Research Journal of

Environmental Toxicology

ISSN 1819-3420

Academic
Journals Inc.

www.academicjournals.com

Research Journal of Environmental Toxicology 5 (1): 39-48, 2011
ISSN 1819-3420 / DOI: 10.3923/rjet.2011.39.48

Sorption Kinetics of 2,4-Dichlorophenoxyacetic Acid in Selected Agricultural Soils of Malaysia

[1]Mehdi Sameni, [1]B.S. Ismail and [2]M. Halimah
[1]School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi, Selangor, Malaysia
[2]Malaysian Palm Oil Board, P.O. Box 10620, 50720 Kuala Lumpur, Malaysia

Corresponding Author: B.S. Ismail, School of Environmental and Natural Resource Sciences, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, Tel: 603 89214183, +60192804174 Fax: 603 89252699

ABSTRACT

The aim of this study was to investigate the sorption kinetics and effects of pH, concentration and temperature on the adsorption of 2,4-D onto soil. Two types of Malaysian ricefield soils were used for this study; namely clay loam and clay soil obtained from the Kerian ricefields in Perak. Agriculture in North West Malaysia relies on the widespread use of herbicides to promote crop performance. Over-application of many herbicides is commonplace, however and may compromise soil and water quality and ultimately human health, within the region. Adsorption experiments were conducted using a batch equilibration technique. The HPLC-UV were used to detect 2,4-D residues in the supernatant. Adsorption equilibrium time was achieved within 2 and 4 h for the clay loam and clay soils, respectively. The percentage of 2,4-D adsorption onto soil was found to be higher in clay loam than in clay soils. Results of the study demonstrated that adsorption of 2,4-D in both soil types was higher at low pH and with increased pH the adsorption decreased. Likewise, the adsorption of 2,4-D was found to be sensitive to temperature, with low temperature significantly increasing the adsorption capacity of the soil. Results also suggested that 2,4-D sorption by soil is concentration dependent.

Key words: Adsorption, pH, temperature, equilibrium time and 2,4-dichlorophenoxyacetic acid

INTRODUCTION

Among the numerous agrochemicals being used, 2,4-Dichlorophenoxy acetic acid (2,4-D), a member of the phenoxy herbicide group, has been widely applied to control broad leaf weeds (Simard and Legere, 2002; Grotzschel *et al.*, 2004). It is widely used as a herbicide in Malaysian agriculture to control a wide range of broad leaf weeds in such crops as rice, oil palm, cocoa and rubber (Cheah *et al.*, 1997; Akma *et al.*, 2009). 2,4-D is generally preferred by farmers because of its low cost and good selectivity. It is considered moderately toxic to humans; the maximum allowable concentration in drinking water is 100 ppb (Hameed *et al.*, 2009).

While 2,4-D has been proven useful as a chemical herbicide, its impact on environmental contamination is of great concern because it has been suspected to cause endocrine disruption (Rawlings *et al.*, 1998). Contamination by 2,4-D has been reported in groundwater aquifers and surface water (Wood and Anthony, 1997; Balinova and Mondesky, 1999) and this finding has led to the study of the mechanism for its adsorption in soils.

This study presents a study of the adsorption equilibrium time and the effects of pH, temperature and concentration of 2,4-D in the soil. Two types of Malaysian ricefield soils were used in this study, namely clay loam and clay soil, obtained from the Kerian ricefields. Adsorption of 2,4-D by the soils was studied at the low 2,4-D concentrations that are likely to occur in the soil environment (mostly <10 mg L^{-1}). The standard application rate of 2,4-D on an agricultural field in 0.28 to 2.3 (kg ha^{-1}) (Tomlin, 2003).

MATERIALS AND METHODS

Reagents: All reagents used in the present study were of analytical grade. Methanol and hydrochloric acid were obtained from Merck and 2,4-D standard of 99.7% purity was purchased from the laboratories of Dr. Ehrenstorfer Co., Germany.

