Adsorption - Desorption of Metolachlorand 2,4-D on Agricultural Soils

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Abstract— Adsorption - desorption behavior of metolachlor [2-chloro-N- (2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide)] which is nonionic herbicide, and 2,4-D (2,4- dichlorophenoxyacetic acid) as anionic herbicide have been studied, by performing batch equilibrium experiments on six agricultural soil samples which has different texture. The adsorption processes of metolachlor and 2, 4-D on the soil solid matrix exhibited moderate rate of accumulation with 20.30% and, 24.71 % respectively after 0.5h. Data revealed that the adsorption- desorption of metolachlor and 2, 4-D on the selected soil samples followed the first order rate law. Linear and Freundlich models were used to describe the adsorption- desorption of the two pesticides. Variation in adsorption affinities of the soils to the pesticides was observed, distribution coefficient K_d values for adsorption process varied between 1.882 - 3.025 mlg^{-1} and 2.123- 3.989 mlg^{-1} for metolachlor and 2,4-D respectively , and for desorption process varied between 4.222- 10.986 and 4.755- 14.54 mlg^{-1} for metolachlor and 2,4-D respectively. Freundlich coefficient K_F for metolachlor and 2,4-D ranged between 0.105-0.312 and 0.119-0.355 mlg^{-1} for adsorption processes. The value Freundlich coefficient for desorption process K_{Fdes} ranged from 0.479 to 1.130 mlg^{-1} and 0.284 to 1.012 mlg^{-1} for metolachlor and 2,4-D respectively. Values of equilibrium constant K_o conducted by the ratio between the constant rate of adsorption to the constant rate of desorption, equilibrium constant for metolachlor and 2,4-D on selected soil samples were in the following from 1.345 to 1.572 and from 1.157 to 1.706 respectively. All desorption isotherms exhibited hysteresis. Higher desorption hystersis (for metolachlor and 2,4-D was less readily desorbed).

Index Terms— Adsorption –desorption kinetics and isotherms, HPLC, Metolachlor, 2, 4-D.

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1 INTRODUCTION

PESTICIDES are the most extensively used agrochemicals in the agricultural fields throughout the world. It has been estimated that pesticides application however, most of the pesticides enter the environment, and contaminate soils, water and air, throughout the world, the accumulation of pesticides in food and drinking water has been generally recognized as dangerous[1]. The adsorption desorption behavior of pesticides in soil are primarily regulated by soil texture. As soil have a great role in the environment by controlling the organic compounds because of their sorption capability, it is also an important factor governing the migratory behavior of the pesticide in soil and ground water and may also influence the uptake and metabolism by plants or microorganisms and the other organisms present in soil [2], [3]. The Equilibrium for adsorption-desorption processes was attained for most of the systems in 4-24h. Desorption was slower than sorption, it has generally been characterized by an initial rapid rate followed by a much slower approach to an apparent equilibrium. The initial reaction has been associated with diffusion of the pesticides to and from the surface of the sorbent[4]. The purpose of the desorption kinetics study is to investigate whether a chemical is reversibly or irreversibly adsorbed on a soil, which plays an important role in the behavior of a chemical in field soil

[5], [6]. Hysteresis which is commonly observed in pesticide adsorption-desorption studies with soils. Once adsorbed, some adsorbats may react further to become covalently and irreversibly bound, while others may become physically trapped in the soil matrix. Moreover, hysteresis may increase with adsorbent- adsorbate contact time [7], [8]. The selected herbicides were used in corn crops and cotton as preemergence and post-emergence weed control. Metolachlor belongs to chloroacetanilide herbicides its persistence in the soil, its soluble in water, and poorly bound to most soils so it leaching down towards the ground water [9], [10]. The acidic model: 2, 4-D is anionic herbicide (auxin mimic family) which used to kill or suppresses unwanted plants by its chemical structure through the herbicide's mode of action mechanism (biochemical or physical) [11], [12]. Its adsorption involved ionic interaction with positive charges in soil and also the less energetic Van der Waals forces and charge transfer[13], [14].

2 METHDLOGY

2.1 Soils

Fresh soil samples were taken from six soil samples were collected from six main agricultural, representing a range of physico-chemical properties. Subsamples of homogenized soils were analyzed for moisture content, organic matter content, particle size distribution, texture, pH, loss on ignition and exchangeable basic cations the detail were characterized in previous article[15].

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2.2 Pesticide

Analytical grad substituted Metolachlor (purity 97.8%), and 2, 4-D (purity 98%) were both purchased from Riedal-de Haen, Sigma-Aldrich company ltd. All chemicals used were of analytical grade reagents and used without pre-treatments. Standard stock solutions of the pesticides were prepared in deionised water.

