




Adsorption-desorption of cypermethrin and chlorfenapyr on Jordanian soils

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Received: 7 December 2018 / Accepted: 10 July 2019 / Published online: 25 July 2019
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Abstract

In this study, adsorption kinetic experiments were conducted on agricultural soil samples from Southern Jordan to investigate the adsorption behavior of the heavily used insecticide cypermethrin and the pesticide chlorfenapyr. Soil samples classified as sand and loamy sand with 1.77–2.02% organic matter content were collected from two locations within 0–30 cm depths in Tafilah, Jordan, and tested as adsorbents, and it was found that the adsorption of the two substances followed pseudo-second-order kinetics which implies that the adsorption process is chemisorption. The second-order rate constants were 1.01–2.03 g/mg h for cypermethrin and 11.38–13.03 g/mg h for chlorfenapyr. Adsorption isotherm experiments were also carried out at a constant temperature and variable initial adsorbate concentrations and it was found that the Langmuir model provided a slightly better fit to the adsorption data in comparison with the Freundlich model. The Langmuir maximum adsorption capacities were 8.88–9.08 mg/g for cypermethrin and 36.23–45.25 mg/g for chlorfenapyr while the Langmuir constants were 0.0123–0.0157 L/mg for cypermethrin and 0.003–0.0037 L/mg for chlorfenapyr. Higher adsorption rates were observed in the loamy sand soil due to the higher organic matter, clay, and silt contents. Nonetheless, it was concluded that the leaching potential of these substances to groundwater is low due to the physical nature of these chemicals as well as the adsorption behavior of the soil.

Keywords Adsorption · Cypermethrin · Chlorfenapyr · Groundwater Contamination · Pesticides · Insecticides

Introduction

Due to the extensive use of pesticides and insecticides in the agricultural sector worldwide, quantifying the fate of these compounds is essential to limit their mobility and minimize their environmental footprint. Adsorption of pesticides and insecticides by agricultural soil determines the fate of these substances and their leaching to groundwater. Adsorption is typically governed by several factors such as soil texture, pH, cation exchange capacity, surface area, ionic strength, and the

soil's organic matter (OM) content (Kodešová et al. 2011; Spark and Swift 2002). There exist several laboratory and field studies on the adsorption-desorption of pesticides and insecticides and the pertinent environmental impacts of these substances. Many of those studies reported a high leaching potential beyond the rooting zone, thus posing a threat to groundwater. Therefore, it is necessary to understand the adsorption behavior of herbicides and insecticides in agricultural soil to assess the groundwater contamination potential.

Cypermethrin is a synthetic pyrethroid compound used as an insecticide in large-scale agricultural applications. It has a molar mass of 416.3 g/mole, and it has been reported that this chemical is less toxic to humans due to its poor dermal absorption, less tissue accumulation, and rapid metabolism (Aggarwal et al. 2015; Weister 1992). Chlorfenapyr is a pesticide derived from the halogenated pyrroles and has a molar mass of 407.6 g/mole. It is classified as slightly hazardous according to the World Health Organization (Raghavendra et al. 2011). These two substances are used heavily in agriculture in Jordan and it is important to investigate their behavior and fate in the soil environment (Abdel-Wali et al. 2012; Elbetieha et al. 2001).

Editorial handling: Maurizio Barbieri

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Jordan is a small Arab country located on the South West of Asia and is known for its limited freshwater resources. The water shortage problem in Jordan became more severe over the past few years due to the increased demand, insufficient annual precipitation, and groundwater over-exploitation and contamination (Al-Qinna et al. 2011). Due to the significance of the agricultural sector in the Jordanian economy, and to conserve the valuable and limited water resources in Jordan, it is imperative to understand the retention and mobility of insecticides and pesticides in the agricultural soil and their potential to leach into groundwater.

