African Journal of Engineering Research
Vol. 4(2), pp. 26-35, July 2016
ISSN: 2354-2144
Full Length Research Paper

Physical characteristics of adsorption–desorption of Fipronil in the soil

Layla Balasem Almalike[1], Anis A. Al-Najar[2] and Zaki N. Kadhim[2]*

[1]Department of Petrochemical Engineering, Techn. Eng. College, Southern Technical University, Basrah, Iraq.
[2]Department of Chemistry, College of Science, University of Basrah, Iraq.

Accepted 24 May, 2016

ABSTRACT

The adsorption-desorption processes of Fipronil have been performed by using batch equilibrium experiments on eight agricultural soils samples from different locations in south of Iraq, Nasiriya, Amara, and mostly Basrah soils. The kinetics study for adsorption-desorption processes proved that first order rate law is ogled. Thermodynamic parameters (ΔG^0, ΔH^0 and ΔS^0) were also calculated for adsorption process of Fipronil at 288.15, 298.15, and 308.15 K. The negative values for each of ΔG^0, ΔH^0 and ΔS^0 parameters confirmed that Fipronil adsorption processes are high at lower temperature and done via enthalpy effect. The effect of organic matter and clay content on the adsorption of Fipronil in soil samples was studied. Also the adsorption effect caused by surfactants like cationic polyacrylamide (PAM), anionic polyacrylic acid (PAA), and nonionic polyvinyl alcohol (PVA) on the solid liquid interface was investigated. Batch adsorption technique was employed for the metal ions adsorption in soils. The amount of metal ions adsorbed increased with time. Copper ion has more adsorption rates than nickel and iron ions.

Keywords: Fipronil, adsorption, desorption, thermodynamic parameters, surfactants, metal ions.

*Corresponding author. E-mail: zekinasser99@yahoo.com.

INTRODUCTION

Our recent works (Layla et al., 2015; Layla et al., 2015) on the chemical kinetic and thermodynamic of adsorption-desorption of both Cypermethrin and Bispyribac-sodium pesticide were carried out by using batch equilibrium experiments on eight agriculture soil samples collected from different locations in south of Iraq. Such works suggested that the quantification of the linear adsorption coefficient (K_d) for soils plays a vital role to predict fate and transport of those pesticides in the soil-water environment.

Besides that, it was found that adsorption-desorption processes obeyed first order rate law. Also, thermodynamic parameters, ΔG^0, ΔS^0, ΔH^0 and equilibrium constant K_0, have revealed spontaneous and exothermic nature of adsorption process and indicated the phenomena of physical adsorption. Finally, the effect of organic matter, clay content, surfactants, and some selected metal ions were investigated.

In the present work, another widely used pesticide, Fipronil, has been testified exactly in the same way as for the other previous two mentioned pesticides (Layla et al., 2015; Layla et al., 2015).

Fipronil, 5-amino-1-[2,6-dichloro-4-trifluoromethyl)phenyl-4-(trifluoromethyl)sulfinyl]pyrazole-3- carbo nitrile (Mohammad et al., 2006), structure is shown in Figure 1.

Fipronil is a pesticide in a new family of insecticides called phenyl pyrazoles (Bobe et al., 1998). Fipronil is a commercial insecticide that was discovered and developed by Rhône-Poulenc Research Station in Ongar, England between 1985 and 1987 (Tingle et al., 2000) 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 (Tingle et al., 2000). Approximately 119,000 lbs. of Fipronil was used in California in 2006 (Amrith and Tresca, 2007).

MATERIALS AND METHODS

All chemicals and solvents used in these experiments

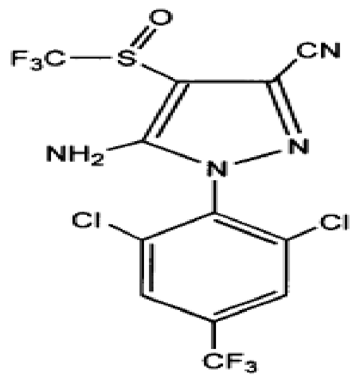

Figure 1. Structural formula of Fipronil.

Table 1. Soil pH, texture, moisture, organic carbon and organic matter for soil before pollution.

Soil properties	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
pH value	7.67	8.34	7.84	8.19	8.21	7.82	8.03	7.83
Clay (%)	43.01	43.01	51.87	53.56	25.25	22.45	22.79	49.41
Silt (%)	52.49	52.49	52.49	45.30	22.10	25.67	74.31	34.08
Moisture content	1.95	2.10	1.49	5.90	3.66	1.43	1.49	5.90
Organic carbon %	0.13	0.38	0.19	1.02	0.32	1.98	0.19	1.02
Organic matter %	6.697	9.321	4.863	2.373	0.434	4.525	4.863	2.373
CEC (meq $100g^{-1}$)	43.13	8.94	1.98	5.40	0.118	10.87	7.02	10.83

were very pure and purchased from Aldrich, Germany. Stock solutions of Fipronil were equally mixed and diluted with methanol to make spiking mixture and working standard solutions. All experimental techniques were done exactly as previously carried out with the other two pesticides (Layla et al., 2015; Layla et al., 2015). The absorbance was measured at 280 nm against blank solution. A linear relationship was obtained between the absorbance and the concentration of Fipronil within the range (2 to 15 ppm) (Talli et al., 2005).