HPLC condition: An Agilent HPLC 1100 Series fitted with a UV detector set at 214 nm was used. The column used was C_8-NH_4 (4.6 mm I.D.×250 mm length, 5 μm particle size). The mobile phase was MeOH and buffer (H_2O with + potassium sodium 3.4 g L^{-1} + hydrochloric acid in pH 2.3), in the ratio of 30:70. The flow rate of the mobile phase and injection volume were 1 mL min^{-1} and 20 μL, respectively.

Preparation of soil: The experiments were conducted with two soils types, clay loam and clay soil, which had been collected from a depth of 0-15 cm from the Kerian rice fields. The top layer of soil was collected from an area of about 100×100 cm, air dried and sieved through a 2 mm mesh sieve to remove debris and large particles. The sieved soil samples were stored at 4°C to minimize the effects of microbial activity. Soil was analyzed and the characteristics of each soil are presented in Table 1. The clay soil was determined to have more than 22% higher clay content than the clay loam soil. The clay loam soil had total carbon content more than 64% higher than the clay soil. All soil data are expressed on a dry weight basis.

Determination of adsorption equilibrium time: The equilibrium time of 2,4-D in the soil samples was evaluated. The adsorption values for the two soil types were determined in accordance with the batch equilibrium method as described by Walker and Exposito (1998).

Two g samples of each soil type were air dried, sieved and put into 27 centrifuge tubes. Ten mL of 2,4-D at 10 μg mL^{-1} were added into each test tube and the mixtures were shaken for 1, 2, 4, 5, 6, 7, 8, 9 and 13 h, using an orbital shaker at 150 rpm. Then, the tubes (with the mixtures) were centrifuged at 3500 rpm for 20 min until the separation of the liquid and solid phases occurred.

The concentration of 2,4-D in the clear supernatant was determined using HPLC. The experiments were repeated thrice and the average values were recorded. A blank without 2,4-D was also analyzed. The amount of adsorption at equilibrium, q_e (g g^{-1}), was calculated using the formula below:

Table 1: Physico-chemical properties of the selected clay loam and clay soils

Soil type	pH	Organic carbon (%)	Coarse sand (%)	Fine sand (%)	Silt (%)	Clay (%)	Bulk density (g cm^{-3})
Clay loam	5.82	5.94	3.13	31.04	26.76	39.07	1.29
Clay	6.17	2.10	8.20	13.03	28.51	50.26	1.24

$$q_e = \frac{(C_O - C_e)V}{W}$$

where, C_0 and C_e (mg L^{-1}) represent the liquid-phase concentrations of 2,4-D at the initial stage and at equilibrium, respectively; V (mL) is the volume of the solution and W (g) the mass of dry adsorbent.

Effect of concentration on adsorption: Two grams each of dried and sieved soil were put into 12 test tubes. Then, 10 mL of 2,4-D at 2, 4, 6 or 8 μg mL^{-1} were added separately into test tubes with three replications for each concentration. A blank containing no 2,4-D was also prepared. The mixtures were shaken for equilibrium time using an orbital shaker at 150 rpm. The suspensions were then centrifuged at 3500 rpm for 20 min to separate the liquid and solid phases. The concentration of 2,4-D in the clear supernatant was determined using HPLC.

The results from the sorption experiments were evaluated by the Freundlich equation, $S = K_f C^{1/n}$, rewritten as $\log S = \log K_f + (1/n) \log C$, where S is the amount of herbicide sorbed to the soil. The difference between the initial and final herbicide concentration (after equilibration) was used to estimate the sorbed amounts in μg g^{-1} soil; C is the concentration (μg mL^{-1}) of the herbicide in the water phase after equilibrium; K_f is the Freundlich sorption coefficient; and 1/n is the slope of the sorption isotherm.