The objectives of this study are to investigate the adsorption behavior of cypermethrin and chlorfenapyr on agricultural soils in Tafilah, Jordan. Soil samples from two locations were analyzed and tested for the adsorption of the aforementioned substances. Kinetic and equilibrium adsorption experiments were conducted and based on the adsorption parameters, the groundwater leaching potential was evaluated.

Materials and methods

Materials and chemicals

Surface soil samples were collected from two locations with intensive agricultural activities in Tafilah, Jordan (Fig. 1). The two locations are soil 1 (Ais 30.83 N, 35.64 E) and soil 2 (Abur 30.80 N, 35.72 E), and the samples were collected in triplicate from 0–30 cm depths from each location.

All chemicals used in this study including cypermethrin and chlorfenapyr were of analytical grade purchased from Sigma Aldrich Ltd. Stock solutions in 10,000 ppm of cypermethrin and chlorfenapyr were prepared by adding 1 g of the respective chemical into a 100-mL volumetric flask filled with acetonitrile. Pyrex conical flasks were cleaned with distilled water and acetone and dried at 110 °C for 30 min prior to their use in the experiments.

Soil testing

Soil samples brought from the two locations were classified using sieve analysis and hydrometer tests according to the ASTM D422 method. Soil samples were sieved through IS sieve no. 10 (2 mm), and the fraction passing through the sieve was collected and preserved in air-tight plastic containers for further analysis. The total organic matter of the soil was determined by the Walkley-Black chromic acid wet oxidation method by drying 1 g of soil and adding 10 mL of 1.0 N $K_2Cr_2O_7$ and 20 mL of concentrated H_2SO_4 gradually over 1 min in a 250-mL conical flask. After 30 min, 200 mL of distilled water and 0.30 mL of 0.025 M ortho-phenanthroline-ferrous complex were added and a greenish cast color to dark-blue

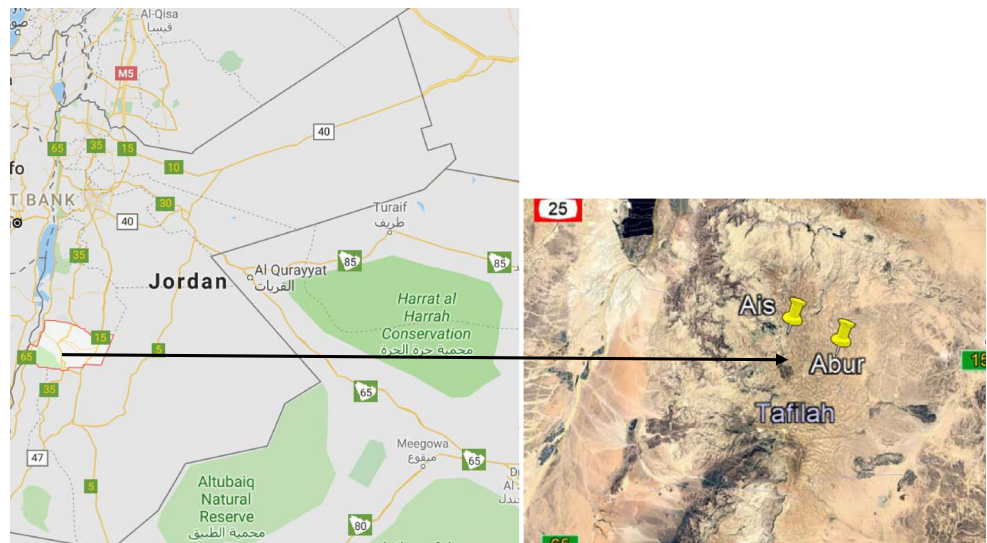
green was observed. The mixture was titrated using 0.4 N ferrous sulfate until the color changed from blue to orange (Walkley and Black 1934). The soil specific gravity was determined by the Pycnometer method (ASTM D854). The soil properties are presented in Table 1.

