177 *Egypt. J. Chem.* **Vol. 66,** No. 4, pp. 219 - 222 (2023)

Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Validation of adsorption-desorption kinetic models for fipronil and thiamethoxam agrichemicals on three types of Egyptian soils

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Abstract

To achieve the objectives of this study, the batch sorption and desorption kinetic experiments were performed to obtain the equilibrium time for fipronil and thiamethoxam in three types of Egyptian soil (clay soil, sandy clay loam soil and sandy loam soil). Equilibrium between the insecticides solution and the soil for adsorption and desorption appeared at 30, 24, 6 and 30 hours in clay soil, 0.5,12, 12 and 12 hours in sandy clay loam soil and 3, 1, 24 and 30 hours in sandy loam soil for fipronil and thiamethoxam, respectively. The adsorption rate of fipronil was higher and it had stronger affinity to three tested soils compared to thiamethoxam. Nevertheless, both pesticides showed stronger affinity to clay soil than to sandy clay loam soil and sandy loam soil. Using five kinetic models; Elovich, Intraparticle diffusion, modified Freundlich, Pseudo-first-order rate and Pseudo-second-order rate were tested to describe the experimental data. The model that gives a relatively high correlation coefficient was used to test the validity of mathematical models (R^2). The best model is Pseudo-second-order rate equation fits with experimental data for fipronil and thiamethoxam on adsorption and desorption kinetic in three types soil ($R^2 \geq 0.9$). Elovich kinetic model fit the experimental data quite well for adsorption in clay soil for two insecticides, adsorption and desorption in sandy clay loam soil for thiamethoxam, adsorption in sandy loam soil for fipronil and desorption in sandy clay loam soil for thiamethoxam with high values of $R^2 \geq 0.9$. Its application of Intraparticle diffusion, the modified Freundlich model, and the Pseudo-first-order rate equation was limited.

Keywords: Adsorption-desorption; kinetic; modeling; soil; fipronil; thiamethoxam.

1. Introduction

Adsorption-desorption kinetic studies of pesticides in soil are of very importance to determine the parameters control the fate and behaviour of pesticides in the environment [1]. Sorption kinetics is the measure of the adsorption uptake with respect to time at a constant concentration and is employed to measure the rate of solute aggregate which gave the residence time [2]. Adsorption and desorption should take place in a balanced state. The equilibrium time could be achieved within 1 or few hours to 1 day, but sometimes it required few days, or months. The rapid equilibration time has been documented in many experiments, with the adsorption equilibrium of parathion being reached in less than one minute. Also, that of bromacil is almost instantaneously. The equilibrium time of cyanazine adsorption is 1 hour, organophosphorous and carbamates in soil is 2 hours as a physical adsorption [3]. The adsorption of carbofuran in soil reached equilibrium within 23 hours [4]. Studied the adsorption kinetics of atrazine and diuron in clay loam soil and concluded that the equilibrium time for two herbicides is three hours [5]. However, the adsorption of aldrin by soil and clays was not change within 5 minutes to 5 days [3]. On clay loam soil and sandy loam soil, the kinetics of adsorption and desorption were studied using the batch equilibration technique to estimate the equilibration time of chlorantraniliprole, dinotefuran, bispyribac sodium, and metribuzin, the equilibrium was obtained at 24 hours [6].

Many mathematical adsorption and desorption kinetic models have been presented to describe the data over the years. There are two main types of the models; adsorption reaction and adsorption diffusion. Diffusion across the liquid layer surrounding the particles, diffusion in the liquid contained in the pores or along their walls (intraparticle diffusion), and adsorption-desorption between the adsorbate and active sites are the three types of adsorption diffusion models. Adsorption reaction models, on the other hand, are based on the entire adsorption process [7]. Equations of equilibrium and transport kinetics could be used to model adsorption. However, the adsorption kinetic is always described by an empirical approach using different models [8]. The rate of adsorption can be calculated using kinetic modeling. Due to the availability of unoccupied sites for adsorption, the adsorption may be quick at first (up to 10 - 15 minutes).

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Receive Date: 13 June 2022, **Revise Date:** 03 August 2022, **Accept Date:** 04 August 2022, **First Publish Date:** 04 August 2022
DOI: 10.21608/EJCHEM.2022.143450.6289

Following that, the adsorption slows down until the maximum adsorption capacity is attained. The duration of contact time is termed equilibration time till that point [9]. The adsorption reaction models such as; Pseudo-first-order, Pseudo-second-order, Second order equation and Elovich. Also, the adsorption diffusion models such as; Double-exponential, Intraparticle diffusion and Liquid film diffusion model.

Fipronil is a pesticide in a new family of insecticides called phenyl pyrazoles. Fipronil is a commercial insecticide that was discovered and developed by Rhône-Poulenc Research Station in Ongar, England between (1985 and 1987) and entered the world market in 1993, and was registered for use in the U.S.A. in 1996. In 1997 production of fipronil was estimated to be 480 tons per annum and to 800 tons per annum in 2000. Approximately 119,000 lbs of fipronil was used in California in 2006 [10]. Thiamethoxam, is a second-generation chlorothiazolylmethyl neonicotinoid discovered and developed by Ciba Crop Protection in 1996. It has been marketed as Cruser® for seed and Actara® for foliar treatment since 1998 [11]. In this study it was validation for sorption kinetic models; Elovich, Intraparticle diffusion, modified Freundlich, Pseudo-first-order rate and Pseudo-second-order rate of fipronil and thiamethoxam on three type's Egyptian soil

2. Materials and methods

2.1. Tested insecticides

Fipronil, 5-Amino-1-[2,6-dichloro-4-(trifluoromethyl) phenyl]-4 (trifluoromethanesulfinyl)-1H-pyrazole-3-carbonitrile. Technical 99 % a.i. Solubility (20ºC) in water 3.78 mg L^{-1}. **Thiamethoxam**, 3-[(2-Chloro-1,3-thiazol-5-yl) methyl]-5-methyl-1,3,5-oxadia-zinan-4-ylidene, nitramide. Technical 98.5 % a.i. Solubility in water 4100 mg L^{-1}.

2.2. Tested soils

Clay soil, sandy clay loam soil, and sandy loam soil are the three most frequent types of Egyptian soil. The soil samples were taken from the surface layer (0-20 cm) in several areas with no pesticide history. The clay soil came from the Faculty of Agriculture's Agricultural Research Station, Abis farm, and the sandy clay loam soil came from the Elnahda region, Elamria, Alexandria Governorate, and the sandy loam soil came from the Bangar Elsokar region. The physical and chemical parameters were determined at the University of Alexandria's Department of Soil and Water Sciences, Faculty of Agriculture, and the results are shown in Table (1). 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 [12]. Soil pH was measured using 0.01 M calcium chloride ($CaCl_2$) in a 1:2 w/w soil: solution slurry. The organic matter content was determined by dichromate oxidation according to the Walkley-Black method [13].