Effect of pH on adsorption: Ten milliliter of 2,4-D at 10 μg mL^{-1} solution were added to a test tube containing 2 g of the soil. The pH of the solution was adjusted either to 3, 7 and 10 using diluted HCl and NaOH. All sample preparations were carried out in triplicate. The test tubes and their contents were shaken using a shaker at 150 rpm. The tubes were subjected to 2 and 4 h of shaking for the clay loam and clay soils, respectively. Each experiment was repeated thrice. The test tubes (with the mixture) were centrifuged at 3000 rpm for 20 min. The concentration of 2,4-D in the supernatant was determined using HPLC.

Effect of temperature on adsorption: The experiment was carried out using the batch adsorption equilibrium method. The concentration of the herbicide solution used was 2 μg mL^{-1} and the incubation temperature was either 30, 35 or 40°C. Each treatment was done in triplicate. The resultant supernatant was collected for analysis by HPLC.

Statistical analysis: All the experiments were carried out in completely randomized block designs with three replications. All data were statistically analyzed with single factor Analysis of Variance (ANOVA). Any significance reported represents $p = 0.05$.

RESULTS AND DISCUSSION

Adsorption equilibrium time: Figure 1 shows the amount of 2,4-D adsorbed by soil at different time intervals. 2,4-D adsorbed on to soil decreases with increase of time. Adsorption equilibrium times of 2,4-D in clay loam and clay soils were characterized by an initial rapid adsorption, which eventually reached a constant and this could be due to limited surface on the soil particles for 2,4-D adsorption. Kumar and Philip (2006) have reported that the rate of adsorption of endosulfan was not significant after the short initial phase of rapid sorption, perhaps due to limited soil surface for adsorption of the pesticide on to the soil particles. It was also observed that there was a rapid

Table 2: The amount of adsorption ($\mu g\ g^{-1}$) and the percentage adsorption of 2,4-D in clay and clay loam soils

Soil	Initial amount ($\mu g\ mL^{-1}$)	Amount absorbed	
		$\mu g\ g^{-1}$	%
Clay loam	2	8.20±0.17	82.00
	4	17.44±0.10	87.21
	6	26.25±0.08	87.51
	8	35.30±0.20	88.24
Clay	2	7.13±0.06	71.28
	4	5.44±0.11	77.21
	6	23.93±0.10	79.76
	8	32.46±0.23	81.14

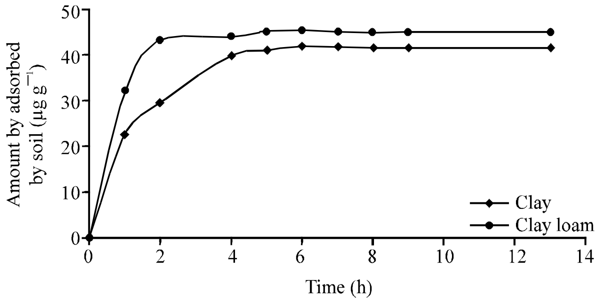

Fig. 1: Adsorption equilibrium times of 2,4-D on clay and clay loam soils. SD±3%

adsorption of 2,4-D to the clay loam soil in the initial 2 h. The adsorption of 2,4-D then became very slow and reached a constant after 2 and 4 h for clay loam and clay soils, respectively. The amount of 2,4-D adsorbed onto the soil after equilibrium time was about 79.28 and 87.56% for clay and clay loam soil, respectively. It was observed that the adsorption of 2,4-D was higher in the clay loam soil with its higher level of organic matter than in the clay soil. After equilibrium time no significant adsorption was observed. Standard deviations were found to be within ±3%. Further, the error bars for the figures were very small (smaller than the symbols used to plot the graphs) and hence are not shown.

Effect of 2,4-D concentration on adsorption: Preliminary studies showed that 2,4-D attained equilibrium at 2 and 4 h by adsorption onto clay loam and clay soils, respectively. Table 2 shows that the amount of 2,4-D adsorbed onto the clay loam was 8.2, 17.44, 26.25 and 35.30 ($\mu g\ g^{-1}$) at concentrations of 2, 4, 6 and 8 $\mu g\ mL^{-1}$, respectively, whereas in the clay soil, the percentages adsorbed were 71.28, 77.21, 79.76 and 81.14% for the same respective concentrations. The percentage 2,4-D adsorbed was higher in clay loam than in clay soils.