Adsorption experiments

The adsorption kinetic experiments were carried out in batch mode using 250-mL conical flasks filled with 5 g of soil and 5 mL of the 10,000-ppm cypermethrin stock solution to yield 200-ppm cypermethrin concentration or 1.5 mL of the 10,000-ppm chlorfenapyr stock solution to yield 60-ppm chlorfenapyr concentration and the volume was completed to the mark with distilled water. The experiments were conducted on a shaker plate at 150 rpm for a period of 24 h at room temperature (25 ± 2 °C). Ten milliliters (cypermethrin) and 5 mL (chlorfenapyr) of samples were collected at time intervals of 0.083, 0.25, 0.5, 1, 2, 4, 6, and 24 h. Cypermethrin was extracted from the samples using the QuEChERS method as described by Schenck and Hobbs (2004), in which 10 mL of the sample was placed in a 50-mL centrifuge tube and then 10-mL acetonitrile was added to the sample, shaken for 1 min until the mixture became uniform, and 4 g $MgSO_4/1$ g $NaCl/0.5$ g sodium citrate were added and the solution was shaken vigorously for 2 min and then centrifuged for 5 min at 3,000 rpm. Chlorfenapyr on the other hand was extracted using solvent extraction according to the EPA Method 1664 in which 5 mL of *n*-hexane was added to 5 mL of sample in a 20-mL centrifuge tube and the mixture was centrifuged for 5 min at 3,000 rpm to separate the organic phase from the aqueous phase (EPA 1999). The extracted liquid (*n*-hexane layer) was then filtered using 0.22- μ m syringe to eliminate the undesirable polar substances and analyzed using Varian 3800 gas chromatography equipped with Varian 2000 mass spectrometer detector with Varian 8400 autosampler and Varian capillary column CP-Sil 8 CB (25 mm \times 0.25 mm id, 0.12- μ m film thickness). The carrier gas was a high purity helium with a flow rate of 1 mL/min and the injection volume was 1 μ L.

The adsorption equilibrium experiments were conducted for the two soils with an adsorbent quantity of 5 g and cypermethrin concentrations of 50, 100, 150, and 200 ppm and chlorfenapyr concentrations of 15, 30, 45, and 60 ppm in 250-mL conical flasks. The mixtures were agitated on shaker plates at 150 rpm for 2 h (estimated equilibrium time) at 25 ± 2 °C. After that, 10-mL (cypermethrin) and 5-mL (chlorfenapyr) samples were collected, extracted as described above, filtered using 0.22- μ m syringe filters, and analyzed using GC-MS.

Fig. 1 Soil sampling locations



Data processing

The amount of pesticides uptake (q_e) by soils and the percentage removal of pesticides ($R\%$) in the solution are calculated as shown in Eqs. 1 and 2 (Khalifa et al. 2016; Setiabudi et al. 2016):

$$q_e \text{ (mg/g)} = \frac{C_o - C_e}{m} \times V \tag{1}$$

$$R\% = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where C_o is the liquid phase concentration at time zero (mg/L); C_e is the liquid phase concentration at equilibrium (mg/L); V is the solution volume (L); and m is the mass of adsorbent used (g).

Several kinetic models can be applied to examine the controlling mechanism of pesticides adsorption by soil such as pseudo-first-order and pseudo-second-order

models. Pseudo-first-order model typically represents reversible reactions with an equilibrium being established between liquid and solid phases whereas pseudo-second-order model is based on the assumption that the rate limiting factor is chemisorption (chemical adsorption) in which ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and finding sites that maximize their coordination number with the surface. The linearized forms of these two models are as follows (Ghrab et al. 2018; Khalifa et al. 2016; Setiabudi et al. 2016):

$$\text{Pseudo-first-order : } \log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

$$\text{Pseudo-second-order : } \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

where q_e is the adsorption capacity at equilibrium (mg/g); t is the time (h); q_t is the adsorption capacity at time t (mg/g); k_1 is the pseudo-first-order adsorption constant (h^{-1}); and k_2 is the pseudo-second-order adsorption constant (g/mg h).