2.3 Adsorption Experiments

Adsorption of two pesticides from aqueous solution was determined at temperature (25±1 C°) employing a standard batch equilibrium method [16], [17]. Duplicate airdried soil samples were equilibrated with different pesticide concentrations (3, 5, 10, and 15 μg ml^{-1}) were for both pesticides at the soil solution ratios 4:8, and 5:10 for metolachlor and 2,4-D respectively in 16 ml glass tube fitted with Teflon-lined screw caps. The samples plus blanks (no pesticide) and control (no soil) were thermostated and placed in shaker for 0.5, 1, 3, 6, 9, 12 and 24h for metolachlor and 0.5, 1, 1.5,2, 2.5, 3, 3.5, 4, 6 and 24h for 2,4-D. The tubes were centrifuged for 20 min. at 3000 rpm. One ml of the clear supernatant was removed and analyzed for the pesticide concentration [18], [19]. Pesticide identification was done by PerkinElmer series 200 USA family high performance liquid chromatography (HPLC) equipped with a changed loop (20μl), C_{18} reversed phase column, flow rate 1.0 ml min^{-1}, and a variable wave length UV detector at wavelength 220 nm 200 nm for metolachlor and 2,4-D respectively. Separation of metolachlor in aqueous phase was achieved with a mobile phase of ratio 80:20 acetonitrile to water, while for 2, 4-D 60:40 (acidified with 1gL^{-1} phosphoric acid). Under these conditions the retention time of metolachlor, and 2, 4-D was 5.37, 4.69 min respectively. Each sample was injected twice to determine the pesticide content by integrating the obtained peak with the respective standard pesticides. The pesticide content was average of two measurements, with no more than 5% deviation between the measurements.

2.4 Dedsorption Experiments

Desorption processes were done as each test tube was placed in a thermostated shaker at (25±1 C°) after equilibration for 24 h with different pesticide concentrations (3, 5, 10 and 15 μg ml^{-1}) the samples were centrifuged, 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of water and this repeated for four times [20]. The resuspended samples were shaken for mentioned time previously for the kinetic study for each pesticide.

3 DATA ANALYSIS

3.1 Adsorption-Desorption Kinetics

The rate constants for adsorption of each pesticide on soils were calculated using the first order rate expression[21].

$$\log\left(C - C_t\right) = \log C - \frac{k}{2.303}t \quad (1)$$

Where k : k_a is the rate constant for adsorption (h^{-1}), t the time (h), C is C_o the concentration of pesticide added (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 as linear plots of log (C_o – C_t) against t of both pesticides demonstrated in (Table 1&2). The same equation used to describe the process of desorption in all experiments and on all soil samples [22]. Where k is k_{des} is the desorption rate constant (h^{-1}), C_t is the amount of released pesticides at time t and C is C_e is the amount of released pesticides at equilibrium and k_{des} is the slope of straight line which is equal to coefficient release rate of k_{des}. A plot of log (C_e – C_t) versus t should give a straight line with slope –k_{des}/ 2.303 and intercept of log C_e of both pesticides demonstrated in (Table 1&2).

3.1.2 Equilibrium Constant

Considering the experimental equilibrium constant k_o can be conducted by the ratio of adsorption rate constant k_a to the desorption rate constant k_{des}, K_o were calculated using the following expression[23].

$$K_o = \frac{k_a}{k_{des}} \quad (2)$$

It indicates that adsorption in the systems studied may be viewed as a reaction in which a solute molecule collides with an adsorption site to form the adsorption complex. Desorption may be viewed as "unimolecular" process by which the adsorption complex dissociates to a free site and solute molecule. The large difference in the equilibrium adsorption arise mainly from the difference in the rate of desorption.

3.2 Adsorption-Desorption Isotherms
3.2.1 Distribution Coefficient

The distribution coefficient (K_d) was calculated by the using the following expression[20], [22].

$$C_s = K_d C_e \quad (3)$$

The distribution coefficient (K_d) was calculated by taking the ratio of adsorption concentration in soil (C_s) and equilibrium concentration in solution (C_e), and averaged across all equilibrium concentration to obtain a single estimate of K_d of both pesticides demonstrated in (Table 3&4).