The fact that more 2,4-D was adsorbed in the clay loam than in the clay soil may be due to the high organic matter content in the clay loam soil. This is attributed to the fact that soil organic matter content plays a major role in the adsorption of organic compounds in the soil, as has been noted in previous studies (Ismail *et al.*, 2002; Kah and Brown, 2007; Gaultier *et al.*, 2008).

Analysis of variance confirmed that the 2,4-D adsorbed was significantly affected by the different levels of concentration in both the soil types ($p<0.05$), confirming the results of Vinod *et al.* (2006).

The sorption coefficient (K_d) was obtained using the equation:

$$C_s = K_d \times C_{aq}$$

Where:

C_s = Mass of solute adsorbed per unit mass of adsorbent, as μg g^{-1}
K_d = Adsorption constant, as mL g^{-1}
C_{aq} = Measured solute concentration in solution at equilibrium, as μg mL^{-1}

The K_d values for the clay and clay loam soils are shown in Table 3. The Freundlich sorption coefficient (K_f) was derived from the interception of the linear form of the Freundlich equation

$$(\text{Log}\,[C_s] = \text{Log}\,K_d + 1/n\,\text{Log}\,[C_{aq}])$$

and the Freundlich sorption exponent (1/n) from the slope. The extent of sorption and the curvature of the isotherm are described by the K_f and the 1/n values, respectively. The 1/n values, which are the values for the slope of the line, were obtained using the least square fit (Fig. 2, 3) of the adsorption isotherm; the values are shown in Table 3.

The 1/n values observed for the clay loam and clay soils were below unity, indicating that the relative adsorption decreased with increasing solution concentration (Cheah *et al*., 1997). The

Table 3: Percent organic matter (OM), K_{oc}, Distribution coefficient (k_d) and Ferundlish constants (k_f and n) for the adsorption of 2,4-D in soils

Soil	%OM	K_{oc}	R^2	K_f	1/n	K_d
Clay loam	5.94	569.36	0.98	31.52	0.85	33.83
Clay	2.10	862.85	0.99	18.33	0.74	18.12

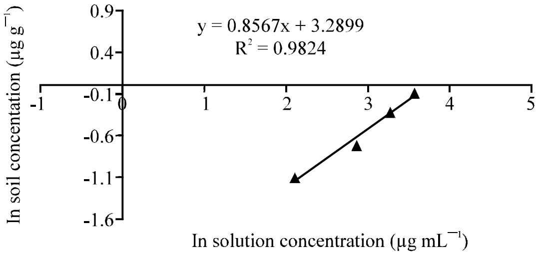

Fig. 2: Freundlich adsorption isotherm of 2,4-D in the clay loam soil at room temperature

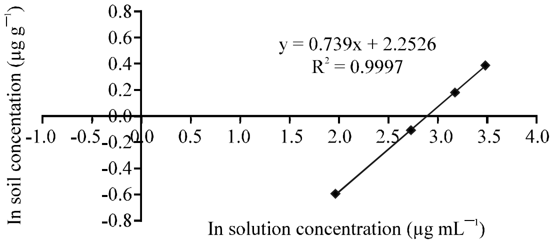

Fig. 3: Freundlich adsorption isotherm of 2,4-D in the clay soil at room temperature

results conformed to the percentages of 2,4-D adsorbed to the clay and clay loam soil, as shown in Table 3. A similar observation has been made by Vinod *et al.* (2006).

The correlation coefficients for clay and clay loam soil were 0.99 and 0.98, respectively, at room temperature. The study found that the K_d of the clay loam soil was higher than that of the clay soil, possibly due to the higher organic matter content in the clay loam soil (Table 3), confirming the results of Shareef and Shaw (2008). The normalized sorption coefficient (K_{oc}) for organic matter was also calculated for each soil and concentration individually, using the equation:

$$K_{oc} = K_d \times 100/OC$$

where, OC is the content of organic carbon in the soil expressed as %.