The adsorption equilibrium was studied by conducting isotherm experiments (adsorption experiments conducted at isothermal temperatures and different adsorbate concentrations). The adsorbate amount per unit mass of adsorbent and the concentration of adsorbate remaining in solution data can be fitted with the Freundlich and Langmuir models (Kundu and Gupta 2006). The Freundlich model is an empirical model used for heterogeneous systems while the Langmuir model assumes that adsorption cannot proceed beyond monolayer coverage with no interaction among the adsorbed molecules. The

Table 1 Soil physical and chemical properties (average of three replicates)

Soil properties	Soil (1) (Ais)	Soil (2) (Abur)
Specific gravity	2.64	2.63
pH	9.30	9.31
Clay (%)	2	3
Silt (%)	7	9
Sand (%)	91	88
Organic matter (%)	1.77	2.02
Soil classification	Sand	Loamy sand

linearized forms of the two models are as follows (Hameed et al. 2007; Kano et al. 2000):

$$\text{Freundlich isotherm : } \log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

$$\text{Langmuir isotherm : } \frac{1}{q_e} = \frac{1}{q_m K_L} \times \frac{1}{C_e} + \frac{1}{q_m} \quad (6)$$

where C_e is the equilibrium concentration (mg/L); q_e is the adsorption capacity at equilibrium (mg/g); q_m is the maximum adsorption capacity (mg/g); K_f is the Freundlich capacity factor (mg/g)(L/mg)^{1/n}; (1/n) is the Freundlich intensity parameter; and K_L is the Langmuir constant (L/mg).

The soil-water partitioning coefficient (K_d) and the soil adsorption coefficient (K_{OC}) are calculated as shown in Eqs. 7 and 8 (Delle Site 2001):

$$K_d = \frac{\text{Concentration of a chemical in soil}}{\text{Concentration of a chemical in water}} = \left(\frac{q_e}{C_e} \right) \times 1000 \quad (7)$$

$$K_{OC} = \frac{K_d}{f_{OM}} \quad (8)$$

where f_{OM} is the fraction of organic matter.

Results and discussion

Adsorption kinetics

The adsorption kinetics can be modeled using pseudo-first-order or pseudo-second-order models. The coefficient of determination (R^2) value between the experimental data and the predicted values and the mean squared error (MSE) were used to judge the goodness of fit of these models. A relatively high R^2 value and a low MSE value indicate that the model fits the experimental data well.

Figure 2 illustrates the relationship between the adsorbate concentration remaining in solution and time. Rapid adsorption was observed for cypermethrin and chlorfenapyr and equilibrium was attained after 2 h in both soil samples. After equilibrium, minimal variations in the concentration of less than 4% for chlorfenapyr and less than 2% for cypermethrin were observed over the remaining 24 h. Kumar and Philip (2006) indicated that the adsorption of pesticides was rapid and reached pseudo equilibrium within a short period of 1.5 h in sandy soils and 4 h in clay and composted soils. Beck and Jones (1996) also reported that herbicide adsorption takes place mostly in the first hour of the sorption experiments. For hydrophobic pesticides, the rapid

adsorption is a surface phenomenon so the vacant sites in the soil particles are filled up rapidly in the initial stages. A slow migration and diffusion often follow leading to a drastic decrease in adsorption and eventually reaching the steady state (Gao et al. 1998).

