_{id} values indicate better adsorption, which is related to improved bonding between the sorbate substance and sorbent particles.⁴⁰ Regarding the intercept values, the C_{id} values for desorption of fenitrothion in clay soil and sandy clay loam soil are smaller than those for adsorption, meaning that the initial amount of adsorption was greater than that of desorption. The straight lines did not pass through the origin but had a significant intercept, which is due to the wide distribution of pore sizes in the tested soil.

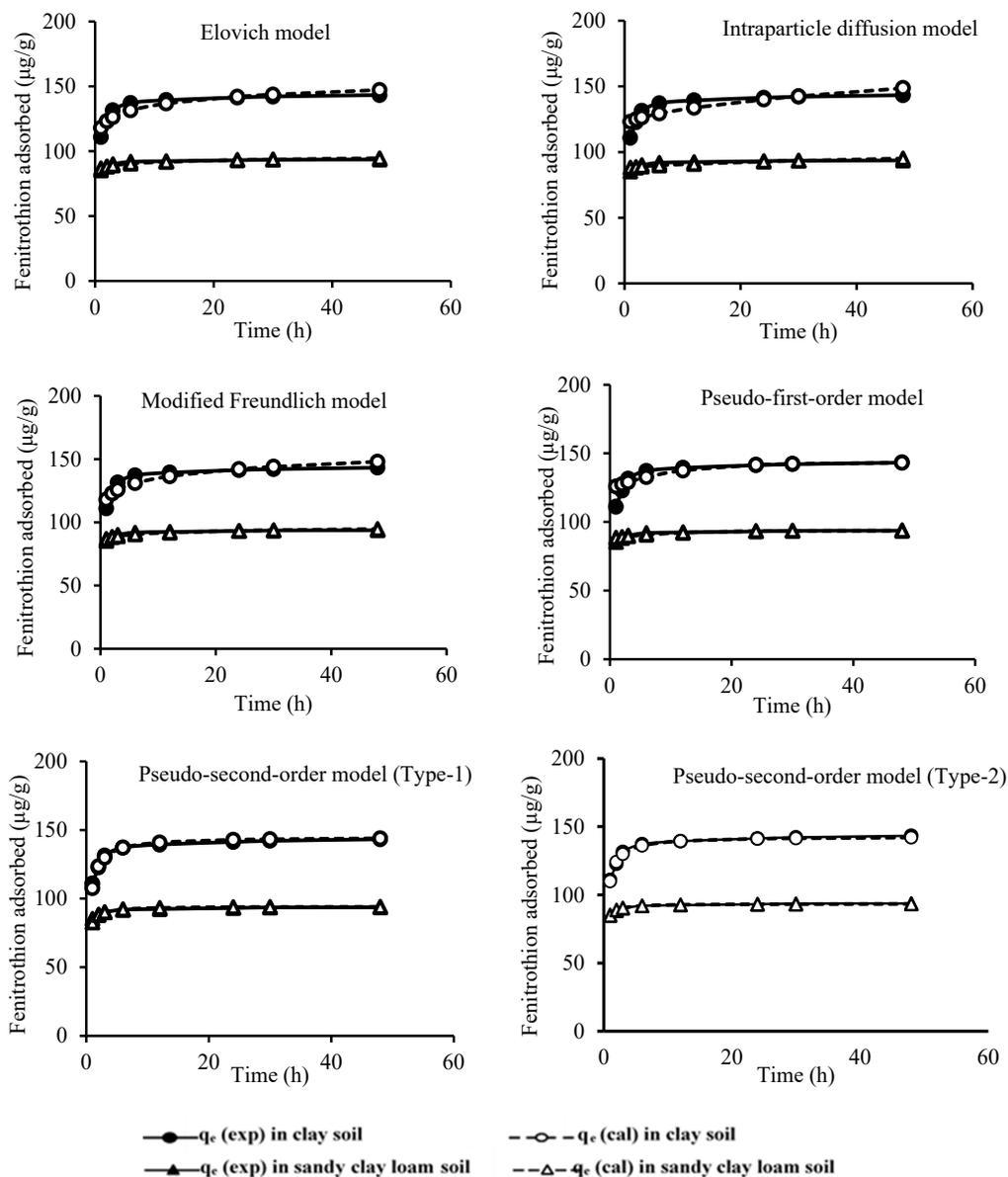


Fig. 5. Kinetic curves of experimental and calculated data from models for the adsorption of fenitrothion in soils.