The K_{oc} values of 569.36 and 862.85 Lkg^{-1} were determined for the clay loam and clay soils, respectively (Table 3). Typically, highly soluble pesticides such as 2,4-D are more weakly adsorbed in a given soil than those with low solubility. Figure 2 and 3 show the best fit Freundlich adsorption isotherm for the clay and clay loam soils studied. Association with soil organic matter is commonly assumed to be a major mechanism of pesticide sorption in soil and thus the K_{oc} is commonly calculated as a measure of pesticide sorption to soil organic matter.

Figure 4 shows that increasing the 2,4-D concentration from 2-8 $\mu g\ mL^{-1}$ resulted in an increase in the K_d values by 46% greater for clay loam than for clay soil. The organic matter content levels of these soils were 5.94 and 2.10% for the clay loam and clay soils, respectively. A previous study Shareef and Shaw (2008) on 2,4-D found that adsorption was positively correlated with soil organic matter content.

Effect of pH on adsorption: Soil pH is largely controlled by fine soil particles and their associated exchangeable cations. The effect of pH on adsorption of 2,4-D on clay and clay loam soils was investigated at varying pH values of 3, 7 and 9 (Fig. 5). Results showed that pH affected the

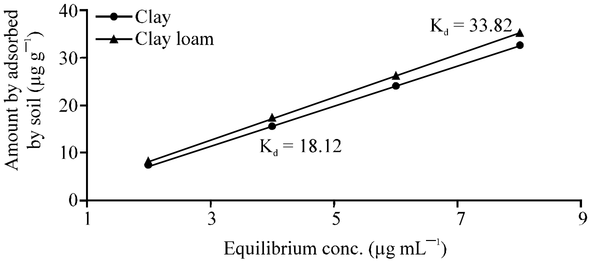

Fig. 4: Adsorption isotherms of 2,4-D in clay and clay loam soil

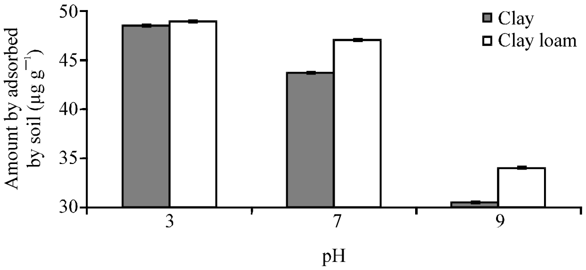

Fig. 5: Effect of pH on the adsorption of 2,4-D on clay and clay loam soils

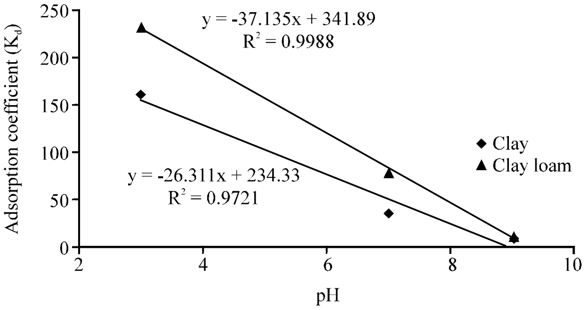

Fig. 6: Relationship of adsorption (K_d) and soil pH

adsorption of 2,4-D on clay and clay loam soils. It was observed that the adsorption of 2,4-D was higher at low pH for both soil types. At pH 9, the amounts of 2,4-D adsorbed on to the clay loam and clay soil were 34.00 and 30.52 $\mu g\ g^{-1}$, respectively. Analysis of Variance (ANOVA) confirmed that there were significant effects ($p = 0.05$) of pH on the adsorption of 2,4-D in clay loam and clay soils. Johnson *et al.* (1995) and Hameed *et al.* (2009) showed that adsorption of the phenoxy acid 2,4-D was lower at pH 7 than at pH 5. Results showed that the amount of 2,4-D adsorbed onto clay loam at varying pH was higher than that onto clay soil (Fig. 5).