The adsorption kinetics for cypermethrin using first- and second-order models are presented in Fig. 3. The first 5 min of the experiment had a low removal efficiency which was around 12% in soil 1 and 31% in soil 2. However, after an hour, the percent removal increased to 43% in soil 1 and to 45% in soil 2. As indicated earlier, equilibrium occurred after about 2 h where the percent removals were 50% and 53% for soil 1 and soil 2, respectively. The rate constants were computed based on the fitted equations for each model and it was found that the first-order rate for cypermethrin (k_1) was 2.21 h⁻¹ for soil 2 while it was 2.81 h⁻¹ for soil 1. On the other hand, the second-order rate constants (k_2) were 2.03 g/mg h and 1.01 g/mg h for soils 2 and 1, respectively. By comparing the two models, it is clear that the adsorption of cypermethrin followed the pseudo-second-order model better than the first-order model, as the R^2 values were approximately 1.00 for the second-order model for both soils as opposed to 0.98 and 0.93 for soils 1 and 2, respectively, using the first-order model. Additionally, the MSE values favored the selection of the second-order model because the second-order MSE values were 0.0005 and 0.0001 for soils 1 and 2, respectively, compared with 0.0148 and 0.0326 for soils 1 and 2, respectively, using the first-order model. Due to the fact that the second-order pseudo model represented the adsorption data better, the process of adsorption is chemisorption in which the adsorbent-adsorbate interaction is through the valency forces (Bajeer et al. 2012).

The adsorption kinetics for chlorfenapyr is illustrated in Fig. 4. The first 5 min had a high percent removal of 62% in soil 1 and 68% in soil 2 and this removal increased to 66% in soil 1 and 76% in soil 2 after equilibrium (after 2 h). Similar to cypermethrin, the second-order model predicted the adsorption data better as the R^2 values were clearly higher in the second- compared with the first-order model regardless of the soil sample. Additionally, the second-order MSE values were significantly lower than the first-order values which suggest that chlorfenapyr adsorption is chemisorption as well. The chlorfenapyr first-order rate constants for soils 1 and 2 were 0.505 h⁻¹ and 1.388 h⁻¹, respectively, whereas the second-order rate constants for soils 1 and 2 were 11.38 g/mg h and 13.03 g/mg h, respectively. For both chemicals, it is clear that the adsorption in soil 2 was higher compared with that in soil 1 as the second-order rate constants were higher for soil 2.

Fig. 2 Plot of the adsorbate remaining concentration in solution (mg/L) versus time (h) using 5 g of soil

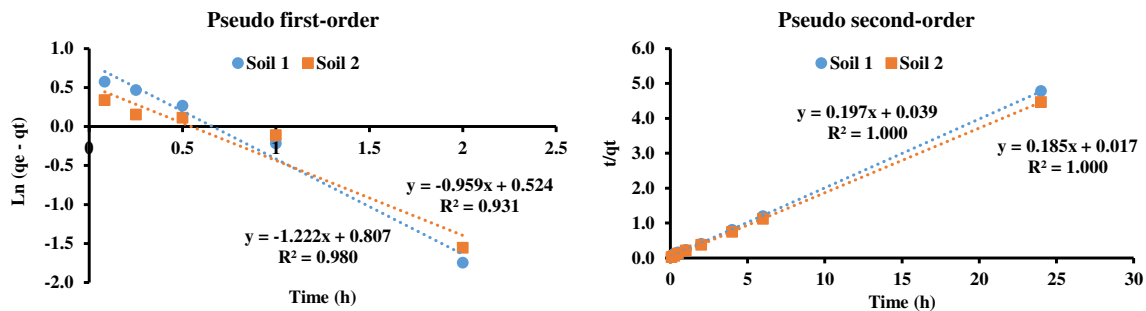
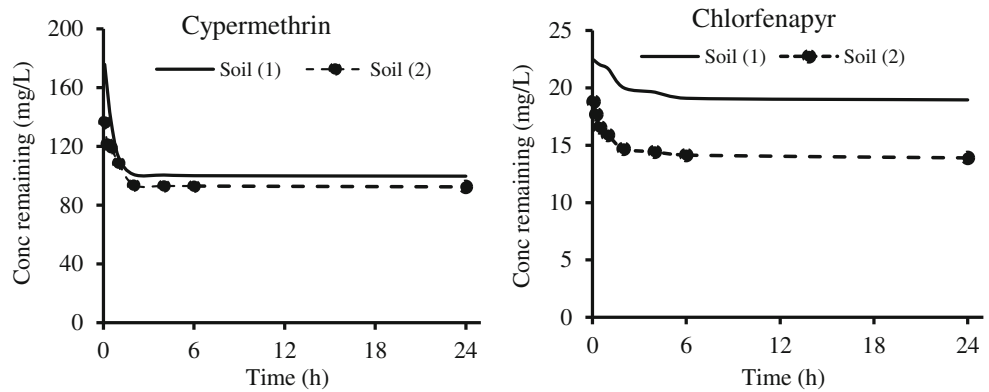