Soil analysis

Eight fresh soil samples were selected from the top layer (0 to 15 cm depth), which is supposed to have the highest organic content. The rest of all experiments and techniques were performed exactly as given before (Layla et al., 2015; Layla et al., 2015). Several tests have been conducted in Table 1.

Adsorption study

Kinetic study

Such study as before (Layla et al., 2015; Layla et al., 2015) was carried out in batch mode using 10 ml centrifuge tubes with Teflon screw caps with (1 g) of solid: solution mass ratio of (1:10) and 1 ml of 3, 5, 10, and15 µg ml^{-1} of technical Fipronil solution. The studies were first conducted in duplicate for all soils, without any Fipronil, on an orbital shaker for a period of 24 h at room temperature (298.15 ± 1 K). Then to each test tube, the appropriate concentration of pesticide was added. After equilibration for 0.5, 1, 2, 3, 6, 24, 48 and 72 h, the suspension was then centrifuged for 30 min at 3500 rpm, and 1 ml aliquot of each clear supernatant solution was removed and analyzed on UV-Visible spectrophotometer (Ban wart et al., 1972).

Desorption

After completion of the adsorption study process, the entire reaction mixture was centrifuged and the supernatant in the conical flask was decanted carefully and analyzed for the residual Fipronil concentration. The rest of all specified and related experiments were done as before (Layla et al., 2015; Layla et al., 2015).

Pesticide surfactant suspension and metal ions

The amount of each studied pesticide sample adsorbed in the presence of cationic, anionic and nonionic surfactants as well as metal ions was determined by using the batch equilibration technique. The selected surfactants comprised cationic polyacrylamide (PAM), anionic polyacrylic acid (PAA), and nonionic polyvinyl alcohol (PVA) surfactants, while metal ions included $CaCl_2$, $FeSO_4$ and $NiCl_2$. Four concentrations of each pesticides 3, 5, 10 and 15 µg ml^{-1} were used. A 24 h batch equilibrium experiment was conducted to compare and contrast differences in adsorptive properties of Fipronil. A surfactant and metal ions concentration of 3, 5, 10, and 15 µg ml^{-1} were used and air-dried soils were weighed into 15 ml stopper centrifuge tubes, the soils were then treated with the same ratio as mentioned before in kinetic study. The solutions of surfactants were equilibrated by shaking for 24 h for pesticides in mechanical shaker thermostatted at 25°C the time had previously been confirmed to be sufficient for equilibrium to be reached. Following equilibration, the suspensions were centrifuged for 30 min at 3500 rpm. To determine the pesticide concentration at equilibrium, a 1ml aliquot of clear supernatant solution was removed and analyzed by UV. All measurements were carried out in duplicate (Chen et al., 2006).

RESULTS AND DISCUSSION

Effect of time on concentration of Fipronil

Figure 2 illustrates the concentration of controlled solution during the period of the batch experiments for Fipronil. It is clear that there was no significant loss of pesticide from the solution during the experiments carried out by the used equipment (Shariff, 2011).

Effect of concentration of Fipronil on adsorption of soils

As previously reported for both Cypermethrin and Bispyribac-sodium (Layla et al., 2015; Layla et al., 2015) results of Fipronil, showed exactly that an extremely rapid rate of the pesticide being removed from solution within the first few hours of the 24 h sorption experiments. Whilst, a second phase of slow sorption appeared to occur as well over the remaining 48 h of the experiment, the duration of which presides any definite conclusions on long term sorption phenomena (Shariff, 2011). Again, this suggests that the 24 h "equilibrium" distribution coefficients may be adequate to characterize the sorption of these chemicals in the field. So sorption coefficients which were derived by using batch techniques that gave the reproducible results are unaffected by losses arising from the sorption to the experimental apparatus (Sharma et al., 2013).

Kinetics study of adsorption on soils

Sorption rate constants were estimated by using the first order rate expression for the pesticide (Griffin and Jurinak, 1973; Shariff and Hassan, 2012) which can be formulated as:

$$C_t = C_0 e^{-K_1 t} \tag{1}$$

$$K_1 = \left(\frac{2.303}{t}\right) \log \left[\frac{C_0}{C_0 - C_t}\right] \tag{2}$$

Where k_1 is the rate constant (h^{-1}), t the time (h), C_0 the initial concentration of pesticide (µg ml^{-1}) and C_t the amount adsorbed (µg ml^{-1}) at time t. In all cases, first order equation provided satisfactory fit for the data by linear plots of $\log(C_0\text{-}C_t)$ according to Mondal et al. (2013).