2.3. Experiments

Adsorption kinetics of tested insecticides

A kinetic study was carried out to determine the equilibration time for the sorption of each tested fipronil and thiamethoxam on the tested soils. A known weight of soil (1g) was placed in a vial with a measured volume of 0.01M $CaCl_2$ solution containing a known concentration (15 µg mL^{-1}) of the tested insecticides (1:5 soil : solution). Polypropylene centrifuge tubes (25 mL) containing the soil and the insecticides solution were mechanically shaken at 150 rpm in the dark at room temperature. After time intervals of 0.5, 1, 3, 6, 12, 24, 30, 50, 72 and 96 hours, the tubes were centrifuged at 4000 rpm for 15 minutes and the supernatant was measured using UV-Visible Spectrophotometer for each tested insecticides [5, 6, 14].

Desorption kinetics of tested insecticides

Desorption studies for concentration (15 g mL^{-1}) were carried out immediately following the adsorption experiments utilising a parallel system. A decant refill procedure was utilised at the end of the sorption experiment, with 5 mL of fresh 0.01 M $CaCl_2$ background solution supplied to each tube for evaluating the desorption equilibrium at times (0.5, 1, 3, 6, 12, 24, 30, 50, 72 and 96 hours). In the dark, at room temperature, tubes were mechanically shaken at 150 rpm. The liquid phase containing desorbed insecticide was examined using a UV-visible Spectrophotometer after centrifugation. 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 retained solution [14].

2.4. Mathematical kinetic models

Several mathematical kinetic models were investigated to find the fit model and to determine the characteristic parameters for the insecticides adsorption and desorption processes. Five kinetic models were tested to describe the experimental data of fipronil and thiamethoxam in clay soil, sandy clay loam soil and sandy loam soil. The experimental values of the adsorbed or desorbed solute and the equilibrium concentration for each pesticide in each soil were applied in the linearized equation of different models in order to determine the model parameters [15, 16].

Table (1): Physical and chemical properties of the tested soils

Soil code	Texture class	Water holding capacity (%)	EC (m mohs/cm) at 25˚C	pH	OM (%)	Total carbonate (%)	Soluble cations conc. (meq L^{-1})	Soluble anions conc. (meq L^{-1})
A	Clay	46	1.32	8.25	3.31	7.87	18.17	13.30
B	Sandy clay loam	38	5.03	8.15	1.54	44.64	50.30	50.30
C	Sandy loam	35	2.33	8.20	1.32	44.09	31.50	23.30

Elovich equation

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

Intraparticle diffusion equation

Table 2 shows the empirical and linearized variants of the equation. Where $q_t =$ the amount of pesticide adsorbed or desorbed in time t; $K_d =$ apparent diffusion rate coefficient. If the reaction follows the parabolic diffusion law, a plot of $q_t$versus $t^{1/2}$ should yield a linear relationship [17].

Modified Freundlich equation

The modified Freundlich equation is exhibited in Table (2). Where $q_t =$ adsorbed or desorbed pesticide (mg g^{-1}); $C_o =$ initial pesticide concentration (mg L^{-1}); $t =$ reaction time (min); $K_d =$ desorption or sorption rate coefficient (min^{-1}) and $\frac{1}{m} =$ constant.

Pseudo-first-order rate equation

Table 2 shows the non-linear and linear forms of the Pseudo-first-order equation. Where $q_t =$ amount of pesticide adsorbed or desorbed in time t; $q_e =$ amount of pesticide adsorbed or desorbed at equilibrium and $K_1 =$ apparent adsorption or desorption rate coefficient.

Pseudo-second-order rate equation

Table (2) shows the Pseudo-second-order equation. Where K_2 is the second-order adsorption rate constant (g mg^{-1} min^{-1}). For the boundary conditions$t = 0\ to\ t = t\ and\ q = 0\ to\ q = q$, and rearranging, the linearized form can be obtained. If the Pseudo-second-order kinetic is applied, the plot of $\frac{t}{q}$ against t should give a linear relationship, from which q_e and k_2 can be determined from the slope and intercept of the plot.

3. Results and discussion

3.1. Adsorption and desorption kinetics

Adsorption and desorption is one of the key mechanisms that determines the behavior and occurrence of insecticides in the environment [18]. Adsorption kinetics is examined by plotting adsorption over time at a constant concentration, which indicates the rate of solute adsorption. As a result, monitoring the kinetics yields the equilibrium time [14, 16]. The equilibration time of tested pesticides fipronil and thiamethoxam on soil was investigated using a batch sorption kinetic experiment. Figure 1 shows the adsorption and desorption of fipronil and thiamethoxam on clay, sandy clay loam, and sandy loam soil versus time at 15 g mL^{-1} at room temperature. The kinetics of adsorption and its associated desorption showed two separate stages, with a fast process in the beginning and a slow process later on. The rapid stage could be attributed to the compound immediately filling surface empty spots in soil particles, followed by a slow migration and diffusion into the soil organic matter matrix and mineral structure. Equilibrium between the insecticide solution and the soil in the adsorption appeared at (30 and 24 hours) in clay soil, (0.5 and 12) hours in sandy clay loam soil and (3 and 1 hour) in sandy loam soil for fipronil and thiamethoxam, respectively. While equilibrium occurred between the pesticide solution and the soil in desorption at (6 and 30 hours) in clay soil, (12 hours) in sandy clay loam and (24 and 30 hours) in sandy loam for fipronil and thiamethoxam, respectively. Moreover, Figure (1), showed that the adsorption rate of fipronil was higher and it had stronger affinity to three tested soils compared to thiamethoxam. Time-dependent adsorption fate indicates that thiamethoxam have very low sorption potential for the soil. Slow sorption behavior over the test period observed for thiamethoxam could be attributed to their high solubility and low octanol : water (log K_{OW}) partition coefficient [18]. Nevertheless, both pesticides showed stronger affinity to clay soil than to sandy clay loam soil and sandy loam soil, may be due to higher clay content and organic matter in clay soil comparing with sandy clay loam soil and sandy loam soil. Adsorption of pesticide is reported to be enhanced with high soil clay and soil organic matter content [14, 19]. According to previous studies, the fipronil equilibrium time was 12 hours onto soils; silt clay loam, loam, silt loam and sandy clay loam [20], while was 24 hours on sediment [21]. Thiamethoxam have achieved equilibrium at 24 hours in clay loam, sandy loam, sandy clay loam and loam soil [18, 22, 23], while Banerjee et al found equilibrium time 48 hours on silty clay, clay and sandy loam soil [24].