3.2.2 Freundlich Coefficient

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation[22], [23].

$$\log C_s = \log K_F + \frac{1}{n}\log C_e \quad (4)$$

C_s and C_e were defined previously, K_F is Freundlich adsorption coefficients, and n is a linearity factor, it is also known as adsorption intensity, $1/n$ is the slope and $\log K_F$ is the intercept of the straight line resulting from the plot of $\log C_s$ versus $\log C_e$ as shown in fig 1a&b. The values of K_F and $1/n$ calculated from this regression equation showed that Freundlich adsorption model effectively describes isotherms for both pesticides in all cases. Desorption isotherms of both pesticides were fitted to the linearzed form of the Freundlich equation [24].

$$\log C_s = \log K_{Fdes} + \frac{1}{n_{des}}\log C_e \quad (5)$$

Where C_s is the amount of pesticides still adsorbed ($\mu g\ g^{-1}$), C_e is the equilibrium concentration of pesticides in solution after desorption ($\mu g\ mL^{-1}$), and K_{Fdes} ($\mu g\ g^{1-nfdes}$ /$ml^{nfdes}\ g^{-1}$) and n_{fdes} are two characteristic constants of both pesticides desorption [25]. The value of the K_{Fdes} and n_{fdes} constants of both pesticides demonstrated in (Table3&4).
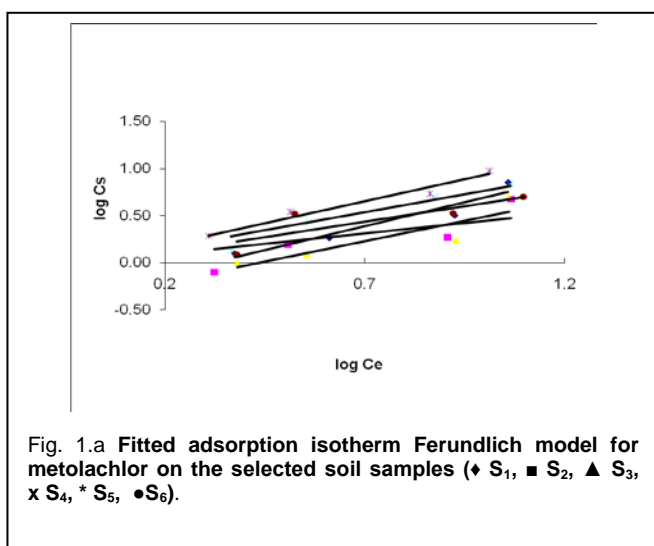

Fig. 1.a **Fitted adsorption isotherm Ferundlich model for metolachlor on the selected soil samples (♦ S₁, ■ S₂, ▲ S₃, x S₄, * S₅, ●S₆).**

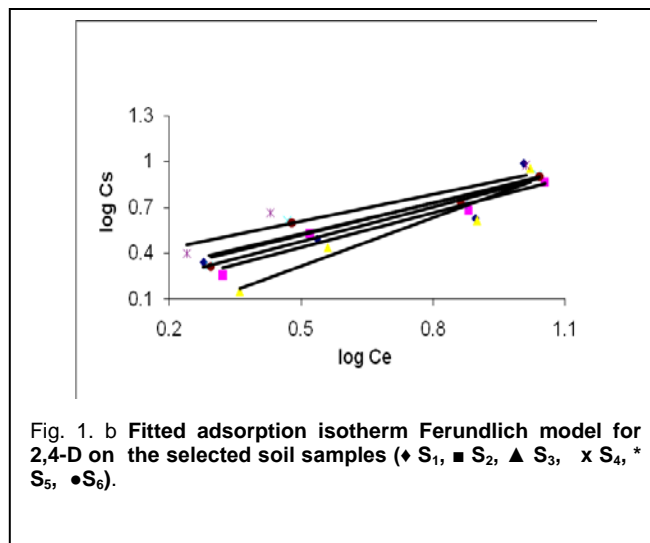Fig. 1. b **Fitted adsorption isotherm Ferundlich model for 2,4-D on the selected soil samples (♦ S₁, ■ S₂, ▲ S₃, x S₄, * S₅, ●S₆)**.

3.3 Hysteresis Coefficient

A study of both pesticides desorption isotherms show positive hysteresis coefficients H_1 on the six selected soil samples. Hysteresis coefficients (H_1) can be determined by using the following equation [25].

$$H_1 = \frac{n_a}{n_{des}} \quad (6)$$

Where n_a and n_{des} are Ferundlich adsorption and desorption constants, respectively, indicating the greater or lesser irreversibility of adsorption in all samples, the highest values corresponding for which the highest adsorption constant was obtained. The coefficient H_1 is a simple one and easy to use, Data in table 5 demonstrated H_1 values for metolachlor, and 2, 4-D respectively.