The calculated values of k_1 were summarized in Table 2 for Fipronil. Values of k_1 were determined also graphically from the slope of a linear plot of log (C_0-C_t) against t. Figure 3 illustrates the final results which support that the adsorption of the studied pesticides followed first order kinetics; such results are in accordance with those obtained for other system. The calculated K_1 values were oscillated from 0.54 to 2.97, for Fipronil. This can be attributed to the value of octanol water partition coefficient K_{ow} 4.01 for Fipronil. The standard error (S.E) values were from 0.0001 to 0.078 for Fipronil. Results indicated that adsorption occurred across organic matter and its chemistry that related to the selected soils.

Adsorption isotherm

The most simple and widely used model of the equilibrium adsorption isotherms is that given by a linear relationship, by which it is assumed that the amount of the solute adsorbed by the soil matrix and the concentration C_s of the solute in the soil solution is given by the relationship:

$$K_d = C_s / C_e \tag{3}$$

Where all symbols were identified elsewhere (Layla et al., 2015; Layla et al., 2015). The K_d values for Fipronil were ranged from 9.032 to 16.950 ml g^{-1} (Table 3).

The adsorption isotherms are well fitted to the Freundlich model. It can be expressed as:

$$C_s = K_f C_e^n \tag{4}$$

All symbols are given in Konda (2002). Adsorption isotherm parameters were calculated by using the linearized form of Freundlich equation:

$$log\ Cs = log\ K_f + n\ log\ Ce \tag{5}$$

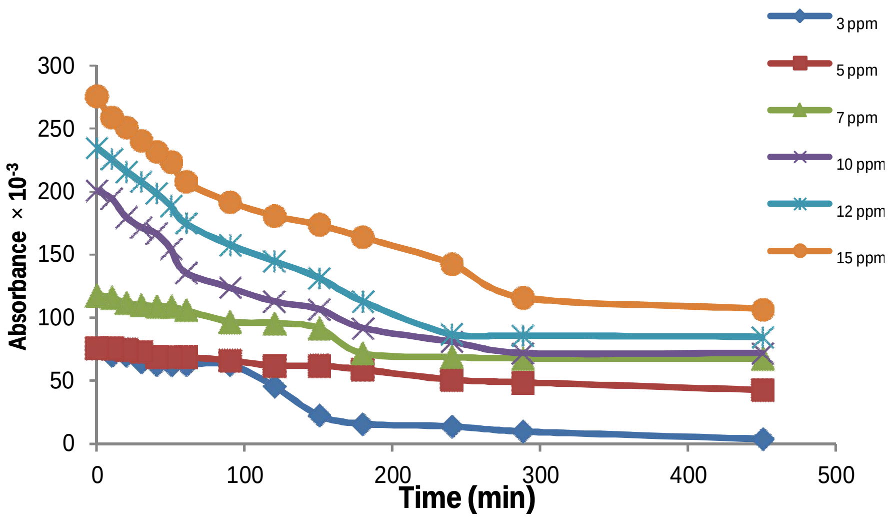

Figure 2. Variation of absorbance with time for Fipronil.

Table 2: Adsorption rate constants calculated for Fipronil on the selected soil samples.

Soil	Conc (ppm)	K (calc h^{-1})	S.E	R^2	Soil	Conc (ppm)	K (calc h^{-1})	S.E	R^2
S_1	3	0.54	0.024	0.73	S_5	3	0.69	0.02	0.98
	5	0.62	0.018	0.8		5	0.88	0.009	0.76
	10	0.67	0.014	0.85		10	1.18	0.004	0.73
	15	0.83	0.0001	1		15	1.32	0.003	0.78
S_2	3	1.12	0.013	0.77	S_6	3	1.1	0.01	0.78
	5	1.29	0.009	0.99		5	1.29	0.007	0.77
	10	1.33	0.005	0.93		10	1.56	0.005	0.76
	15	1.45	0.005	0.9		15	1.7	0.004	0.76
S_3	3	0.79	0.031	0.71	S_7	3	1.7	0.004	0.76
	5	0.89	0.018	0.67		5	2.97	0.013	0.7
	10	0.5	0.008	0.75		10	0.79	0.078	0.78
	15	1.17	0.006	0.99		15	1.17	0.003	0.75
S_4	3	0.55	0.019	0.92	S_8	3	1.3	0.002	0.95
	5	0.58	0.02	0.89		5	1.07	0.011	0.72
	10	0.79	0.012	0.81		10	1.23	0.007	0.97
	15	0.69	0.019	0.85		15	1.49	0.008	0.9

Values of K_f calculated from the linearized form of Equation 5 by plotting of log C_s versus log C_e, were also summarized in Table 3. K_f values oscillated between 13.813 and 54.954 ml g^{-1} and their trend of K_f are in the following order: $S_8 > S_3 > S_2 > S_6 > S_5 > S_7 > S_1 > S_4$.