Table (2): Kinetic models of adsorption and desorption, as well as their linear versions

Models	Empirical formula	Linear form	Plot
Elovich	$\frac{dq_t}{d_t} = \alpha\ exp(-\beta q_t)$	$q_t = \left(\frac{1}{\beta}\right) ln(\alpha\beta) + \left(\frac{1}{\beta}\right) ln\ t$	$q_t\ vs.\ ln\ t$
Intraparticle diffusion	$q_t = K_d t^{1/2}$	$q_t = C_{id} + K_{id} t^{½}$	$q_t\ vs.\ t^{½}$
Modified Freundlich	$q_t = K_d\ C_o t^{1/m}$	$lnq_t = ln(K_{mf} C_o) + \frac{1}{m} lnt$	$lnq_t\ vs.\ lnt$
Pseudo-first order	$q_t = q_e(1 - e^{k_1 t})$	$ln(q_e - q_t) = lnq_e - k_1\ t$	$ln(q_e - q_t)\ vs.\ t$
Pseudo-second order	$\frac{dq}{dt} = K_2\ (q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$	$\frac{t}{q_t}\ vs.\ t$

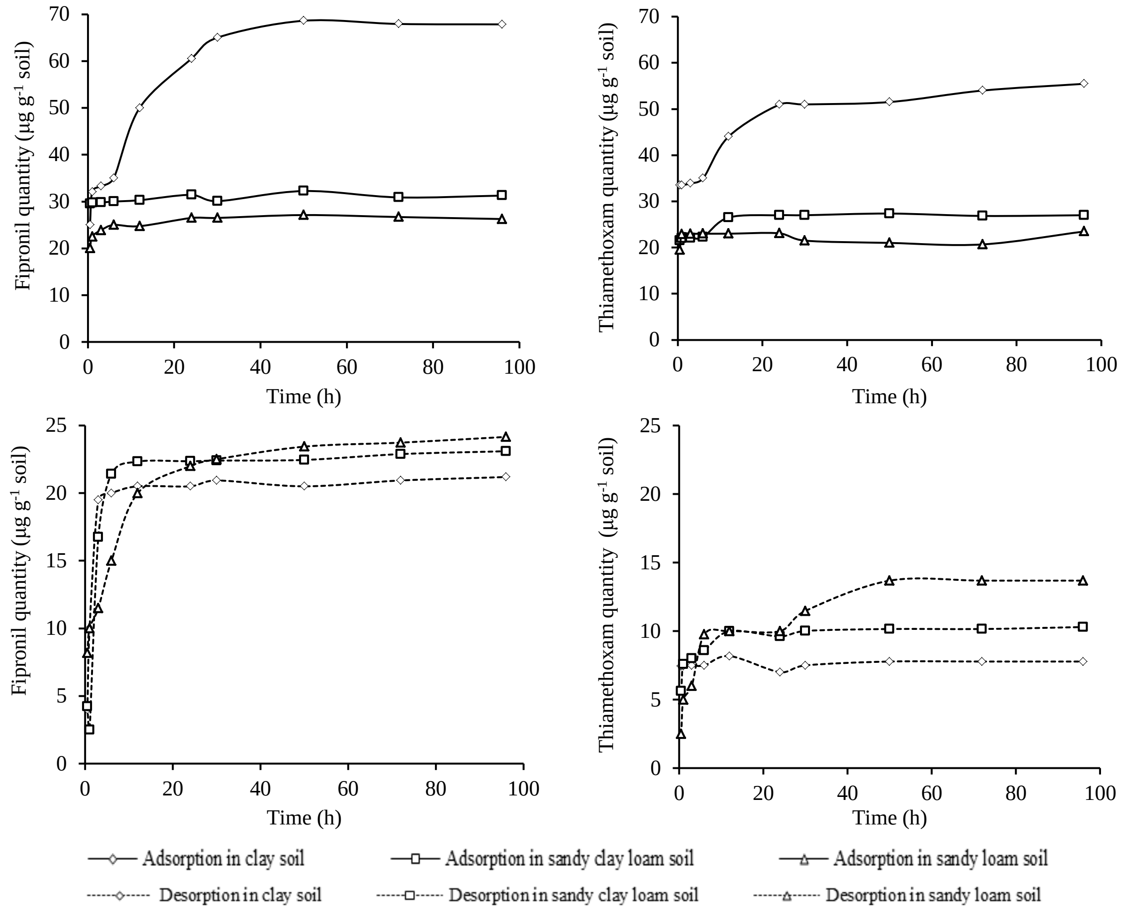

Figure (1): Adsorption and desorption kinetics of fipronil and thiamethoxam in Egyptian soils a period.

3.2. Modeling of insecticide sorption kinetics

The adsorption and desorption kinetics of fipronil and thiamethoxam on three Egyptian soils were analyzed using different mathematical kinetic models. To find the valid model and to determine the characteristic parameters for the pesticide adsorption and desorption process, five kenietic models (Elovich, Intraparticle diffusion, Modified Freundlich, Pseudo-first-order rate and Pseudo-second-order) were applied to describe experimental data of tested insecticides.

Elovich model

Elovich equation plots of adsorption and desorption kinetics of insecticides in soil exhibited linear relationships exist between "qt" and "ln t" for each soil type, are represented in Figure (2). The Elovich equation parameters, α and β were calculated from the slope and intercept of the linear plots and reported in Table (2). The amount of fipronil and thiamethoxam adsorbed in clay soil is higher than that in sandy clay loam and sandy loam soil. According to Fouad et al., α represents the chemisorption rate at zero coverage and β based on the extent of surface coverage and chemisorption activation energy [16]. When comparing parameter α ($\mu g\ g^{-1}\ h^{-1}$) and β ($\mu g\ g^{-1}$) for the three soils, it was observed that the α and β values for adsorption were higher (5.101×10^{32} and 1.652×10^{8} in insecticide fipronil) and (2.287×10^{7} and 7.554×10^{81} in insecticide thiamethoxam) for α and (2.577 and 0.849 in fipronil) and (0.765 and 8.734 in thiamethoxam) for β compared to that of desorption (3.676 x 10 and 6.322 x 10) in fipronil and (1.765 x10 and 5.428×10^{3}) in thiamethoxam for α and (0.258 and 0.295) in fipronil and (0.472 and 1.246) in thiamethoxam for β in sandy clay loam soil and sandy loam soil, respectively, While the opposite in clay soil desorption is higher than adsorption in two pesticides for α and β values (Table 3). The Elovich equation is fit with experimental adsorption data more than desorption data in clay soil in two insecticides, as indicated by higher values of determination coefficient (R^2 = 0.924 and 0.888) compared to (R^2 = 0.706 and 0.091) while the opposite in sandy clay loam soil and sandy loam soil; R^2 was (0.779, 0.956, 0.961 and 0.893) for desorption and (0.618, 0.832, 0.889 and 0.024) for adsorption in fipronil and thiamethoxam, respectively. Elovich model parameters of fipronil and atrazine in the sugarcane trash ash were 99.8 and 21812.5 $mg\ kg^{-1}\ min^{-1}$, 158.7 and 84.0 $kg\ mg^{-1}$, 0.783 and 0.720 for α, β and R^2, respectively [25]. Parameters of carbofuran at concentrations 45 and 4.5 µM were 7.99-0.73, 6.30-0.48, 0.85-0.30 and 3.41-0.70 $mg\ kg^{-1}$ for α, 0.60-0.19, 0.69-0.14, 0.77-0.14 and 0.78-0.14 $mg\ kg^{-1}$ for β and 0.97-0.97, 0.94-0.99, 0.98-1.00 and 0.96-099 for R^2 in clay loam, loam, sandy loam and loamy sand soil, respectively [26].