Thus, a straight line is forced to pass through the origin.¹³ Additionally, when comparing the results of adsorption and desorption obtained from laboratory experiments of fenitrothion (Fig. 5 and Fig. 6) with the results calculated from the intraparticle diffusion equation in the two soils, they found almost identical results in the case of adsorption, while the curves were mismatched in the case of desorption. The intraparticle diffusion model has been used to describe the substance adsorption on a porous adsorbent.⁴¹ In general, the adsorption process controlled by the intraparticle diffusion model is due to the preferential sorption of sorbate in the micropores.⁴² Most likely, sorbate transport through the particle-sample interphase on the pores of the adsorbent particles, as well as adsorption on the available surface of the sorbent, is responsible for the adsorption process.

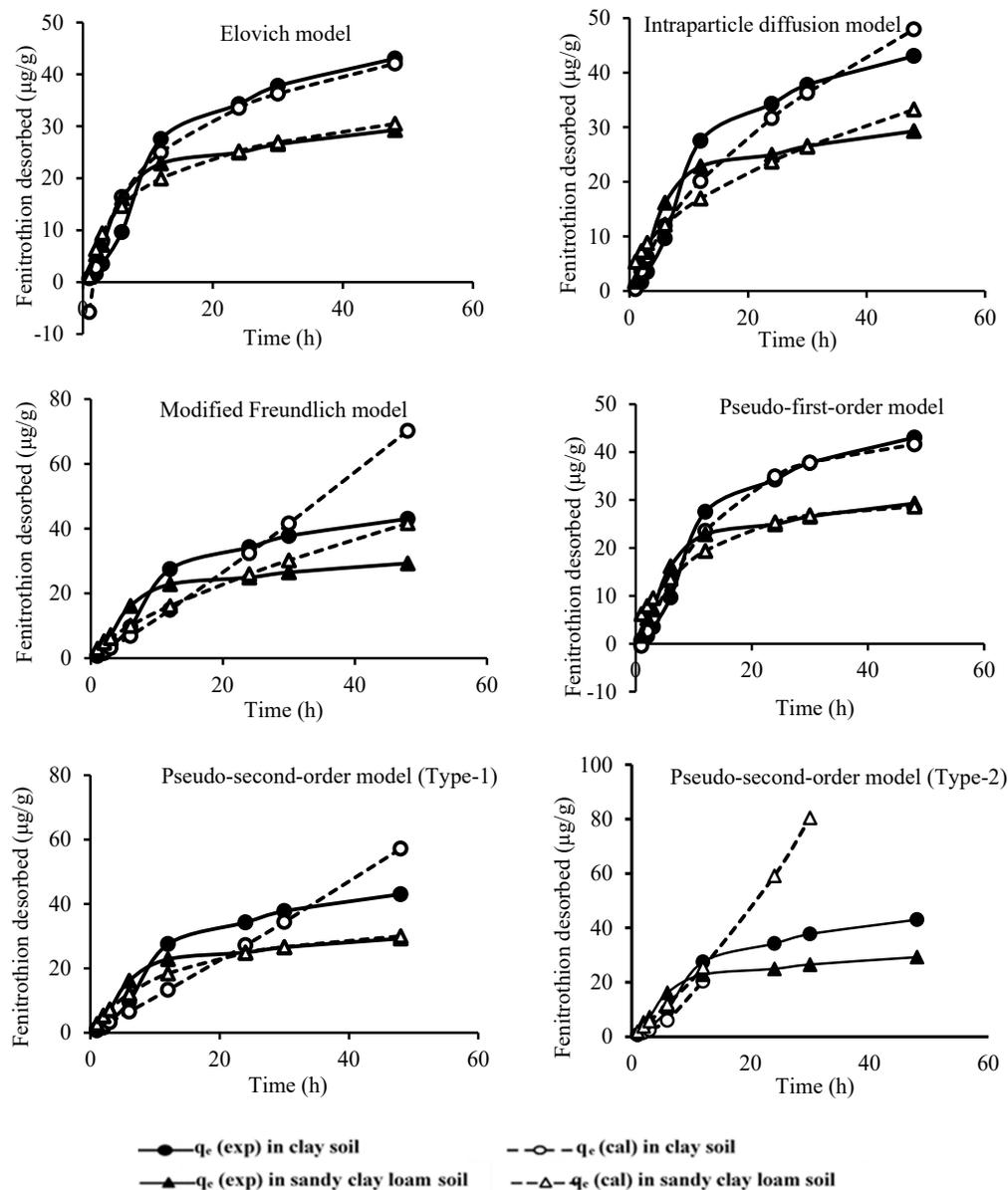


Fig. 6. Kinetic curves of experimental and calculated data from models for the desorption of fenitrothion in soil.

Modified Freundlich model

Modified Freundlich plots of $\ln q_t$ (amount of pesticide adsorbed or released mg g^{-1}) versus $\ln t$ (time of reaction) for the soil types are shown in Fig. 3 and Fig. 4. The modified Freundlich equation parameters K_{mf} (the initial adsorption rate ($\text{L g}^{-1} \text{min}^{-1}$)) and $1/m$ (the Kuo-Lotse constant) were calculated from the intercept and the slope of the linear plots, respectively. The parameter values for the adsorption and desorption of fenitrothion are shown in Table 3. In general, the adsorption rate coefficient " K_{mf} " values of the two soils were greater than the desorption rate coefficient values in both the clay and sandy clay loam soils. The K_{mf} values in clay soil were the highest for adsorption, whereas; they were the lowest for desorption compared to those in sandy clay loam soil. The constant ($1/m$) values were lower for adsorption (0.059 and

0.022) than for desorption (1.116 and 0.683) in the two soil types of clay and sandy clay loam soil, respectively. The $1/m$ values were greater in the clay soil than in the sandy clay loam soil for adsorption and desorption. Adsorption kinetic parameters are helpful for predicting, the adsorption rate and provide valuable information for modeling and designing related processes.