The extent of hysteresis was quantified by using hysteresis coefficient (ω), it was defined on the discrepancy between the sorption and desorption isotherms, and calculated by using Freundlich parameters estimated from sorption and desorption isotherms separately, (ω) expressed as[26].

$$\omega = (\frac{n_a}{n_{des}} - 1)x100 \quad (7)$$

Recently Zhu et. al [27] proposed an alternative hysteresis coefficient (λ) based on the difference in the areas between adsorption and desorption isotherms, they derived the following expression for the parameter λ for the traditional isotherms

$$\lambda = (\frac{n_a + 1}{n_{des} + 1} - 1)x100 \qquad (8)$$

3.4 Organic Matter Normaliz Adsorption Coefficient

The linear or distribution coefficient (K_d) is related to soil organic carbon (OC) and soil organic matter (OM) by the following equations [28].

$$\%OC = \frac{\%OM}{1.724} \qquad (9)$$

$$K_{OM} = \frac{100K_d}{\%OM} \qquad (10)$$

$$K_{OC} = \frac{100K_d}{\%OC} \qquad (11)$$

4   RESULT AND DISCUTION

4.1 Adsorption-Desorption Rate

Data in Table 1&2 showed that adsorption –desorption of the both pesticides in all cases followed first order rate law [29], [30], (values of rate constants for adsorption and desorption of metolachlor on selected soil samples were in the range from 1.001 to 1.886 h^{-1} and 0.132 to 2.153h^{-1} respectively, and the value of R^2 for adsorption-desorption of metolachlor on selected soil samples ranged from 0.762 to 0.976 and from 0.735 to 0.995 respectively. The value of standard error (S.E.) for adsorption-desorption of metolachlor on selected soil samples ranged from 0.100 to 0.204 and from 0.084 to 0.244 respectively. Values of rate constants for adsorption-desorption of 2, 4-D on selected soil samples were in the range from 1.073 to 2.683 h^{-1} and 0.731 to 1.277h^{-1} respectively, and the value of R^2 for adsorption-desorption of 2,4-D on selected soil samples ranged from 0.729 to 0.988 and from 0.739 to 0.987 respectively. The value of standard error (S.E.) for adsorption-desorption of 2,4-D on selected soil samples ranged from 0.195 to 0.269 and from 0.192 to 0.202 respectively. The values of rate constant for adsorption k_a for the both pesticides are greater than desorption rate constant k_{des}. Thus desorption during the first few hours is likelyto come from the or more accessible sites and /or from the low-energy –release sorption mechanisms, whereas metolachlor sorbed on less accessible sites and/or

more strongly adsorbed sites is not susceptible to desorption initially and is subsequently subject to slow release over time [31], [32]. Data in table 1&2 demonstrated the values of equilibrium constant K_o equilibrium constant for metolachlor, and 2, 4-D on selected soil samples were in the following from1.345 to 1.572 and from 1.157 to 1.706 respectively.

4.2 Adsorption-Desorption Isotherms

Preliminary studies have shown that more than 90% of the 2,4-D sorption occurs within 2h. Orgam et al .1985 [33] suggested that microbial degradation occurred only in solution phase and not when the pesticide was sorbed. K_d values for adsorption process varied between 1.882 - 3.025 mlg^{-1} and 2.123- 3.989 mlg^{-1} for metolachlor and 2,4-D respectively, and for desorption process varied between 4.222- 10.986 and 4.755- 14.54 mlg^{-1} for metolachlor and 2,4-D respectively. Freundlich coefficient K_F for metolachlor and 2,4-D ranged between 0.105-0.312 and 0.119-0.355 mlg^{-1} for adsorption processes. The value Freundlich coefficient for desorption process K_{Fdes} ranged from 0.479 to 1.130 mlg^{-1} and 0.284 to 1.012 mlg^{-1} for metolachlor and 2,4-D respectively. Ferundlich desorption isotherms were determined on the soils used in the adsorption isotherms experiment, the K_{Fdes} values indicate that a small proportion of the chemical has desorbed into solution [34], [35]. In present study, the value of n were less than unity for S_3 in the adsorption of metolachlor indicating the non-linear relationship between concentration of metolachlor and the soil, while a linear relationship between the other soils and metolachlor. The adsorption processes for 2, 4-D on soil samples, the values of n>1 indicating a linear relationship between as shown in fig 1 a & b. The variable slopes of the adsorption isotherm obtained for different soil systems studied reveal that the both pesticides adsorption on soil complex phenomena involving different types of adsorption sites with different surface energies .The value of n_{fdes} describes nonlinearity curvature in the desorption isotherm and is often used as an index of hysteresis. Results obtained in the present work showed that the values of n_{des} values were smaller than the values for the other works [36], [37]. Data in table 5 demonstrated H_1 values for metolachlor and 2,4-D from the selected soil samples in the range from 1.450-2.352 and 0.568-2.595 respectively, indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases, and indicate the increased difficulty of the sorbed analyte to desorb from the matrix. The calculated values of hysteresis coefficient (ω) for adsorption-desorption of for metolachlor and 2, 4-D on the selected soil samples were summarized in table 5 ranged from 90 to 135 and from -43 to 159 respectively. Whereas hysteresis coefficient (ω) is only applicable for the traditional type isotherms of the successive desorption [38], [39]. The data in table 5 demonstrated hysteresis coefficient (λ) according to equation 8 for adsorption-desorption of for metolachlor and 2,4-D from the selected soil samples were ranged from 132 to

678   and from 72 to 750 respectively.