Intraparticle diffusion model

The linearized plots of qt versus $t^{1/2}$ according to Intraparticle diffusion model for the adsorption and desorption of fipronil and thiamethoxam on three kinds of soil are shown in Figure 3. The intraparticle diffusion plot lines did not cross through the origin for both insecticides in adsorption and desorption, showing that intraparticle

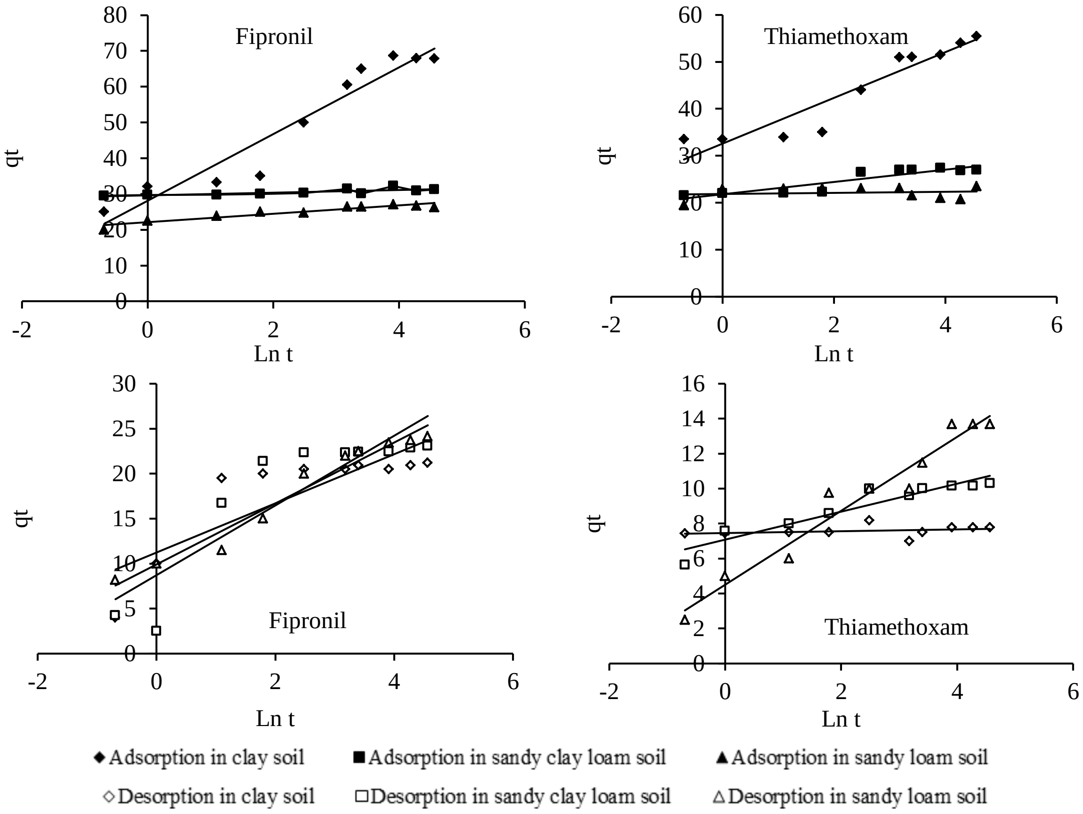

Figure (2): Elovich model plots of insecticides adsorption and desorption kinetics in soils.

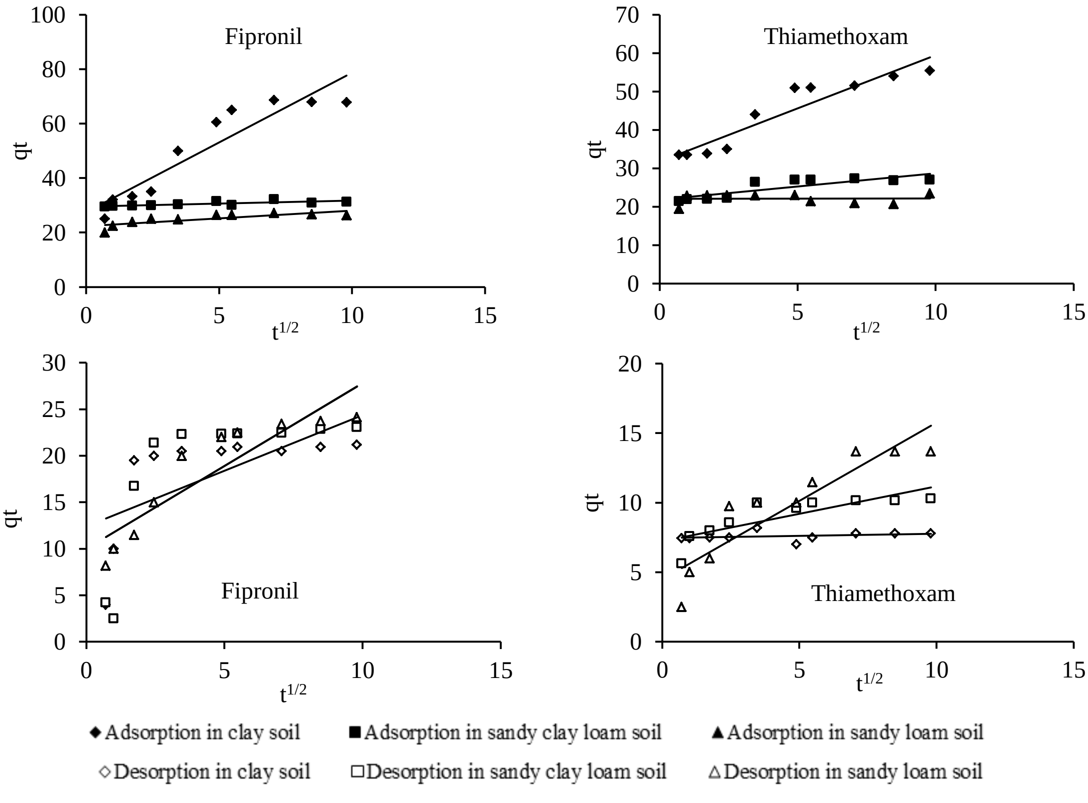

Figure (3): Intraparticle diffusion model plots of insecticides adsorption and desorption kinetics in soils.

Table (3): Kinetic parameters for adsorption and desorption of insecticides in soils