²⁷ The correlation coefficients (R^2) were 0.832 and 0.886 for adsorption; and 0.951 and 0.887 for desorption on clay soil and sandy clay loam soil, respectively. In addition, the values of the normalized standard deviation (Δq_e %) and SSE presented in **Table 3** were lower for adsorption than for desorption of fenitrothion in the two soil types. Furthermore, the excellent agreement between the experimental data and calculated data for fenitrothion adsorption is illustrated in **Figs. 5** and **Fig. 6**. Therefore, the modified Freundlich equation appeared to be successful in describing the sorption kinetics of fenitrothion from the two studied soils. The modified Freundlich equation was used by several researchers to describe heavy metal sorption and the sorption of organic compounds.^{16,43}

Pseudo-first-order rate model

A linear form of the pseudo-first-order equation applied for the adsorption and desorption of fenitrothion is shown in **Fig. 3** and **Fig. 4**. The results show that with adsorption time, the values of $\ln(q_e - q_t)$ are very different, and these values are nonlinear. As noted by the results, the values of $\ln(q_e - q_t)$ are equal to zero at approximately 15 hours in the case of sandy clay loam soil. It was important to observe that the distribution of the points corresponding to the relationship between $\ln(q_e - q_t)$ against t , around the trendline, was better for desorption than for adsorption. The values of the adsorption and desorption rate parameters; K_1 (h^{-1}) and q_e calculated from the pseudo-first-order model ($\mu g\ g^{-1}$) and the statistical parameters; R^2 , Δq_e (%) and SSE are listed in **Table 3**. The " K_1 " values for adsorption and desorption were 0.100, and 0.109 and 0.073, and 0.077 min^{-1} in clay soil and sandy clay loam soil, respectively. The pseudo-first-order rate equation fit relatively well with the experimental data for fenitrothion ($R^2 \geq 0.9$), particularly for adsorption kinetics, because the values of Δq_e (%) and SSE were lower (1.538-5.455 and 0.143-2.369, respectively) for adsorption kinetics. The fitness of the pseudo-first-order rate equation for the adsorption of fenitrothion was also confirmed by the agreement of the predicted kinetic data from the model with the experimental kinetic data in the two tested soils (**Fig. 5** and **Fig. 6**). According to Daneshvar *et al.*, the linear fit is better when the SSE is low. In general, the pseudo-first-order kinetic model is widely used for describing soil adsorption kinetics.^{18,44}