5 CONCLUSION

The batch kinetics experiments were used to differentiate the behavior of two pesticides on six agricultural soil samples. The experimental data were evaluated by employing first-order rate law, the regression equations relating that the highest values are in first-order which is the most suitable to be used. Accessibility of soil organic OC and clay content and the chemical nature of the constituents determined the adsorption affinity of the soil. All desorption isotherms exhibited hysteresis. Higher desorption hystersis (both was less readily desorbed), the increasingly difficult desorption with decreasing solute concentration which can be explained by the limited number of the available sites for the high-energy. Most of these sites were occupied at low solute concentrations, whereas at high solute concentrations, more molecules are taken up by low-energy binding sites and therefore they can more readily desorbed. This could also be explained by the possible hysteresis effect taking place during desorption involving various forces that caused the amount of compounds retained to be higher after desorption than after adsorption at the unit of equilibrium concentration.

REFERENCES

[1]   Pimentel, D., and L. Levitan, "Amounts applied and amounts reaching pests. Bioscience. 36 (1986):86-91.

[2]   Benny Chefetz. "Sorption of Phenantgrene and Atrazine by Plant Cuticular fractions", Environmental Toxicology and Chemistry. 22 (2003):2492-2498.

[3]   Riaz Ahmad, Kookana, R. S., & Angus M. A. "Sorption of Amiteryn and Imazethapyr in Twenty-Five Soils from Pakistan and ". J. Environ. Sci. Health. B36 (2001): 143-160.

[4]   Garrison Sposito." Chemical Equilibrium and Kinetics in Soils" .Wiely. New York .1994.

[5]   Singh, U.S.; Tripathi, R.K.; Kumar, J., & Dwivedi, T.S., "Uptake, Translocation, Distribution and Persistende of Metalaxyl i.e, Pearl Millet (Pennisetum Americanum (L) Lecke.)".T. Phytopathol. 117 (1986):112-115.

[6]   Hamaker J W. "The Application of Mathematical Modeling to the Soil Persistence". Proc. BCPC Symposium: Persistence of Inscticide and Herbicides. (1967): 181-199.

[7]   Kishk, M.F.; Abu-Sharar, M.T.; Bakry, M.N. & Abu-Donia, B. M. "Sorption-Desorption Characteristics of Methyl- Parathion by Clays". Arch. Environ. Contam. Toxicol.. 8 (1979):637-645.

[8]   Thanh H. Dao "Competitive Anion Sorption Effects on Dairy West Water Dissolved phosphorus Extraction with Zeolite-based Sorbents". Food, Agriculture & Environment.3 (2003):263-269.

[9]   Wauchope, R. D., Buttler., T. M. Hornsby A. G., Augustijn-Beckers, P. W. M. and Burt, J. P. SCS/ARS/CES "pesticide properties database for environmental decisionmaking". Reviews of Environment Contamination and Toxicology. 123(1992):1-157

[10] L. J. Krutz, S. A. Senseman, K. J. Mclnnes, D. W. Hoffman, and D. P. Tierney. Adsorption an Desorption of Metolachlor and Metolachlor Metabolites in Vegetated Filter Strip and Cultivated Soil" J. Environ. Qual. 33 (2004):939-945.

[11] McCall, P. J., S. A. Vron, and S. S. Kelly. "Fate of uniformly carbon-14 ring labeld 2,4,5- Trichlorophenoxyacetic acid and 24-Dichrlorophenoxyacetic acid. J. Agric. Food Chem. 29: 100-107

[12] Parker, L. W., and K. G. Doxtader "Kinetics of microbial degradation of 2, 4-D in soil: effects of temperature and moisture". J. Environ. Qual. 12(1983):553-558.

[13] Kahan, S. "Equilibrium and Kinetic Studies of the Adsorption Studies of the Adsorption of 2, 4-D and Picloram on Humic Acid". Canadian Journal of soil Science. 53(1973):429-434.

[14] Nearpass, D.C. "Adsorption of Picloram by Humic Acids and Humin". Soil Sci.1. 121 (1976):272-277.

[15] M. Rounak Shariff., "Compost Adsorption Desorption of Picloram in the Presence of Surfactant on Six Agricultural Soils". International Journal of Scientific & Engineering Research. 2(2011):2229-5518.