Modeling	Parameters	Clay soil		Sandy clay loam soil		Sandy loam soil	
		Adsorption	Desorption	Adsorption	Desorption	Adsorption	Desorption
	Insecticide	Fipronil					
Elovich	α (μg g^{-1} h^{-1})	191.185	1.673E+02	5.101E+32	3.676E+01	1.652E+08	6.322E+01
	β (μg g^{-1})	0.107	0.366	2.577	0.258	0.849	0.295
	R^2	0.924	0.706	0.618	0.779	0.889	0.961
Intraparticle diffusion	K_{id}	5.120	1.196	0.216	1.780	0.572	1.783
	C_{id}	27.438	12.413	29.555	10.014	23.342	10.010
	R^2	0.864	0.418	0.591	0.508	0.648	0.833
Modified Freundlich	K_{mf}	1.929	0.611	1.973	0.405	1.469	0.663
	1/m	0.206	0.237	0.013	0.371	0.050	0.220
	R^2	0.939	0.628	0.627	0.681	0.873	0.955
Pseudo-first-order	K_1 (h^{-1})	0.069	0.043	0.027	0.053	0.038	0.087
	q_e (μg g^{-1})	21.724	3.222	1.611	5.815	2.109	19.188
	R^2	0.317	0.503	0.099	0.650	0.195	0.853
Pseudo-second-order	K_2 (g $μg^{-1}$ h^{-1})	0.0046	0.0495	0.1957	0.0163	0.1860	0.0026
	q_e (μg g^{-1})	70.423	21.277	31.348	23.810	26.596	-11.521
	R^2	0.997	1.000	1.000	0.995	1.000	0.853
Modeling	Insecticide	Thiamethoxam					
Elovich	α (μg g^{-1} h^{-1})	3924.859	1.567E+61	2.287E+07	1.765E+01	7.554E+81	5.428E+03
	β (μg g^{-1})	0.205	19.268	0.765	0.472	8.734	1.246
	R^2	0.888	0.091	0.8323	0.956	0.024	0.893
Intraparticle diffusion	K_{id}	2.767	0.031	0.688	0.395	0.006	1.125
	C_{id}	31.811	7.452	21.852	7.224	22.081	4.507
	R^2	0.887	0.099	0.712	0.668	0.0002	0.834
Modified Freundlich	K_{mf}	2.198	0.498	1.455	0.466	1.451	0.286
	1/m	0.114	0.007	0.054	0.099	0.006	0.289
	R^2	0.890	0.088	0.835	0.853	0.027	0.896
Pseudo-first-order	K_1 (h^{-1})	0.038	-0.008	0.199	0.046	-0.019	0.043
	q_e (μg g^{-1})	20.277	0.228	7.773	5.815	0.697	8.165
	R^2	0.914	0.005	0.824	0.741	0.255	0.762
Pseudo-second-order	K_2 (g $μg^{-1}$ h^{-1})	0.0081	0.3184	0.0915	0.1150	0.1224	0.0003
	q_e (μg g^{-1})	3121.001	60.750	738.422	106.721	498.246	1612.877
	R^2	0.998	0.999	1.000	1.000	0.993	0.810

diffusion was not the only rate determining step and that boundary layer diffusion may have influenced adsorption to some extent. In the intraparticle diffusion model, the intercept value indicates the thickness of the boundary layer. The distance from the adsorbent at which the concentration of the diffusing species reaches 99 percent of the bulk concentration is known as the boundary layer thickness. Adsorption capabilities are higher in thicker layers. Adsorption is generally controlled by intraparticle diffusion due to the adsorbent's microporosity [25]. With increasing temperature, both adsorbents' intraparticle diffusion rates were shown to decrease [26]. The model parameter values of K_{id} and C_{id}, and statistical parameters R^2 were presented in Table (3).

The K_{id} and C_{id} values in adsorption and desorption kinetic of fipronil were 5.120, 27.438, 1.196 and 12.413 for clay soil, 0.216, 29.555, 1.780 and 10.014 for sandy clay loam soil and 0.572, 23.342, 1.783 and 10.010 for sandy loam soil, while in thiamethoxam were 2.767, 31.811, 0.031 and 7.452 for clay soil, 0.688, 21.852, 0.395 and 7.224 for sandy clay loam soil and 0.006, 22.081, 1.125 and 4.507 for sandy loam soil, respectively. Intraparticle diffusion model it is suitable in only two cases; adsorption in clay soil and desorption in sandy loam soil for two pesticides and not suitable in all other cases.

Modified Freundlich model

Kuo and Lotse were the first to create the modified Freundlich kinetic model. It was utilised to look into the adsorption mechanism and the rate of potential control over mass movement and chemical reactions [28]. When compared to the Freundlich model, the modified Freundlich model has improved R^2 values [29]. Modified Freundlich plots of ln qt (amount of pesticide adsorbed or released mg g^{-1}) versus ln t (time of reaction) for the soil types are shown in Figure (4). The modified Freundlich equation parameters K_{mf} (is the initial adsorption rate (L g^{-1} min^{-1}) and 1/m (is the Kuo-Lotse constant) were calculated from the intercept and the slope of the linear plots, respectively. The parameter values for adsorption and desorption of two insecticides are shown in Table (3). In general, the adsorption rate coefficient "K_{mf}" values of the three soils were higher than desorption rate coefficient values of fipronil and thiamethoxam in three soil types of clay, sandy clay loam and sandy loam soil. The constant (1/m) values in adsorption and desorption kinetics were 0.206, 0.237, 0.013, 0.371, 0.050 and 0.220 for fipronil, 0.114, 0.007, 0.054, 0.099, 0.006 and 0.289 for thiamethoxam in clay, sandy clay loam and sandy loam soil, respectively. The adsorption kinetic parameters are helpful for prediction of adsorption rate, which gives valuable knowledge for modeling and designing the processes [17]. The correlation coefficient values (R^2) were (fipronil; 0.939, 0.627 and 0.873 & thiamethoxam; 0.890, 0.835, 0.027) for adsorption and (fipronil; 0.628, 0.681 and 0.955 & thiamethoxam; 0.088, 0.853 and 0.896) for desorption of on clay soil, sandy clay loam soil and sandy loam soil, respectively. A modified Freundlich kinetics model accurately represented the adsorption-desorption data of simazine on a loam soil and its components [30], the heavy metals sorption [31, 32, 33] and the sorption of organic compounds [29, 34].

Pseudo-first-order rate model

Pseudo-first-order equation firstly had been called Lagergren first order rate equation, given by Lagergren [35]. The first-order sorption kinetic model correlated with the concentration and the time [8]. A linear form of Pseudo-first-order equation applied for adsorption and desorption of fipronil and thiamethoxam are shown in Figure (5). The values of adsorption and desorption rate parameters; K_1 (h^{-1}) and qe calculated from the Pseudo-first-order model (µg g^{-1}) and also statistical parameter; R^2 were listed in Table (3) The "K_1" values for adsorption and desorption were 0.069, 0.043, 0.027, 0.053, 0.038 and 0.087 for fipronil, and 0.038, -0.008, 0.199, 0.046, -0.019 and 0.043 for thiamethoxam in clay soil, sandy clay loam soil and sandy loam soil, respectively. Pseudo-first-order equation is fit for describing experimental results in desorption from sandy loam soil for fipronil (R^2 = 0.853), adsorption in clay soil (R^2 = 0.914) and sandy clay loam soil (R^2 = 0.824) for thiamethoxam. Pseudo-first-order kinetic model is commonly used to describe adsorption kinetics in soil [36]. It was the best model for the 2, 4-D

Pseudo-second-order model

Since its introduction in 1999 to describe adsorption kinetics, the Pseudo-second-order equation has been frequently employed in liquid-phase systems [39]. According to Pan and Xing, linearized Pseudo-second order is more compatible with data on adsorption kinetics [36]. In the Pseudo-second-order rate equation, the rate-limiting step is the adsorption on surfaces that includes chemisorption, because the solute adsorption from its solution is related to physicochemical interactions between the two substances [40]. The adsorption and desorption kinetic parameters of insecticides, determined from the linear form of the Pseudo-second-order equation, are presented in Table (3) and Figure (3). Values of K_2 (g µg^{-1} h^{-1}) for adsorption and desorption were 0.0046, 0.0495, 0.1957, 0.0163, 0.1860 and 0.0026 for fipronil, and 0.0081, 0.3184, 0.0915, 0.1150, 0.1224 and 0.0003 for thiamethoxam in clay soil, sandy clay loam soil and sandy loam soil, respectively. The calculated qe values (µg g^{-1}) were the highest for thiamethoxam adsorption in clay soil (3121), sandy clay loam soil (738) and sandy loam soil (498), while was desorption of thiamethoxam in sandy loam soil (1612). The Pseudo-second-order rate equation fits relatively with experimental data for two insecticides in adsorption and desorption on three soils, ($R^2 \geq 0.9$). The kinetic evaluation illustrated that the Pseudo-second order equation provided good fits to various pesticide adsorption on soil, fenitrothion and trifluralin [41], 2,4-D and carbofuran [42, 43], glyphosate [44], diuron [45]. If the adsorption process good fits to Pseudo-second-order equation, it demonstrates an inclination towards chemisorption.