As with other acidic pesticides, the decrease in adsorption of 2,4-D as soil pH increased is due to the lower adsorption potential of the dissociated anionic form compared with the undissociated molecular form (Nicholls and Evans, 1991; Akma *et al.*, 2009). Thus, adsorption coefficients were log-transformed to evaluate whether they formed a linear pattern against soil pH, which is to be expected for acid dissociation at pH values around the P_{ka} (Dyson *et al.*, 2002). With the amphoteric compounds imazaquin and imazethapyr containing acid and basic functional groups, adsorption has been found to decrease as soil pH rose from 3 to 9 (Loux and Reese, 1992). In addition, organic matter content can also account for some of the variance in adsorption not accounted for by soil pH, particularly since the molecular form is likely to adsorb to organic matter. Indeed, in 21 soils with a pH ranging from 6 to 8, Fontaine *et al.* (1991) demonstrated that the relationship between soil pH and the adsorption of the weak acid flumetsulam only became clear when plotted against the adsorption coefficient, K_{oc}, adjusted for organic carbon content. Thus, in this study organic carbon adsorption (K_{oc}) was also plotted against soil pH. Figure 6 shows that for clay and clay loam soil the K_d value decreased as soil pH increased.

The R^2 value of more than 0.97 is consistent with the claim that soil pH has a strong influence on adsorption of 2,4-D onto the soil. Johnson *et al.* (1995) showed that adsorption of the phenoxy acid 2,4-D was lower at pH 7 than at pH 5.

Figure 7 shows that the K_{oc} value decreased as soil pH increased. This confirms that soil pH and organic carbon are the soil properties predominantly responsible for most of the behavior of adsorption in soils. Walker *et al.* (1989) found similar results in a study on chlorsulfuron and metsulfuron-methyl adsorption in 23 soil samples, in which adsorption was correlated negatively with soil pH and positively with organic carbon.

Effect of temperature on adsorption: Figure 8 shows that the adsorption of 2,4-D onto the soil decreases as the temperature increases from 30 to 40°C. In the adsorption process, soil temperature could have a direct effect on the phase distribution of pesticides. Adsorption usually increases as temperature decreases and desorption is favored by increasing temperature. Furthermore,

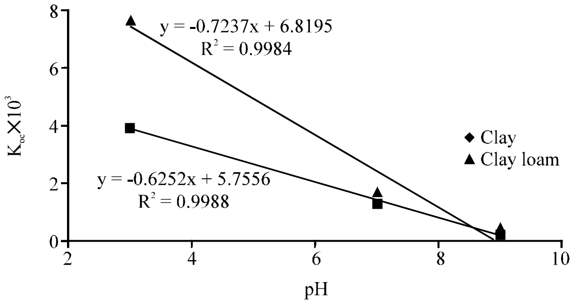

Fig. 7: Adsorption (K_{oc}) and soil pH

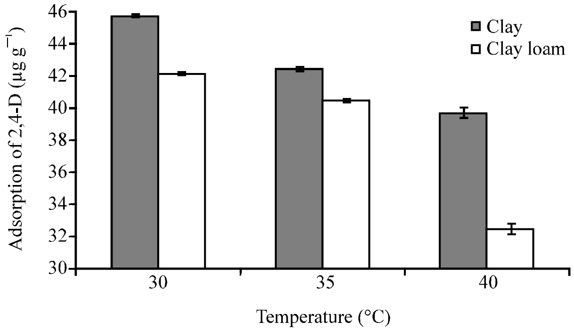

Fig. 8: Effect of temperature on the adsorption of 2,4-D in clay and clay loam soils

Table 4: The amount of adsorption ($\mu g\ g^{-1}$) and the percentage adsorption of 2,4-D at 30, 35 and 40°C in clay loam and clay soils

	Clay loam		Clay	
	Amount absorbed		Amount absorbed	
Temperature (°C)	$\mu g\ g^{-1}$	%	$\mu g\ g^{-1}$	%
30	45.70±0.08	91.40	42.09±0.09	84.19
35	42.45±0.10	84.89	40.40±0.16	80.81
40	39.66±0.32	79.31	32.48±0.33	64.97

temperature could indirectly influence adsorption by its effect on pesticide-water interactions (Vinod *et al*., 2006).