Fig. 3 Cypermethrin pseudo first- and second-order kinetic fits

Adsorption isotherms

The adsorption of cypermethrin and chlorfenapyr was modeled using the Freundlich and Langmuir isotherms at 25 ± 2 °C assuming an equilibrium time of 2 h for both chemicals in both soils. The quality of fit for each model was assessed using the R^2 and MSE values. The linearized Freundlich and Langmuir isotherms for the two chemicals are shown in Figs. 5 and 6.

Both models fit the adsorption equilibrium data well for the two chemicals with high R^2 values. However, the R^2 values for the Langmuir model were slightly higher than those in the Freundlich model and the MSE values for

Langmuir were smaller than those for the Freundlich model for both substances and regardless of the soil sample. Therefore, it can be concluded that the adsorption of cypermethrin and chlorfenapyr follows the Langmuir model in the studied soils in which adsorption cannot proceed beyond monolayer coverage and all sorbent surface sites are equivalent (Sohn and Kim 2005; Boparai et al. 2011). This can be due to the lower adsorbate concentration in the solution, which was insufficient to impose a competition for the abundantly available adsorption sites in the soil. The isotherm parameters are summarized in Table 2.

The Freundlich n values were 1.52 and 1.61 for cypermethrin and 1.02 for chlorfenapyr. These values tend to be between 1 and 10 with greater values implying stronger