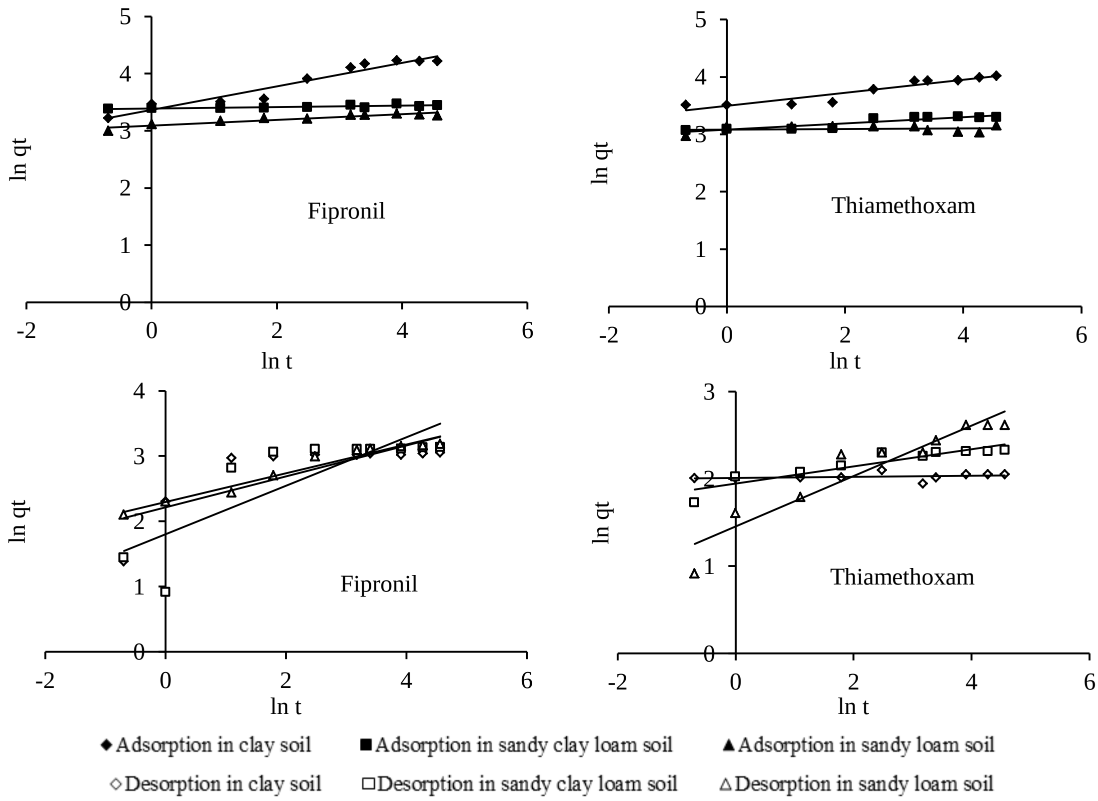

Figure (4): Modified Freundlich model plots of insecticides adsorption and desorption kinetics in soils.

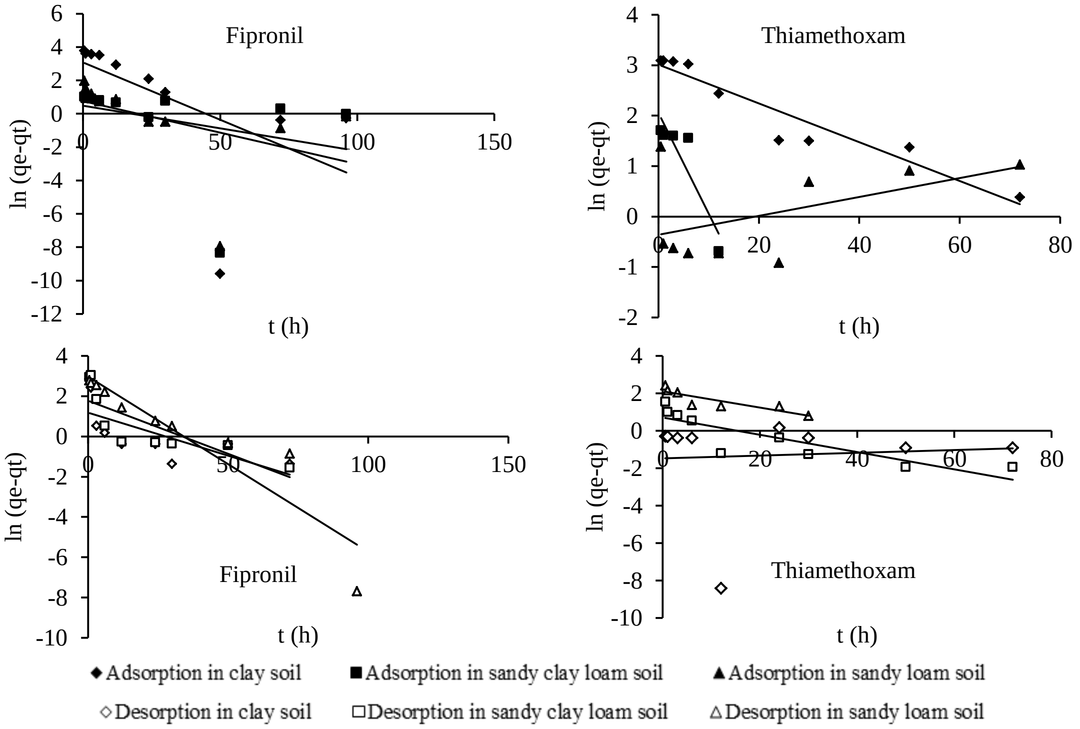

Figure (5): Pseudo-first-order model plots of insecticides adsorption and desorption kinetics in soils.