Data from the batch adsorption on the selected soil samples will conform to Langmuir equation (Samriti, 2007) by:

$$C_s = C_m \frac{K_l C_e}{1 + K_l C_e} \qquad (6)$$

Where C_s and C_e are defined before, C_m is the maximum amount of pesticide adsorbed (adsorption maxima μg g^{-1}), and it reflects the adsorption capacity and K_l is Langmuir adsorption coefficient, (binding energy coefficient) (mlg^{-1}). The linear form of Langmuir equation is:

$$\frac{C_e}{C_s} = \frac{1}{C_m K_l} + \frac{C_e}{C_s} \qquad (7)$$

Values of K_l were obtained by plotting C_e/C_s versus C_e,

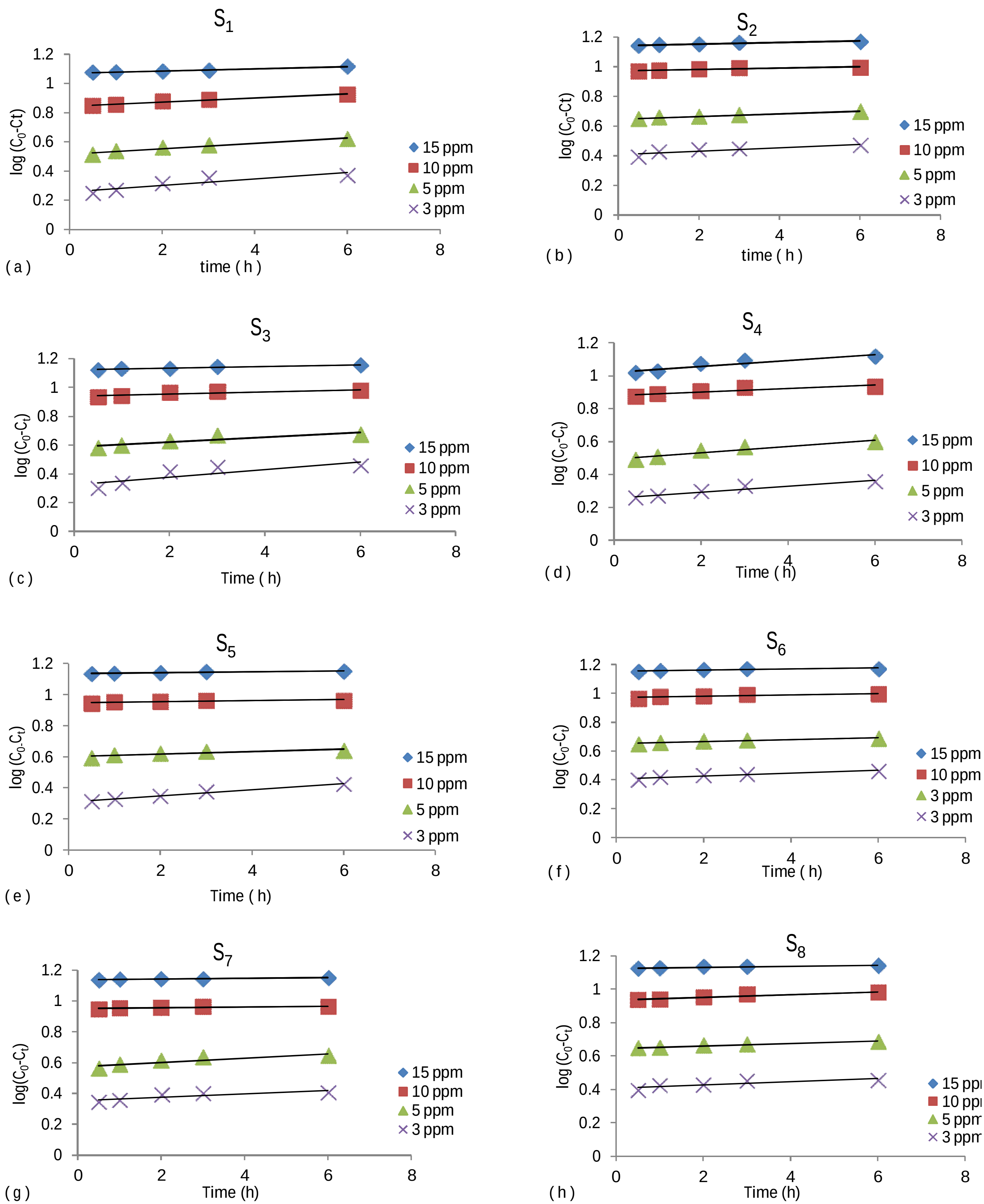

Figure 3. Application of 1st order rate law for Fipronil on the selected soil samples (a) S_1, (b) S_2, (c) S_3, (d) S_4, (e) S_5, (f) S_6, (g) S_7, and (h) S_8.

Table 3. Adsorption isotherm parameters for the linear, Freundlich and Langmuir models for Fipronil.