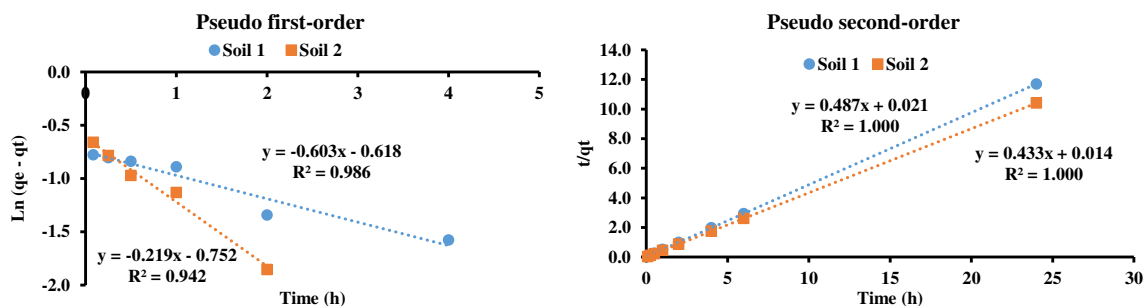


Fig. 4 Chlorfenapyr pseudo-first- and second-order kinetic fits

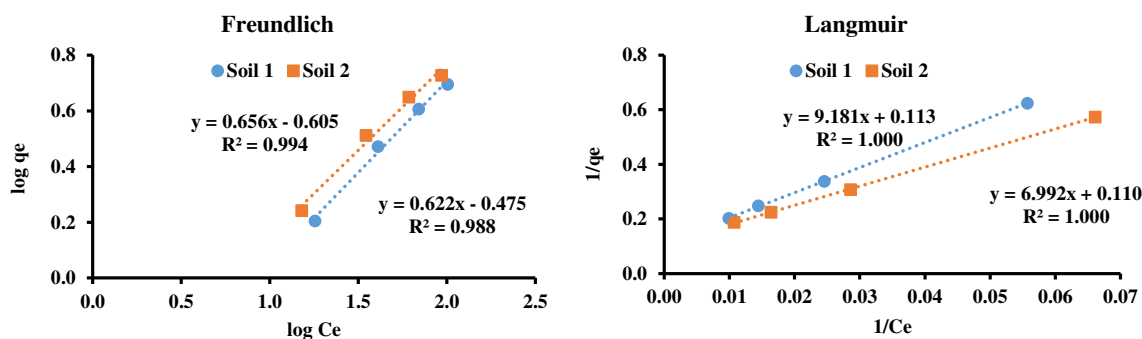


Fig 5 Linearized Freundlich and Langmuir model fits for cypermethrin adsorption

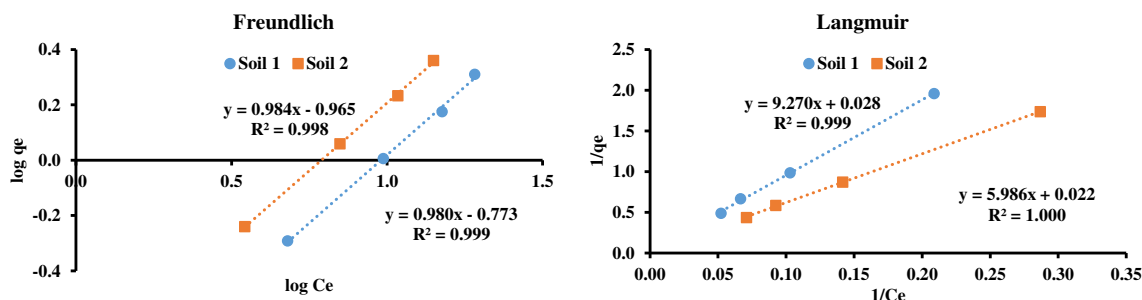


Fig. 6 Linearized Freundlich and Langmuir model fits for chlorfenapyr adsorption

interaction between soil and pesticides and are indicative of chemisorption (Boparai et al. 2011; Öztürk and Bektaş 2004). On the other hand, Almalike et al. (2015) reported that the Freundlich capacity factor (K_f) for cypermethrin ranged from 9.2 to 46.5 mg/g/(L/mg)^{1/n} in South Iraq soil which has relatively high organic content. Singh and Singh (2004) studied the adsorption of cypermethrin in sandy loam and silt loam soils with 0.75–2.16% OM content and found that the Freundlich capacity factor ranged from 9.2 to 22.9 mg/g/(L/mg)^{1/n}. For chlorfenapyr, Sun et al. (2013) reported that the K_f values in soil samples ranged from 469.87 to 607.16 mg/g/(L/mg)^{1/n}.

The Langmuir maximum adsorption capacities (q_e) of cypermethrin ranged from 8.88 mg/g to 9.08 mg/g, whereas the corresponding chlorfenapyr values ranged from 36.23 mg/g to 45.25 mg/g. The higher adsorption of soil 2 (loamy sand) in comparison to soil 1 (sand) for both chemicals is due

to the higher OM content in soil 2. Under low organic content, small amounts of herbicides can be adsorbed due to the hydrophobic nature of these substances, whereas the adsorption coefficient increases with an increase in the soil's OM content (El-Nahhal and Hamdona 2017). The adsorption of nonionic molecules such as herbicides and pesticides onto soil is a partitioning process which depends primarily on the OM content in the soil or in clay minerals. The higher clay and silt content in soil 2 may also have contributed to the high adsorption rates due to the larger surface area available for attachment, besides that adsorption of organic compounds onto clay minerals enhances their adsorption capacity (El-Nahhal and Safi 2008; El-Nahhal 2003; Nir et al. 2000). Chlorfenapyr adsorption was higher than cypermethrin in both soils and this is possibly due to the differences in the molar mass, as the adsorption potential decreases with an increase in molar mass (Ghabbour and Davies 2007).