Pseudo-second-order model

The t/q_t values increased gradually for the adsorption of fenitrothion, and these values continued to increase as the contact time increased to 48 h. This pattern can be related to the number and availability of adsorption sites in the studied soils over time. According to **Fig. 3** and **Fig. 4**, each kinetic curve has almost constant slope values and very low intercept values. Additionally, a similar trend was obtained from the kinetic curves for the desorption of fenitrothion in sandy clay loam soil. The adsorption and desorption kinetic parameters of fenitrothion, determined from the linear form of the pseudo-second-order equation, are presented in **Table 3**. The values of K_2 ($g\ \mu g^{-1}\ h^{-1}$) for adsorption and desorption were 0.020 and 0.350×10^{-5} in the clay soil and 0.075 and 0.002 in the sandy clay loam soil, respectively. The calculated q_e values ($\mu g\ g^{-1}$) were the highest for fenitrothion adsorption in clay soil (144.928) and sandy clay loam soil (94.340). The results for the adsorption of fenitrothion with low Δq_e and SSE values as well as $R^2 = 1$ of the pseudo-second order kinetic model (type-1) indicate the validity of this model for predicting the pesticide kinetic process under the experimental conditions for the adsorption of fenitrothion in the two studied soils. As shown in **Table 3**, a very low value of R^2 (0.233) for the desorption of fenitrothion was recorded in the clay soil. Thus, the pseudo-second-order model cannot describe the kinetics of desorption of fenitrothion from clay soil. This observation was supported by the relatively identical plots of the experimental adsorption data with the predicted data of fenitrothion in clay soil and sandy clay loam soil (**Fig. 5** and **Fig. 6**).

To confirm that the pseudo-second-order model is valid for describing the adsorption but invalid for describing the desorption of fenitrothion, another expression (type-2) of the pseudo-second-order model was tested. The linear form (type-2) of the model is applied between $1/q_t$ against $1/t$, the intercept is $1/q_e$ and the slope is $1/K_2 q_e^2$. The trendlines for the adsorption kinetics of fenitrothion in clay soil and sandy clay loam soil were almost parallel, whereas, the trendlines for fenitrothion desorption in the two soil types; increased gradually with $1/t$. The adsorption and desorption kinetic parameters of fenitrothion, determined from the linear type-2 form of the pseudo-second-order equation, are presented in **Table (3)**. The values of K_2 ($g\ \mu g^{-1}\ h^{-1}$) for adsorption were 0.023 and 0.104, and those for desorption were 0.003 and 0.0001 in clay soil and sandy clay loam soil, respectively. The calculated q_e values ($\mu g\ g^{-1}$) were 142.857 and -14.577 in the clay soil and 93.458 and -18.818 in the sandy clay loam soil for the adsorption and desorption processes, respectively. **Table (3)** indicates that the R^2 values were >0.9 and that the values of Δq_e and SSE were low for the adsorption and desorption of fenitrothion in clay soil and sandy clay loam soil. In addition, identical patterns were obtained by plotting the experimental and calculated adsorption quantities of fenitrothion (**Fig. 5** and **Fig. 6**). However, the values of the calculated desorbed quantity of fenitrothion deviated with time; thus, their forward lines did not appear. The linearized pseudo-second order method has high adaptability to adsorption kinetic data.¹⁸ Consequently, the kinetic evaluation illustrated that the pseudo-second-order equation was a good fit for the adsorption of various pesticides on soil or other adsorbents, such as fenitrothion and trifluralin.