The amounts of 2,4-D adsorbed onto the clay and clay loam soils at 30, 35 and 40°C are shown in Table 4. The amounts of 2,4-D adsorbed onto the clay soil at 10 $\mu g\ mL^{-1}$ was 42.09, 40.40 and 32.48 ($\mu g\ g^{-1}$) at temperature of 30, 35 and 40°C, respectively, whereas in the clay loam soil, the percentage absorbed was 91.40, 84.90 and 79.31% at the same respective temperatures. The percentage 2,4-D adsorbed was higher in the clay loam than in the clay soils at all temperatures.

The statistical Analysis of Variance (ANOVA) confirmed that the amount of 2,4-D adsorbed was significantly affected by the different levels of temperature in both the soil types ($p<0.05$), the amount of 2,4-D adsorbed by clay loam being slightly higher than that adsorbed by the clay soil (Fig. 8), confirming the results of Hameed *et al*. (2009).

Adsorption isotherms obtained by the reduced concentration method showed, in contrast to normal adsorption isotherms, an increase in adsorption with increasing temperature, suggesting that the heat effect involved in the adsorption process was mainly influenced by the solubility of

Table 5: Sorption coefficient (K_d), K_{oc} and K_f of clay and clay loam soils at 30, 35 and 40°C

Soil	Temperature (°C)	K_{oc}	K_d	K_f
Clay loam	30	895.62	53.20	17.77
	35	473.06	28.10	6.60
	40	322.73	19.17	2.31
Clay	30	1267.62	26.62	10.81
	35	1002.38	21.05	5.84
	40	441.42	9.27	1.27

the solute. Similar results, emphasizing the significant effect of temperature on adsorption through its solubility effect, have been obtained by Vinod *et al.* (2006) for 2,4-D and Carbofuran adsorption by dust and sludge. In the present study, it was observed that in both soils, the sorption coefficients K_{oc} and K_f decreased with rise in temperature from 30 to 40°C, probably due to the effect of temperature on the weak binding between 2,4-D and the soil particles (Table 5).

CONCLUSION

Experimental investigations were carried out to examine the effects of pH, temperature and herbicide concentration on the adsorption of 2,4-D from aqueous solutions onto clay and clay loam soils. The adsorption of 2,4-D was found to be sensitive to soil pH, with low pH significantly increasing the adsorption capacity of the soil while low temperatures and high 2,4-D concentrations promoted higher adsorption. Organic matter is shown to be a key factor for the sorption of 2,4-D in soil. Even small amounts of organic matter contribute to an increase of 2,4-D sorption.

ACKNOWLEDGMENT

The authors would like to thank Alena Sanusi for editorial comments on the manuscript.

REFERENCES

Akma, N.M.H., A.W. Samsuri, H.K. Ainie and A.B. Rosenani, 2009. Sorption-desorption study of a herbicide 2,4-Dichlorophenoxyacetic acid on acidic tropical soils. Malaysian J. Soil Sci., 13: 119-131.

Balinova, A.M. and M. Mondesky, 1999. Pesticide contamination of ground and surface water in Bulgarian Danube plain. J. Environ. Sci. Health Part B, 34: 33-46.

Cheah, U.B., R.C. Kirkwood and K.Y. Lum, 1997. Adsorption-desorption and mobility of four commonly used pesticides in Malaysia. Agric. Soil. Pestic. Sci., 50: 53-63.