Adsorption model	Parameter	Soils							
		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
Distr. coffi.	K_d (calc.)	16.95	12.922	11.157	14.976	11.675	9.032	11.102	14.733
	S.E	2.668	2.378	2.644	2.653	2.493	2.652	2.668	2.54
	R^2	0.874	0.946	0.947	0.944	0.97	0.974	0.952	0.98
Freundlich	K_f (ml g^{-1})	14.521	24.694	37.316	13.813	21.071	24.547	18.416	54.954
	S.E	0.155	0.159	0.155	0.155	0.152	0.166	0.156	0.154
	n	0.774	1.132	0.493	0.665	0.64	2.551	0.629	0.868
	R^2	0.825	0.926	0.727	0.907	0.948	0.957	0.883	0.989
Langmuir	K_l (ml g^{-1})	0.354	1.819	1.353	1.53	0.675	2.381	0.688	1.11
	S.E	0.003	0.009	0.002	0.002	0.01	0.002	0.001	0.003
	C_m	16.502	19.841	47.393	21.93	25.126	31.348	40.486	90.09
	R^2	0.794	0.999	0.836	0.835	0.967	0.977	0.98	0.95

and data are tabulated in Table 3. Such values of adsorption capacity K_l ranged from 0.354 to 2.380 ml g^{-1} because they can vary among soils due to the quantities and composition of soil components (Samriti, 2007). Values of K_l for adsorption of Fipronil are in the order $S_6 > S_2 > S_4 > S_3 > S_8 > S_7 > S_5 > S_1$. The maximum amount of pesticides adsorption (C_m µg g^{-1}) ranged from 16.520 to 90.090.

Desorption kinetics

Desorption of pesticides was studied in the eight selected soil samples initially treated with different concentrations (3, 5, 10 and 15 µg ml^{-1}) of Fipronil. The amount of pesticides that remained on soils at each desorption stage was calculated as the difference between the initial amount adsorbed (the amount of pesticides sorbed at equilibrium concentration corresponding to the initial concentration) and the amount desorbed (after each removing), all determinations were carried out in duplicate.

The percentage of adsorption is calculated for each test tube at each time, according to the following equation:

$$\%\,\text{Sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (8)$$

where C_i and C_e were defined in Mohammad et al. (2006). While the percentage of desorption is calculated from Equation 9 (Al-Degs et al., 2011):

$$\%\,Desorption = \frac{amount\ \ of\ eluted\ \ pesticide}{total\ \ amount\ \ of\ adsorbed\ \ pesticide} \times 100 \quad (9)$$

Values of % Desorption for adsorption of the three pesticides on the eight selected soil samples are summarized in Table 4. In general, it is obvious that Adsorption % is increasing as concentration of pesticides increases, apart from some exception cases while desorption. This trend is in accordance with study of Adolphe and Michael (2002).

Thermodynamic studies of adsorption

Standard thermodynamic functions of adsorption

Thermodynamic is essential to understand the basic reactions in soils, but unfortunately such investigations of clay and soils are limited. This is particularly true for soils that contain complex mixtures of clay minerals, non-crystalline components, oxides, hydroxides and organic matter (Yaron et al., 2005). So adsorption experiments were conducted at 288.15, 298.15, and 308.15 K to study the thermodynamic (equilibrium) parameters, associated with the adsorption of the studied pesticides on the selected soil samples.

Equilibrium constant, K_0

The values of K_0 were obtained by plotting ln (C_s/C_e) vs. C_s and then extrapolating C_s to zero from Equation 10 (Boparai et al., 2011):

$$\ln K_0 = \ln \frac{C_s}{C_e} \quad (10)$$

The results of equilibrium constants obtained at 288.15, 298.15, and 308.15 K for soils are summarized in Table 5. It is obvious that the trend of thermodynamic

Table 4. Percentage of Fipronil adsorbed (ads%) and desorbed (% des) on the selected soil samples.

Soils	Conc. ppm	% ads	% des	Soils	Conc. ppm	% ads	% des
S_1	3	84.33	39.16	S_5	3	99.38	36.59
	5	88.79	23.94		5	98.54	24.57
	10	89.88	13.47		10	98.91	12.6
	15	87.6	12.5		15	98.67	11.86
S_2	3	99.38	68.06	S_6	3	96.15	57.82
	5	97.82	45.86		5	97.08	44.04
	10	98.19	22.93		10	94.05	25.61
	15	98.43	17.71		15	95.59	20.43
S_3	3	99.38	68.89	S_7	3	96.96	21.1
	5	98.54	46.03		5	97.69	15.96
	10	98.55	24.29		10	97.94	8.34
	15	98.79	17.97		15	98.02	7.06
]S_4	3	95.14	62.04	S_8	3	96.76	21.1
	5	95.26	49.49		5	97.57	15.96
	10	93.63	30.17		10	97.57	8.34
	15	94.66	21.29		15	97.45	7.06

Table 5. Equilibrium constants and standard free energy change at three different temperatures for adsorption of Fipronil on the selected soil samples.