3.3 Comparison of the tested kinetic models

The adsorption and desorption kinetic data of fenitrothion in clay soil and sandy clay loam soil were presented in the form of different kinetic models. The correlation coefficient (R^2), a normalized standard deviation (Δq_e %), comparing the

experimental and calculated adsorption and desorption data and SSE were used to gauge the goodness of validity. The model that produced relatively high R^2 and low values of $\Delta q_e\%$ and SSE, as well as the agreement of the trends of the experimental and calculated model data, is the best fit model for describing the experimental data.⁴⁴⁻⁴⁶ As the efficiency of adsorption and desorption is dominated by their kinetics, kinetic models such as Elovich, intraparticle diffusion, modified Freundlich, pseudo-first-order and pseudo-second-order models are widely used for the analysis of mechanisms and reaction processes. These five kinetic models are commonly used, assuming that at equilibrium time, the maximum adsorption capacity occurs where adsorbate molecules cover the sorption surface.²⁷ Concerning the adsorption kinetic modeling of fenitrothion (**Table 3**) in clay soil and sandy clay loam soil, the results indicated that the highest R^2 values were obtained for pseudo-second-order type-1 and type-2 followed by the pseudo-first-order model. The value of R^2 is closest to 1 for the pseudo-second-order model, indicating that this model (pseudo-second-order) is most suitable for describing the adsorption kinetics of fenitrothion on clay soil and sandy clay soil. In general, the R^2 values varied in the order pseudo-second-order type-1 > pseudo-second-order type-2 > pseudo-first-order > Elovich > modified Freundlich > intraparticle diffusion model. Additionally, low values of $\Delta q_e\%$ and SSE were obtained from all the tested models. Acceptable R^2 , $\Delta q_e\%$ and SSE values were noted for the adsorption of fenitrothion, but some differences between the experimental and theoretical data were detected, as summarized in **Table 4** for the tested soils. A comparison between the experimental and theoretical adsorbed quantity patterns is shown in **Fig. 7**. However, pseudo-second-order equation shows acceptable result fitting. Thus, the pseudo-second-order equation may be applicable for the sorption of fenitrothion on clay soil and sandy clay loam soil.

Table 4. Comparison of the experimental and calculated adsorption quantities of fenitrothion by different models in soils.

Time (h)	q_e (exp)	q_e (cal)					
		Elovich	Intraparticle diffusion	Modified Freundlich	Pseudo-first-order	Pseudo-second-order	
Clay soil							
1	110.941	117.980	123.090	117.931	125.737	107.527	109.890
2	122.782	123.205	124.879	122.820	127.405	123.457	124.224
3	131.410	126.262	126.252	125.773	128.915	129.870	129.870
6	137.119	131.487	129.351	130.987	132.636	136.986	136.054
12	139.368	136.713	133.733	136.417	137.434	140.845	139.373
24	141.317	141.938	139.931	142.072	141.512	142.857	141.093
30	142.129	143.620	142.429	143.942	142.305	143.266	141.443
48	143.270	147.163	148.696	147.962	143.111	143.885	141.970
Sandy clay loam soil							
1	85.313	86.879	88.201	86.886	88.455	82.645	84.746
2	88.241	88.273	88.685	88.240	88.998	88.106	88.889
3	90.079	89.088	89.057	89.041	89.485	90.090	90.361
6	91.865	90.481	89.895	90.428	90.664	92.166	91.884
12	92.405	91.875	91.082	91.837	92.127	93.240	92.664
24	93.127	93.268	92.759	93.267	93.282	93.787	93.059
30	93.504	93.717	93.435	93.733	93.487	93.897	93.139
48	93.709	94.662	95.131	94.720	93.678	94.062	93.258