Table 2 Cypermethrin and chlorfenapyr equilibrium parameters

Substance	Soil	Freundlich				Langmuir			
		K_f (mg/g/(L/mg) ^{1/n})	n	MSE	R^2	q_m (mg/g)	K_L (L/mg)	MSE	R^2
Cypermethrin	Soil (1)	4.031	1.52	2.05×10^{-4}	0.994	8.881	0.012	2.23×10^{-6}	1.000
	Soil (2)	2.983	1.61	4.26×10^{-4}	0.999	9.083	0.016	2.91×10^{-6}	1.000
Chlorfenapyr	Soil (1)	9.217	1.02	2.64×10^{-4}	0.998	36.232	0.003	1.27×10^{-4}	0.999
	Soil (2)	5.930	1.02	5.35×10^{-6}	0.999	45.248	0.004	2.87×10^{-5}	1.000

Table 3 Adsorption classifications based on $\log K_{OC}$ (EPA 2012)

$\log K_{OC}$	Adsorption classifications
> 4.5	Very strong sorption to soil/sediment, negligible migration to groundwater
3.5–4.4	Strong sorption to soil/sediment, negligible to slow migration to groundwater
2.5–3.4	Moderate sorption to soil/sediment, slow migration to groundwater
1.5–2.4	Low sorption to soil/sediment, moderate migration to groundwater
< 1.5	Negligible sorption to soil/sediment, rapid migration to groundwater

Leaching potential of cypermethrin and chlorfenapyr to groundwater

The soil adsorption coefficient (K_{OC}) provides a measure of the ability of a chemical to adhere to the OM in soil and the potential to leach through soil into groundwater (Delle Site 2001). The adsorption classifications based on $\log K_{OC}$ are illustrated in Table 3. Besides K_{OC} , the soil-water partitioning coefficient (K_d), which measures the amount of chemical substances adsorbed onto soil per amount of water, is a good indicator of the leaching potential of contaminants to groundwater (James et al. 2019).

The K_d and K_{OC} results for cypermethrin and chlorfenapyr in both soils are presented in Table 4. The $\log K_{OC}$ values for cypermethrin and chlorfenapyr were in the 3.5 to 4.4 range which, according to the classification provided in Table 3, indicates that these pesticides are strongly adsorbed to the soil and their leaching potential to groundwater is slow to negligible.

Conclusions

In this study, the adsorption of the pesticide chlorfenapyr and the insecticide cypermethrin by agricultural soil samples from two locations in Southern Jordan was investigated. The soil samples were sand and loamy sand with 1.77–2.02% organic matter content. Rapid adsorption was observed for the two chemicals regardless of the soil sample location and equilibrium was reached after 2 h. It was also found that the pseudo-second-order model was a better fit to the adsorption data of both chemicals compared with the first-order model, which implies that the adsorption process is chemisorption. The second-order rate constants were 1.01–2.03 g/mg h for cypermethrin and 11.38–13.03 g/mg h for chlorfenapyr.

Table 4 K_d and $\log K_{OC}$ values for cypermethrin and chlorfenapyr

Chemical	Soil	K_d	$\log K_{OC}$
Cypermethrin	Soil (1)	67.4	3.58
	Soil (2)	84.7	3.62
Chlorfenapyr	Soil (1)	104.4	3.77
	Soil (2)	162.0	3.9

Adsorption isotherm experiments were conducted and it was found that the Langmuir model was slightly a better fit compared with the Freundlich model for both chemicals. The Langmuir maximum adsorption capacities were 8.88–9.08 mg/g for cypermethrin and 36.23–45.25 mg/g for chlorfenapyr whereas the Langmuir constants were 0.0123–0.0157 L/mg for cypermethrin and 0.003–0.0037 L/mg for chlorfenapyr. Finally, the leaching potential of these two chemicals to groundwater was evaluated based on the soil adsorption coefficient and it was found that these two chemicals are strongly adsorbed to the soil and their leaching potential is slow to negligible.

Funding information The authors wish to thank MEDRC Water Research and the Deanship of Scientific Research at the University of Jordan for funding this research.

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