T K	Parameter	Soil							
		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
T_1k	$\ln K_0$	4.8	1.2	3.6	2.8	4.6	3.2	2.4	3.1
	ΔG^0 (kJ.mol^{-1})	-11.49	-2.87	-8.62	-6.7	-11.01	-7.66	-5.74	-7.42
T_2K	$\ln K_0$	2	1	2.7	2.1	1.9	2.6	1.5	2.4
	ΔG^0 (kJ. mol^{-1})	-4.95	-2.47	-6.68	-5.2	-4.7	-6.44	-3.71	-5.94
T_3K	$\ln K_0$	0.8	0.9	2.2	1.65	1.2	2.5	0.2	1.9
	ΔG^0 (kJ.mol^{-1})	-2.04	-2.3	-5.63	-4.22	-3.07	-6.4	-0.51	-4.86

equilibrium constant K_0 is decreasing with increase in temperature for all soil pesticides interaction (Singh et al., 2011). However, for Fipronil the trend was $S_1 > S_5 > S_3 > S_6 > S_8 > S_4 > S_7 > S_2$ soils.

Standard free energy change

The standard free energy for the transfer of pesticide molecules between the solid and aqueous phases was estimated using:

$$\Delta G^o = -RT \ln K_o \quad (11)$$

Where R is the universal gas constant (J.mol^{-1}.K^{-1}) and T (K) is temperature (Seyoum et al., 2012). The values of ΔG^0 for adsorption of the studied pesticides on the selected soil samples at 288.15, 298.15, and 309.15 K were summarized in Table 5. The ΔG^0 values oscillated between -11.493 and -0.512 (kJ mol^{-1}). Values of adsorption at the three temperatures 288.15, 298.15, and 309.15 K of pesticide on soil samples were in the order: $S_1 > S_5 > S_3 > S_6 > S_8 > S_4 > S_7 > S_2$, $S_3 > S_6 > S_8 > S_4 > S_1 > S_5 > S_7 > S_2$, and $S_6 > S_3 > S_8 > S_4 > S_5 > S_2 > S_1 > S_7$, respectively.

Standard enthalpy change

The standard enthalpy change of adsorption (ΔH^o) represents the difference in binding energies between the solvent and the soil with the pesticides; which explains

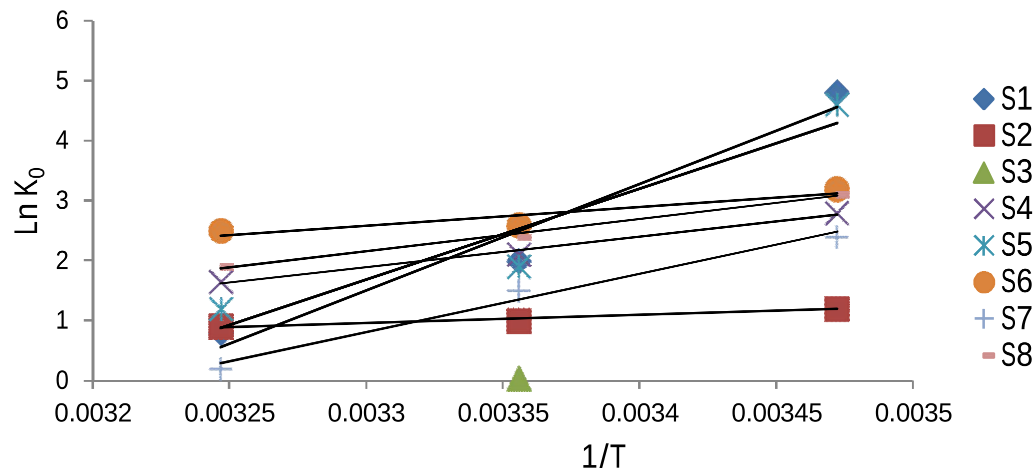

Figure 4. Variation of $\ln K_0$ with 1/T for adsorption of Fipronil.

Table 6. Standard enthalpy and entropy changes (determined graphically) for adsorption of Fipronil.

Parameters	**Soil**							
	S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
ΔH^0 (kJ.mol^{-1})	-147.5	-11.06	-51.62	-42.4	-25.81	-25.81	-81.12	-44.25
ΔS^0 (J.mol^{-1}K^{-1})	-45.97	-28.68	-150.3	-124.5	-73.82	-64.34	-260.4	-128.3
R^2	0.96	0.97	0.98	0.99	0.91	0.87	0.98	0.99

the binding strength of pesticides to the soil (Shariff, 2011). Also, the values of ΔH^0 can be determined graphically from the following equation (Chaudhary and Prasad, 1999):

$$\ln K_0 = -\frac{\Delta H^0}{RT} + \text{const} \quad (12)$$

The enthalpy of adsorption in the range 288.15 to 308.15 K was calculated from the slope of the plot of ln K_0 against 1/T as shown in Figure 4. It is obvious that a straight lines are obtained with each slope equals to -ΔH^0/R. The results are summarized in Table 6. Values of ΔH^0 ranged in from -147.500 to -11.060 kJ mol^{-1}.