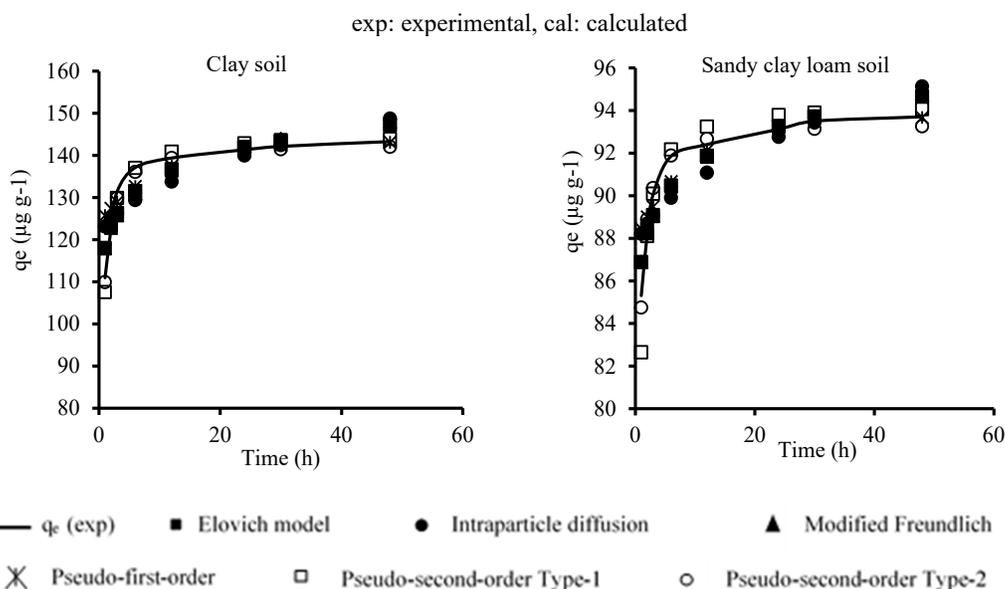


Fig. 7. Comparison of the experimental and calculated adsorption quantities of fenitrothion by different models in soils.

According to the desorption kinetic modeling of fenitrothion on clay soil, the correlation coefficient R^2 was closest to 1, and relatively low values of $\Delta q_e\%$ and SSE were obtained for all the tested kinetic models except for the pseudo-second-order model type-1, which produced $R^2 < 0.008$ (Table 3). For the desorption of fenitrothion in sandy clay loam soil, high values of R^2 and low values of $\Delta q_e\%$ and SSE were obtained from all the tested kinetic models, particularly the pseudo-first-order model, pseudo-second-order model type-1 and type-2 and Elovich model. The relationships between the experimental and theoretical desorption of fenitrothion in clay and sandy clay loam soil quantities are presented in Table 5 and Fig. 8, which show a decrease in the calculated desorption of fenitrothion over a long period of time

Table 5. Comparison of the experimental and calculated desorption quantities by different models for fenitrothion in soils.

Time (h)	q_e (exp)	q_e (cal)					Pseudo-second-order	
		Elovich	Intraparticle diffusion	Modified Freundlich	Pseudo-first-order	Type 1	Type 2	
Clay soil								
1	0.718	-5.759	0.303	0.933	-0.451	1.082	0.744	
2	1.584	2.803	3.631	2.022	2.606	2.168	1.568	
3	3.486	7.811	6.184	3.180	5.448	3.258	2.485	
6	9.633	16.373	11.947	6.894	12.831	6.555	5.991	
12	27.522	24.935	20.097	14.946	23.531	13.267	20.342	
24	34.256	33.497	31.624	32.404	34.902	27.183	-102.9*	
30	37.745	36.253	36.269	41.571	37.783	34.400	-46.5*	
48	43.033	42.058	47.924	70.253	41.619	57.163	-25.5*	
Sandy clay loam soil								
1	1.718	1.045	5.348	2.956	6.370	2.750	1.879	
2	5.294	6.313	7.297	4.748	8.124	5.128	3.797	
3	7.175	9.395	8.793	6.264	9.744	7.206	5.755	
6	16.169	14.664	12.170	10.059	13.896	12.116	11.886	
12	22.831	19.933	16.945	16.154	19.739	18.377	25.435	
24	24.932	25.201	23.698	25.942	25.607	24.778	59.142	
30	26.531	26.898	26.420	30.216	26.999	26.634	80.472	
48	29.269	30.470	33.249	41.662	28.728	30.004	175.3*	

exp: experimental, cal: calculated, *: odd values.