[16] E. Barriuso, Ch. Feller, R.Calvet and C.Cerri. Sorption of atrazine, terbutryn and 2, 4-D herbicides in two Brazilian Oxisols. Elesevier Science Pulishers B. V.Amsterdam. 53(1992):155-167.

[17] Jianhang Lu, Laosheng Wu, John Letey, and Walter J. Farmer. Anionic polyacrylamide effects on soil sorption and desorption of Metolachlor, Atrazine, 2, 4-D, and picloram. 31(2002):1226-1233.

[18] Maria Jose carrizosa, Wilam C. koskinan, and Maria Del Carmen Hermosin.". Interaction of Acidic Herbicides Betazon and Dicarmba with Organo Clays". Soil Sci. Soc. Am. J. 68(2004): 1863-1866

[19] Pignatello, J. J., and L. Q. Huang. "Sorptive reversibility zinc and metolachlor residues in field soil sample" J. Environ. Qual. 20 (1991):222-228.

[20] Mohammed A Ali and Peter J. Baugh. "Sorption, Desorption Studies of Six Pyerethroids and Mirex on Soils using GC/ MS-NICI " Internet. J. Environ. Anal. Chem. 83 (2003):923-933.

[21] Suman, G.& Gajbhiye, v. T. "Adsorption –Desorption, Presestance, and Leaching Beahavior of Dithiopyr in an Auuvial soil of India". J. Environ. Sci. and Health. B37 (2002):573-586.

[22] Soledad M.; Andades R.; Sonia Rodri Guez-Cruz M.; Jesus Sanchez-Martin M., & Maria Sanchez-Camazano, January-March, "Effect of the Modification of Natural Clay Minerals with Hexadecylpyridinium Cation on the Adsorption-Desorption of Fungicides" Intern.J. Environ. Anal. Chem. 84(2004):133-141

[23] OP Banasal. "Kinetics of interaction of three carbamate pesticides with Indian soils: Aligrah district". Pest Manag Sci. 60 (2004):1149-1155.

[24] R. A. Griffin and J. J. Jurinak. "Test of a New Model for the Kinetices of Adsorption-Desorption Processes" Soil Sci Soc. Amer. Proc. 37(1973):869-872.

[25] Zhu, H., and H. M. selim "Hysteretic of metolachlor Adsorption - desorption in soil" J. Soil. Sci Qual. 165 (2000):632-645.

[26] Cass T. Miller and Joseph A. Pedlt. "Sorption-Desorption Hysteresis and Abiotic Degradation of Lindane in a Surface Material". Environ. Sci. Technol. 26 (1992):1417-1427.

[27] H. M. Selim and H. Zhu. "Organic Compounds in Environment Atrazine Sorption-Desorption Hysteriesis by Sugarca Mulch Residue". J. Environ. Qual. 34 (2005): 325-335.

[28] Adlophe Monkiedje and Micheal Spiteller. "Fungicides, mefenoxam and Meta laxly, and their acid metabolite in typical Cameroonian and German soils".chemosphere. 49 (2002):659-668.

[29] Mannion, A. M. "Agricultural and environmental vhange"New York, N. Y.: Johan wiley & Sons.1995

[30] Heatwole, C. D., S. Zacharias, S. Mostaghimi, and T.A. Dillaha. Movement of field-applied atrazine, metolachlor, and bromide in sandy loam soil. Transaction of ASAE. 40 (1997): 1267-1276.EAT

[31] Paola E. Diaz-Flores, Roberto Leyva-Ramos, Jose R. Rangel-Mendez, Marriana Michel Ortiz."Adsorption of 2,4-dichlorophenoxyacetic acid from aqueous solution on activated carbon cloth". Journal of Environmental Engineering and Management". 16 (2006): 249-257

[32] Annemieke Farenhorst and Brent Prokopowich. The effect of propanil Co-application on 2, 4-D sorption by soil . Journal of enviromenral scince and health part b-pesticides, food contaminants, and agricultural wastes. b38 (2003):713-721.

[33] Orgam, A. V., R. E. Jessup, L. T. Ou, and P. S. C. Rao. "Effects of sorption on biological degradation rates of (2,4-dichlorophenoxy) acetic acid in soils. Appl, Environ. Microbiol. 49 (1985):582-587.

[34] L.cox, A. Cecchi, R. Celis, M. C. Hermosin, W. C. Koskinen and J. cavenejo. "Effect of oxygens carbon on movement of simazine and 2, 4-D in soils" Soil Soc Am J. 65(2001):1688-1695.

[35] M. C. Hermosin and J. Cornejo, "removing 2, 4-D from water by organo-clays". Chemospere, 24(1992):1493-1503.