The average value of the correlation factor R^2 is about 0.970 which clearly supported the linear nature of the plot. The amount of energy released during adsorption is changed because the supply of thermal energy is different. The negative values pointing to the formation of an activate complex by coordination or association between the pesticide and exchangeable cations with results loss in the degree of freedom of the pesticide. The different values of ΔH^0 for adsorption of the same pesticide on the selected soils may be correlated to differences in soil constituents (Shariff, 2011). Also, the negative values of ΔH^0 confirmed the exothermic reactions, and suggested that the most probable nature of the adsorption was physical type.

Standard entropy change

The values of standard entropy change ΔS^0 of adsorption were determined by using the following equation:

$$\ln K_0 = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (13)$$

The values of ΔS^0 were determined from the plot of $\ln K_0$ against 1/T as shown in Figure 4 from which straight lines were obtained with a slope of $-\Delta H^0$/R and intercept equals ΔS^0/R. The results were summarized in Table 6. The values of ΔS^0 followed the range -260.410 to -28.680 Jmol^{-1}K^{-1}.

Effect of surfactants and metal ions on adsorption of Fipronil

By comparing the data listed in both Tables 3 and 7, it is concluded that values of K_s for adsorption of pesticides alone in the soils than those are higher in the presence of surfactants. As a conclusion, it is obvious that the trend of adsorption enhancement is as follows: PAM > PVA > PAA. This conclusion came out from the founded fact that the results of K_s (where K_s is the Freundlich affinity constant in the presence of surfactant) increased with

Table 7. Freundlich adsorption coefficient for the adsorption of Fipronil in the presence of PAM, PVA, and PAA on the selected soil samples.

Soils	PAM			PVA			PAA		
	K_s ml g^{-1}	R^2	n	K_s ml g^{-1}	R^2	N	K_s ml g^{-1}	R^2	n
S_1	10.158	0.976	0.749	4.823	0.988	0.4	3.519	0.999	1.434
S_2	9.528	0.844	0.535	7.211	0.994	0.601	5.321	0.915	1.186
S_3	11.429	0.88	1.867	8.67	0.998	1.928	6.012	0.979	1.823
S_4	14.428	0.973	0.65	8.111	0.731	1.031	6.328	0.902	1.901
S_5	11.668	0.976	1.819	9.084	0.995	2.832	7.124	0.99	1.971
S_6	7.773	0.936	1.472	6.003	0.958	1.823	2.109	0.955	2.14
S_7	13.005	0.918	0.948	6.315	0.986	1.768	2.219	0.979	3.152
S_8	14.06	0.995	1.171	13.213	0.928	1.574	12.289	0.971	1.751

Table 8. Adsorption isotherm constants K_l, C_m and regression factor R^2 for pesticide in the presence of metal ions on the selected soil sample.

Metals	Parameter	Soils							
		S_1	S_2	S_3	S_4	S_5	S_6	S_7	S_8
	K_l ml g^{-1}	1.029	1.289	2.833	1.697	1.852	2.546	1.326	2.671
Cu^{2+}	C_m µg g^{-1}	2.063	33.003	29.412	17.857	28.571	7.077	17.544	7.257
	R^2	0.935	0.965	0.986	0.974	0.901	0.922	0.759	0.962
	K_l ml g^{-1}	0.685	0.535	0.668	0.342	1.027	1.375	0.55	0.446
Ni^{2+}	C_m µg g^{-1}	4.329	25.189	12.739	51.813	7.905	5.862	29.586	39.216
	R^2	0.914	0.906	0.853	0.73	0.994	0.826	0.838	0.86
	K_l ml g^{-1}	0.626	0.578	0.469	0.57	0.906	0.708	0.385	0.598
Fe^{2+}	C_m µg g^{-1}	23.148	11.013	9.174	5.302	6.998	9.625	11.013	1.595
	R^2	0.9	0.981	0.974	0.804	1	0.995	0.979	0.945

respect to those obtained in surfactant free system.

The results in Table 8 showed that Langmuir isotherm K_l values for Fipronil in presence of Cu^{2+}, ranged from 1.029 to 2.833 ml g^{-1}, C_m values ranged from 2.063 to 33.003 µg g^{-1}, and with coefficients of determination R^2 ranging from 0.759 to 0.986. While those values in presence of Ni^{2+} ranged from 0.342 to 1.375 ml g^{-1}, C_m values ranged from 4.329 to 51.813 µg g^{-1}, and with coefficients of determination R^2 ranging from 0.730 to 0.994. But values of Langmuir isotherm K_l for Fipronil in presence of Fe^{2+} values ranged from 0.385 to 0.906 mlg^{-1}, C_m values ranged from 1.595 to 23.148 µg g^{-1}, and with coefficients of determination R^2 (correlation factors) ranging from 0.804 to 1.000. So, the trend of adsorption process in the presence of metal ions is in the order: $Cu^{2+} > Ni^{2+} > Fe^{2+}$.