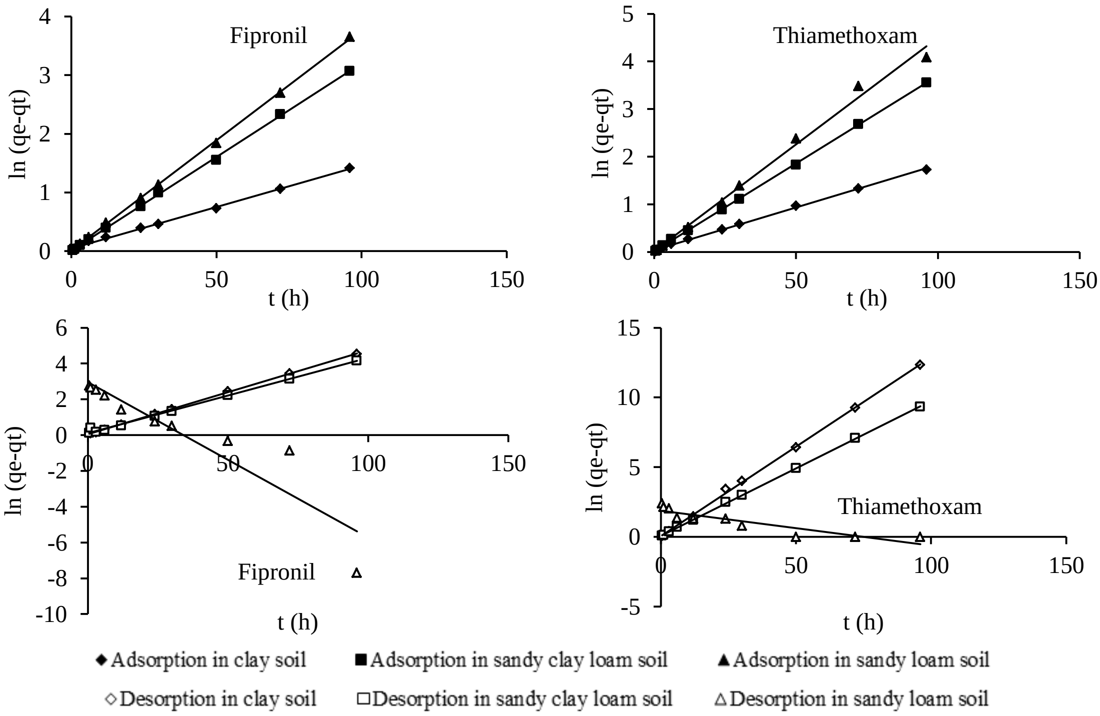

Figure (6): Pseudo-second-order model plots of insecticides adsorption and desorption kinetics in soils.

4. Conclusion

A batch sorption kinetic experiment was conducted to investigate the equilibration time of tested insecticides; fipronil and thiamethoxam on clay soil, sandy clay loam soil and sandy loam soil. The kinetic of adsorption and its corresponding to desorption exhibited two distinct stages, a rapid process in the initial stages followed by a slow process. Equilibrium between the insecticides solution and the soil for adsorption and desorption appeared at 30, 24, 6 and 30 hours in clay soil, 0.5,12, 12 and 12 hours in sandy clay loam soil and 3, 1, 24 and 30 hour in sandy loam soil for fipronil and thiamethoxam, respectively. The adsorption rate of fipronil was higher and it had stronger affinity to three tested soils compared to thiamethoxam. Nevertheless, both pesticides showed stronger affinity to clay soil than to sandy clay loam soil and sandy loam soil, may be due to higher clay content and organic matter in clay soil. Elovich kinetic model fit the experimental data quite well for adsorption in clay soil for two insecticides, adsorption and desorption in sandy clay loam soil for thiamethoxam, adsorption in sandy loam soil for fipronil and desorption in sandy clay loam soil for thiamethoxam with high values of $R^2 \geq 0.9$. Intraparticle diffusion and Modified Freundlich model it is suitable in only two cases; adsorption in clay soil and desorption in sandy loam soil for two pesticides. Pseudo-first-order equation is suitable for describing experimental results in desorption from sandy loam soil for fipronil, adsorption in clay soil and sandy clay loam soil for thiamethoxam. The Pseudo- second -order rate equation fits relatively with experimental data for two insecticides in adsorption and desorption on three soils, ($R^2 \geq 0.9$).

5. References

[1] Palma, G., Demanet, R., Jorquera, M., Mora, M. L., Briceño, G., & Violante, A. Effect of pH on sorption kinetic process of acidic herbicides in a volcanic soil. *Journal of soil science and plant nutrition*, *15*(3), (2015), 549-560.

[2] Saha, D., & Grappe, H. A. 5-Adsorption properties of activated carbon fibers. In: Activated Carbon Fiber and Textiles. A volume in Woodhead Publishing Series in Textiles. By: J. Y. Chen (ed.). Copyright © 2017 Elsevier Ltd. All rights reserved. PP. 143-165.

[3] Delle Site, A. Factors affecting sorption of organic compounds in natural sorbent/water systems and sorption coefficients for selected pollutants. A review. *Journal of Physical and Chemical Reference Data*, *30*(1), (2001), 187-439.

[4] Khuntong, S., Sirivithayapakorn, S., Pakkong, P., & Soralump, C. Adsorption kinetics of carbamate pesticide in rice field soil. *International Journal of Environment Asia, 3*(2), (2010), 20-28.

[5] Fouad, M. R., & El-Aswad, A. F. Competitive and non-competitive adsorption of atrazine and diuron on alluvial soil. *Alexandria Science Exchange Journal, 39*(3), (2018), 527-533.

[6] Fouad, M. R. (2017) Behaviour of some pesticides in soil. A Thesis Presented to the Graduate School Faculty of Agriculture, Alexandria University in Partial Fulfillment of the Requirements For the Degree of Master of Science.

[7] Qiu, H, Lu, L. V, Pan, B., Zhang, Q. J, Zhang, W, & Zhang, Q. X. Critical review in adsorption kinetic models. *Journal of Zhejiang University-Science, 10*(5), (2009), 716-724.

[8] Rodrigues, A. E., & Silva, C. M. What’s wrong with Lagergreen pseudo first order model for adsorption kinetics?. *Chemical Engineering Journal,* 306, (2016) 1138-1142.

[9] Shankara, A., Kongotb, M., Sainia, V. K., & Kumarb A. Removal of pentachlorophenol pesticide from aqueous solutions using modified chitosan. *Arabian Journal of Chemistry, 13*(1), (2020), 1821-1830.

[10] Almalike, L. B., Al-Najar, A. A., & Kadhim, Z. N. Physical characteristics of adsorption–desorption of Fipronil in the soil. *African Journal of Engineering Research, 4*(2), (2016), 26-35.

[11] Rana, S., & Gupta, V. K. Microbial degradation of second generation neonicotinoid: thiamethoxam in clay loam soils. *Journal Pharmacogn Phytochem, 8*(1S), (2019), 294-298.

[12] Gee, G. W., Bauder, J. W., & Klute A. Particle-size analysis. Methods of soil analysis Part 1 Physical and Mineralogical Methods, (1986), 383-411.

[13] Nelson, D. W., Sommers, L. E., Sparks, D., Page, A., Helmke, P., Loeppert, R., Soltanpour, P., Tabatabai, M., Johnston, C., & Sumner, M. Total carbon, organic carbon, and organic matter. Methods of soil analysis Part 3-chemical methods, (1996), 961-1010.

[14] El-Aswad, A. F., Aly, M. I., Fouad, M. R., Badawy, M. E. I. Adsorption and thermodynamic parameters of chlorantraniliprole and dinotefuran on clay loam soil with difference in particle size and pH. *Journal of Environmental Science and Health Part B. 54*(6), (2019), 475-488.

[15] Al-Ghouti, M. A., Da'ana, D. A. Guidelines for the use and interpretation of adsorption isotherm models: A review. *Journal of Hazardous Materials,* 393, (2020), 122383.

[16] Fouad, M. R., El-Aswad, A. F., Badawy, M. E. I., Aly, M. I. Adsorption isotherms modeling of herbicides bispyribac-sodium and metribuzin on two common Egyptian soil types. *Journal of Agricultural, Environmental and Veterinary Sciences, 3*(2), (2019), 69-91.