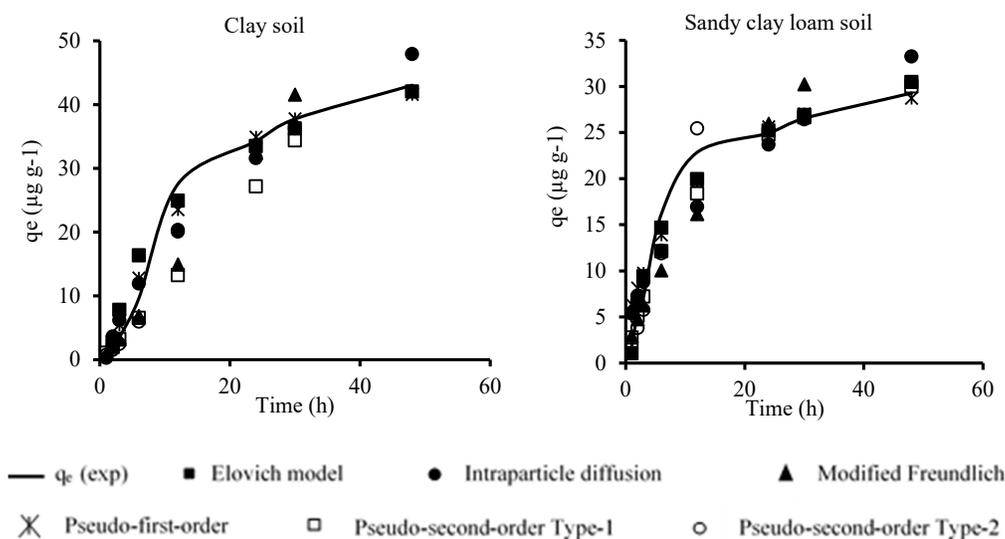


Fig. 8. Comparison of the experimental and calculated desorption quantities by different models for fenitrothion in soils.

In general, the results showed that the pseudo-first-order model followed by the Elovich kinetic model fit the experimental adsorption and desorption data quite well, with high R^2 values and low $\Delta q_e\%$ and SSE values. Accordingly, the pseudo-first-order equation is most suitable for describing the adsorption and desorption kinetics of fenitrothion on clay soil and sandy clay soil. It has been reported that the pseudo-first-order kinetic equation is commonly used to describe the adsorption kinetics of various pesticides in soil,¹⁸ and it is the best model for the adsorption of methoxychlor, 2,4-D, methyl parathion, atrazine and DDT.^{27,47-48} Additionally, the results showed that the pseudo-second-order model type-1 and type-2 fit the experimental adsorption data, and the R^2 values reached unity with low values of $\Delta q_e\%$ and SSE, which indicated that the experimental and theoretical data were in the best agreement. The pseudo-second order model is widely applied in liquid-phase adsorption systems.¹⁴ This material is suitable for the adsorption of various pesticides, such as fenitrothion, trifluralin, 2,4-D, carbofuran, glyphosate, and diuron.^{29,47,49} However, the pseudo-second-order model cannot be used to describe the desorption kinetics because the R^2 of fenitrothion desorption was very low and the relation between the

experimental and calculated data was noncompatible. Moreover, the modified Freundlich model has limited applicability, and the intraparticle diffusion model does not apply practical data on the sorption and desorption of fenitrothion on clay and sandy clay loam soils. However, the modified Freundlich model was used to describe the adsorption of different organic compounds.¹⁶ Because the intraparticle diffusion model cannot describe the adsorption and desorption kinetics of the tested pesticides on two soil types, intraparticle diffusion was not the rate-controlling step for the adsorption or desorption kinetics of fenitrothion on clay soil and sandy clay loam soil.^{13,50-53} This work confirms the high importance of applied sciences in different fields as shown in a lot of papers published before.⁵⁴⁻⁵⁹

Authors' contributions

The experimental studies were carried out by Mohamed Riad Fouad. Ahmed Farahat El-Aswad performed the model analysis and wrote the main manuscript. Maher Ibrahim Aly edited the text. All authors reviewed the manuscript.

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