[36] Kahan, S. "Equilibrium and kinetic studies of the adsorption studies of the adsorption of 2, 4-D and picloram on humic acid". Canadian Journal of soil Science. 53 (1973):429-434.

[37] S. Bas Karan, N.S. Bolan, A. Rahanan and R. W. Tillman. "Effect of oxygenous carbon on the sorption andmovement of atrazine and 2,4-D by soils". Australin Journal of soil reserch. 34 (1990):609-622.

[38] Cludio A. Spadotto and Arthur G. Hornsby. "Organic compounds in the environment soil sorption of acidic pesticides: modeling pH effects". . Environ. Qual. 32 (2003): 949-956.

[39] Jeong -Hunpark, Deenise Kuy, Xianda Zhao, Stephen A. Boyed and Thomas C. Vocie." Kinetic modeling of bioavailability of sorbed. Phase2, 4-chlorophenoxyacetic acid. J. Environ. Qual. 30 (2001):1523-1527.

TABLE 1
ADSORPTION -DESORPTION RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR METOLACH-
LOR ON THE SELECTED SOIL SAMPLES

Soil	Conc ·ppm	Adsorption			Desorption			K_o
		K_{ads} calc (h^{-1})	S.E	R^2	K_{des} calc (h^{-1})	S.E	R^2	
S_1	3	1.285	0.185	0.828	1.187	0.119	0.879	1.360
	5	1.515	0.100	0.942	0.913	0.170	0.776	
	10	1.582	0.104	0.904	1.120	0.128	0.809	
	15	1.001	0.158	0.808	0.796	0.199	0.918	
S_2	3	1.886	0.175	0.801	1.127	0.244	0.899	1.345
	5	1.414	0.193	0.819	1.236	0.176	0.874	
	10	1.382	0.168	0.955	1.117	0.186	0.922	
	15	1.327	0.165	0.849	0.989	0.121	0.802	
S_3	3	1.765	0.171	0.834	1.150	0.158	0.914	1.364
	5	1.609	0.124	0.927	1.111	0.188	0.930	
	10	1.639	0.113	0.843	1.161	0.192	0.963	
	15	1.115	0.154	0.884	1.070	0.193	0.969	
S_4	3	1.422	0.199	0.852	0.981	0.089	0.793	1.370
	5	1.386	0.202	0.848	0.987	0.093	0.892	
	10	1.369	0.204	0.873	0.984	0.094	0.936	
	15	1.261	0.197	0.983	0.983	0.084	0.995	
S_5	3	1.749	0.164	0.973	1.025	0.190	0.979	1.449
	5	1.161	0.971	0.944	0.847	0.185	0.735	
	10	1.281	0.165	0.762	0.985	0.188	0.946	
	15	1.326	0.153	0.976	0.802	0.186	0.967	
S_6	3	1.669	0.197	0.954	1.627	0.194	0.974	1.572
	5	1.744	0.195	0.962	0.132	0.122	0.823	
	10	1.695	0.163	0.933	2.153	0.189	0.902	
	15	1.698	0.159	0.955	0.406	0.168	0.863	

TABLE 2
ADSORPTION -DESORPTION RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR 2,4-D ON THE SELECTED SOIL SAMPLES

Soil	Conc ·ppm	Adsorption			Desorption			K_o
		K_{ads} calc (h^{-1})	S.E	R^2	K_{des} calc (h^{-1})	S.E	R^2	
S_1	3	1.155	0.195	0.929	0.933	0.196	0.963	1.157
	5	1.339	0.198	0.884	1.158	0.192	0.927	
	10	1.350	0.269	0.962	1.065	0.193	0.972	
	15	1.114	0.195	0.872	1.129	0.192	0.947	
S_2	3	1.615	0.205	0.867	1.173	0.192	0.982	1.216
	5	1.114	0.197	0.793	1.128	0.192	0.909	
	10	1.637	0.201	0.940	1.277	0.191	0.987	
	15	1.364	0.196	0.807	1.134	0.199	0.952	
S_3	3	1.953	0.211	0.915	0.868	0.192	0.739	1.706
	5	1.464	0.199	0.898	0.807	0.193	0.846	
	10	1.848	0.207	0.866	1.087	0.198	0.829	
	15	1.379	0.197	0.828	1.133	0.198	0.822	
S_4	3	2.683	0.242	0.988	1.096	0.201	0.843	1.683
	5	1.591	0.202	0.876	0.991	0.198	0.980	
	10	1.362	0.196	0.985	0.999	0.196	0.933	
	15	1.355	0.197	0.942	1.083	0.194	0.954	
S_5	3	1.267	0.196	0.729	0.959	0.195	0.855	1.369
	5	1.247	0.197	0.770	0.731	0.201	0.828	
	10	1.265	0.196	0.827	0.915	0.196	0.962	
	15	1.073	0.195	0.966	0.937	0.196	0.934	
S_6	3	2.161	0.219	0.903	0.993	0.200	0.982	1.494
	5	1.475	0.201	0.864	0.989	0.202	0.902	
	10	1.867	0.207	0.948	0.978	0.195	0.909	
	15	1.829	0.202	0.973	0.987	0.195	0.947	