[17] Ahmed, S. M., Taha, M. R., Taha, O M. E. Kinetics and isotherms of dichlorodiphenyltrichloroethane (DDT) adsorption using soil–zeolite mixture. *Nanotechnology for Environmental Engineering, 3*(1), (2018), 4.

[18] Kurwadkar, S. T., Dewinne, D., Wheat, R., McGahan, D. G., & Mitchell, F. L. Time dependent sorption behavior of dinotefuran, imidacloprid and thiamethoxam. *Journal of Environmental Science and Health, Part B, 48*(4), (2013), 237-242.

[19] Davis, J. W. Physico‐chemical factors influencing ethyleneamine sorption to soil. *Environmental Toxicology and Chemistry: An International Journal, 12*(1), (1993), 27-35.

[20] Singh, A., Srivastava, A., & Srivastava, P. C. Sorption–desorption of fipronil in some soils, as influenced by ionic strength, pH and temperature. *Pest management science, 72*(8), (2016), 1491-1499.

[21] Lin, K., Haver, D., Oki, L., & Gan, J. Persistence and sorption of fipronil degradates in urban stream sediments. *Environmental Toxicology and Chemistry: An International Journal, 28*(7), (2009), 1462-1468.

[22] Dankyi, E., Gordon, C., Carboo, D., Apalangya, V. A., & Fomsgaard, I. S. Sorption and degradation of neonicotinoid insecticides in tropical soils. *Journal of*

Environmental Science and Health, Part B, 53(9), (2018), 587-594.

[23] Smalling, K. L., Hladik, M. L., Sanders, C. J., & Kuivila, K. M. Leaching and sorption of neonicotinoid insecticides and fungicides from seed coatings. *Journal of Environmental Science and Health, Part B, 53*(3), (2018), 176-183.

[24] Banerjee, K., Patil, S. H., Dasgupta, S., Oulkar, D. P., & Adsule, P. G. Sorption of thiamethoxam in three Indian soils. *Journal of Environmental Science and Health, Part B, 43*(2), (2008), 151-156.

[25] Yadav, S., & Singh, N. (2020). Sugarcane trash ash: A low cost adsorbent for atrazine and fipronil removal from water.

[26] Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., & Simal-Gándara, J. Carbofuran sorption kinetics by corn crop soils. *Bulletin of environmental contamination and toxicology, 77*(2), (2006), 267.

[27] Ofomaja, A. E., Naidoo, E. B., & Pholosi, A. Intraparticle diffusion of Cr (VI) through biomass and magnetite coated biomass: A comparative kinetic and diffusion study. *South African Journal of Chemical Engineering, 32*(1), (2020), 39-55.

[28] Kuo, S., & Lotse, E. G. Kinetics of phosphate adsorption and desorption by hematite and gibbsite1. *Soil Science, 116*(6), (1973), 400-406.

[29] Bhatt, A. S., Sakaria, P. L., Vasudevan, M., Pawar, R. R., Sudheesh, N., Bajaj, H. C., & Mody, H. M. Adsorption of an anionic dye from aqueous medium by organoclays: equilibrium modeling, kinetic and thermodynamic exploration. *RSC advances. 2*(23), (2012), 8663-8671.

[30] Farcasanu, R. I., Yamaguchi, T., Moldrup, P., De jonge, L. W., & Fukushima, T. Kinetics and equilibrium of simazine sorption on soil colloids. *Journal of Environmental Chemistry, 8*(2), (1998), 259-266.

[31] Liang, T. J., Hsu, C. N., & Liou, D. C. Modified Freundlich sorption of cesium and strontium on Wyoming bentonite. *Applied radiation and isotopes, 44*(9), (1993), 1205-1208.

[32] Liu, X., Goodfellow, M. R., Yu, Q., & Zheng, C. Correlation of pH dependant equilibrium isotherms of heavy metal biosorption with a modified Freundlich model. *Environmental technology, 25*(12), (2004), 1341-1348.

[33] Wang, X. S., Li, Z. Z., & Tao, S. R. Removal of chromium (VI) from aqueous solution using walnut hull. *Journal of Environmental Management, 90*(2), (2009), 721-729.

[34] Varank, G., Demir, A., Yetilmezsoy, K., Top, S., Sekman, E., & Bilgili, M. S. (2012). Removal of 4-nitrophenol from aqueous solution by natural low-cost adsorbents.

[35] Lagergren, S. K. About the theory of so-called adsorption of soluble substances. *Sven. Vetenskapsakad. Handingarl, 24*, (1898), 1-39.

[36] Pan, B., & Xing, B. Adsorption kinetics of 17α-ethinyl estradiol and bisphenol A on carbon nanomaterials. I. Several concerns regarding pseudo-first order and pseudo-second order models. *Journal of Soils and Sediments, 10*(5), (2010), 838-844.

[37] Hameed, B. H., Salman, J. M., & Ahmad, A. L. Adsorption isotherm and kinetic modeling of 2, 4-D pesticide on activated carbon derived from date stones. *Journal of hazardous materials, 163*(1), (2009), 121-126.

[38] Gupta, V. K., Gupta, B., Rastogi, A., Agarwal, S., & Nayak, A. Pesticides removal from waste water by activated carbon prepared from waste rubber tire. *Water research, 45*(13), (2011), 4047-4055.

[39] Wu, F. C., Tseng, R. L., Huang, S. C., & Juang, R. S. Characteristics of pseudo-second-order kinetic model for liquid-phase adsorption: a mini-review. *Chemical Engineering Journal, 151*(1-3), (2009), 1-9.

[40] Robati, D. Pseudo-second-order kinetic equations for modeling adsorption systems for removal of lead ions using multi-walled carbon nanotube. *Journal of nanostructure in Chemistry, 3*(1), (2013), 1-6.

[41] Lule, G. M., & Atalay, M. U. Comparison of Fenitrothion and Trifluralin adsorption on Organo-zeolites and activated carbon. Part I: pesticides adsorption isotherms on adsorbents. *Particulate Science and Technology, 32*(4), (2014), 418-425.

[42] Gupta, V. K., Ali, I., & Saini, V. K. Adsorption of 2, 4-D and carbofuran pesticides using fertilizer and steel industry wastes. *Journal of Colloid and Interface Science, 299*(2), (2006), 556-563.

[43] Pandiarajan, A., Kamaraj, R., Vasudevan, S., & Vasudevan, S. OPAC (orange peel activated carbon) derived from waste orange peel for the adsorption of chlorophenoxyacetic acid herbicides from water: adsorption isotherm, kinetic modelling and thermodynamic studies. *Bioresource technology, 261*, (2018), 329-341.

[44] Carneiro, R. T., Taketa, T. B., Neto, R. J. G., Oliveira, J. L., Campos, E. V., de Moraes, M. A., & Fraceto, L. F. Removal of glyphosate herbicide from water using biopolymer membranes. Journal of environmental management, 151, (2015), 353-360.

[45] Cáceres-Jensen, L., Rodríguez-Becerra, J., Parra-Rivero, J., Escudey, M., Barrientos, L., & Castro-Castillo, V. Sorption kinetics of diuron on volcanic ash derived soils. *Journal of hazardous materials, 261*, (2013), 602-613.