Dyson, J.S., S. Beulke, C.D. Brown and M.C.G. Lane, 2002. Adsorption and degradation of the weak acid mesotrione in soil and environmental fate implications. J. Environ. Qual., 31: 613-618.

Fontaine, D.D., R.G. Lehmann and J.R. Miller, 1991. Soil adsorption of neutral and anionic forms of a sulfonamide herbicide, flumetsulam. J. Environ. Qual., 20: 759-762.

Gaultier, J., A. Farenhorst, J. Cathcart and T. Goddard, 2008. Regional assessment of herbicide sorption and degradation in two sampling years. J. Environ. Qual., 37: 1825-1836.

Grotzschel, S., J. Koster and D. de Beer, 2004. Degradation of 2,4-dichlorophenoxyacetic acid (2,4-D) by a hypersaline microbial mat and related functional changes in the mat community. Microbial Ecol., 48: 254-262.

Hameed, B.H., J.M. Salman and A.L. Ahmad, 2009. Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones. J. Hazard. Materi., 163: 121-126.

Ismail, B.S., A.O.S. Enoma, U.B. Cheah, K.Y. Lum and M. Zulkifli, 2002. Adsorption, desorption and mobility of two insecticides in Malaysian agricultural soil. J. Environ. Sci. Health Part B, 37: 355-364.

Johnson, W.G., T.L. Lavy and E.E. Gbur, 1995. Sorption, mobility and degradation of Triclopyr and 2,4-D on four soils. Weed Sci., 43: 678-684.

Kah, M. and C.D. Brown, 2007. Prediction of the ionizable pesticides in soils. J. Agric. Food Chem., 55: 2312-2322.

Kumar, M. and L. Philip, 2006. Adsorption and desorption characteristics of hydrophobic pesticide endosulfan in four Indian soils. Chemosphere, 62: 1064-1077.

Loux, M.M. and K.D. Reese, 1992. Effect of soil pH on adsorption and persistence of imazaquin. Weed Sci., 40: 490-496.

Nicholls, P.H. and A.A. Evans, 1991. Sorption of ionisable compounds by field soils Part 1: Acids. Pestic. Sci., 33: 319-330.

Rawlings, N.C., S.J. Cook and D. Waldbillig, 1998. Effects of the pesticides carbofuran, chlorpyrifos, dimethoate, lindane, triallate, trifluralin, 2,4-D and pentachlorophenol on the metabolic endocrine and reproductive endocrine system in ewes. J. Toxicol. Environ. Health A, 54: 21-36.

Simard, M.J. and A. Legere, 2002. Control of volunteer canola with auxinic herbicides: Does cold hardening or plant size matter. Proceedings of the Canadian Weed Science Society National Meeting, Saskatoon, SK.

Shareef, K. and G. Shaw, 2008. Sorption kinetics of 2,4-D and carbaryl in selected agricultural soils of northern Iraq: Application of dual-rate model. Chemosphere, 72: 8-15.

Tomlin, C.D.S., 2003. The Pesticide Manual. 13th Edn., British Crop Protection Council, Hampshire, UK., pp: 13-44.

Vinod, K., G. Imran, A. Suhas and K.S. Vipin, 2006. Adsorption of 2,4-D and carbofuran pesticides using fertilizer and steel industry wastes. J. Colloid Interface Sci., 299: 556-563.

Walker, A. and M.J. Exposito, 1998. Adsorption of isoproturon, diuron and metsulfuron methyl in two soils at high soil-solution ratio. Weed Res., 38: 229-238.

Walker, A., E.G. Cotterill and S.J. Welch, 1989. Adsorption and degradation of chlorsulfuron and metsulfuron-methyl in soils from different depth. Weed Sci., 29: 281-287.

Wood, J.A. and D.H.J. Anthony, 1997. Herbicide contamination of prairie springs at ultratrace levels of detection. J. Environ. Qual., 26: 1308-1318.