TABLE3
ADSORPTION -DESORPTION ISOTHERM PARAMETERSTHE LINEAR AND FREUNDLICH
MODELS FOR METOLACHLOR ON THE SELECTED SOIL SAMPLES

Adsorption Desorption Models		Parameter	Soils					
			S_1	S_2	S_3	S_4	S_5	S_6
Adsorption Distr.Coffi	Adsorption Distr.Coffi	K_d (calc)	2.429	2.628	3.025	2.206	1.882	2.216
		S.E	0.259	0.181	0.149	0.279	0.263	0.277
		R^2	0.785	0.985	0.965	0.879	0.943	0.847
		$K_{OC(ml/g)}$	87	253	95	94	98	147
		$K_{OM(ml/g)}$	1.496	4.361	1.632	1.614	1.695	2.532
	Freundlich Adsorption	$K_{F(ml/g)}$	0.105	0.202	0.214	0.191	0.312	0.169
		S.E	0.286	0.282	0.310	0.322	0.283	0.281
		n_F	1.336	1.668	0.943	1.483	1.684	1.430
		R^2	0.826	0.936	0.921	0.889	0.833	0.923
	Dedsorption Distr.Coffi	K_d (calc)	8.915	6.773	4.222	5.889	9.203	10.986
		S.E	0.099	0.079	0.072	0.068	0.100	0.039
		R^2	0.757	0.765	0.986	0.846	0.968	0.865
	Freundlich Desorption	$K_{Fdes(ml/g)}$	0.817	0.479	1.066	1.130	0.724	0.742
		S.E	0.290	0.234	0.358	0.243	0.133	0.121
		n_{Fdes}	0.767	1.051	0.401	0.692	0.885	0.986
		R^2	0.908	0.857	0.992	0.886	0.998	0.937

TABLE4
ADSORPTION -DESORPTION ISOTHERM PARAMETERSTHE LINEAR AND FREUNDLICH
MODELS FOR 2,4-D ON THE SELECTED SOIL SAMPLES

Adsorption Desorption Models		Parameter	Soils					
			S_1	S_2	S_3	S_4	S_5	S_6
Adsorption	Adsorption Distr.Coffi	K_d (calc)	2.123	2.949	3.857	3.112	2.124	3.989
		S.E	0.279	0.283	0.179	0.207	0.206	0.209
		R^2	0.898	0.797	0.977	0.846	0.968	0.752
		$K_{OC(ml/g)}$	105	284	121	173	758	298
		$K_{OM(ml/g)}$	1.816	4.893	2.081	2.974	13.52	5.144
	Freundlich Adsorption	$K_{F(ml/g)}$	0.178	0.119	0.185	0.175	0.355	0.154
		S.E	0.256	0.280	0.325	0.350	0.254	0.306
		n_F	1.409	1.608	1.128	1.021	1.111	1.516
		R^2	0.944	0.823	0.803	0.979	0.964	0.754
Desorption	Dedsorption Distr.Coffi	K_d (calc)	4.755	14.54	10.21	8.258	4.762	7.039
		S.E	0.113	0.160	0.272	0.093	0.146	0.142
		R^2	0.915	0.765	0.977	0.955	0.853	0.953
	Freundlich Desorption	$K_{Fdes(ml/g)}$	0.720	1.012	0.419	0.303	0.613	0.284
		S.E	0.530	0.578	0.212	0.349	0.380	0.329
		n_{Fdes}	0.543	0.808	1.147	1.799	0.750	1.022
		R^2	0.800	0.978	0.773	0.981	0.959	0.850

TABLE 5
HYSTERSIS COEFFICENT FOR ADSORPTION- DESORPTION FOR METOLACH-
LOR AND 2,4-D ON THE SELECTED D SOIL SAMPLES

Soil	Metolachlor			2,4-D		
	H_1	ω	λ	H_1	ω	λ
S_1	1.742	74	678	2.595	159	304
S_2	1.587	59	173	1.990	99	750
S_3	2.352	135	398	0.983	-1.656	126
S_4	2.143	114	492	0.568	-43.25	73
S_5	1.903	90	132	1.481	48.13	72
S_6	1.450	45	339	0.749	-25.02	16