Conclusions

The batch kinetics experiments were used to investigate the behavior of Fipronil in eight agricultural soil samples. Generally, adsorption increased with concentration, the initial step was characterized as rapid and low energy while the second step was slow and high energy accompanied by slow diffusion to sites within the soil matrix. The magnitude of all K_d, K_f and K_l values were indicated as moderate to low adsorption for all pesticides. Freundlich model more accurately predicted the behavior of pesticides desorption. The values of ΔG^0 increased with rise in temperature.

REFERENCES

Adolphe M, **Michael** S, **2002**. Sorptive behavior of the phenylamide fungicides, mefenoxam and metalaxyl, and their acid metabolite in typical Cameroonian and German soils. Chemosphere, 49(6): 659-668.

Al-Degs YS, El-Sheikh AH, Jaber ST, **2011**. Application of heated date seeds as a novel extractant for diuron from water. Arab J Chem, 6(1): 121–129.

Amrith S, **Tresca** T, **2007**. Environmental Fate of Fipronil, Review. California Environmental Protection Agency.

Ban wart WL, Tabatubi MA, Bremner JM, **1972**. Detemonia of ammonium in soil extracts and water samples by an ammonia electrode. Common Soil Sci Plant Anal, 3: 449-458.

Bobe A, Cooper J, Coste CM, Marie-Anne M, **1998**. Behavior of Fipronil in soil under Sahelian plain field conditions. Pest Sci, 52: 275-281.

Boparai HK, Joseph M, O'Carroll DM, **2011**. Kinetics and thermodynamics of cadmium ion removal by adsorption onto nanozerovalent iron particles. J Hazard Mater, 186:458–465.

Chaudhary K, **Prasad** B, **1999**. Thermodynamics of potassiume exchange rection in entisol and vertisol using a kinetic approach by miscible displacement technique. J Ind Soc So Sci, 47(2): 221-229.

Chen J, Xue-Jun W, Hun-dong, Fu-Liu X, Tao S, **2006**. Numerical Simulation of PAHs Sorption/Desorption on Soil with the Influence of Tween80. J Environ Sci, 18(4):716-720.

Griffin RA, **Jurinak** JJ, **1973**. Test of a new model for the kinetics adsorption-desorption processes. Soil Sci Oc Am Proc, 37:869-872.

Konda LN, **2002**. Investigation of sorption behavior of organic pesticides on soil. Doctoral Program in Environmental Science, Szent Istvan University.

Layla BA, Anis AA, Zaki NK, **2015**. Adsorption and desorption characteristics of bispyribac-sodium pesticide in eight soil in south of Iraq. Int J Sci Eng Res, 6(7): 1689-1700.

Layla BA, Anis AA, Zaki NK, **2015**. Chemical kinetic and thermodynamic of adsorption-desorption of cypermethrin in the soil of South Iraq. Int J Adv Res Technol, 4(9): 17-25.

Mohammad R, Seyed M, Kamyar K, **2006**. Determination of Fipronil residue in soil and water in the rice fields in north of Iran by RP-HPLC method. Acta Chim Slov, 53: 517-520.

Mondal NK, Soumya C, Bikash S, Biswajit D, Songklanakarin, **2013**. Evaluation of carbaryl sorption in alluvial soil. J Sci Technol, 35(6): 727-738.

Samriti S, **2007**. Impact of soil organic matter heterogeneity and soil aggregation on the sorption of herbicides by soils. New Brunswick, New Jersey.

Seyoum YG, Beutel MW, Markus F, Harsh JB, **2012**. Nonsingular adsorption/desorption of chlorpyrifos in soils and sediments: Experimental results and modeling. Environ Sci Technol, 46: 869–875.

Shariff RM, **2011**. Thermodynamic adsorption-desorption of metolachlor and 2,4-D on agricultural soils. Int J Chem, 3(4): 134-146.

Shariff RM, **Hassan** MA, **2012**. Kinetic study of adsorption-desorption of simazine on agricultural soils. Int J Eng Res Dev, 4(12):01-09.

Sharma DK, Gupta A, Kumar N, Gupta A, **2013**. Soil adsorption study of dimethoate to evaluate its leaching potential by spectrophotometry. Arch Environ Sci, 7: 6-14.

Singh RP, Sujata S, Garima S, **2011**. Effect of surfactants on the adsorption and movement of carbaryl in soils. Pest Res J, 1-16.

Talli I, Elke S, Benny C, **2005**. Interactions of organic compounds with wastewater dissolved organic matter: Role of hydrophobic fractions. J. Environ. Qual., 34:552-562.

Tingle C, Rother J, Dewhurst C, Lauer S, King W, **2000**. Health and Environmental Effects of Fipronil. Pesticide Action Network UK.

Yaron D, Zeev A, Benny C, **2005**. Sorption, Desorption Behavior of Atrazine in Soils Irrigated with Reclaimed West Water. Soil Sci Soc Am J, 69:1703–1710.

Citation: Almalike LB, Al-Najar AA, Kadhim ZN, 2016. Physical characteristics of adsorption–desorption of Fipronil in the soil. Afr J Eng Res, 4(2): 26-35.