

Compost Adsorption Desorption of Picloram in the Presence of Surfactant on Six Agricultural Soils

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Abstract— To investigate the effect of different types of surfactants on adsorption behavior of pesticide, picloram [4-amino-3, 5, 6-trichloropicolinic acid] which is an ionic herbicide on six agricultural soil samples, picloram soil –water system-surfactant. The Freundlich adsorption coefficients K_s values for picloram adsorption in the presences of surfactant in three concentration of critical micelles concentration (cmc), batch equilibrium experiments performed of cationic surfactant Hexadecyltrimethylammonium bromide (HDTMA). The K_s values of picloram range between 0.940-1.344, 0.943-1.407, and 0.952-1.434 ml/g, for cmc/10, cmc and cmc*20 respectively. Freundlich adsorption coefficients of picloram in the presence of anionic surfactant sodium dodecyl sulphate (SDS) was determined, the values of K_s obtained were in the range 0.761-1.151, 0.654-1.141, and 0.631-1.099ml/g, for cmc/10, cmc, and cmc*20 respectively. The K_s values for polyoxyethylene sorbitanmonooleate (tween-80) were in the range 0.971 -1.229, 1.104-1.303, and 1.189-1.404 ml/g, for cmc/10, cmc, and cmc*20 respectively. The values of Freundlich desorption coefficients (K_{des}), linearity factor for desorption (n_{des}) and regression factor for desorption (R^2) ranged from 0.839-1.286, 0.267-0.619, and 0.889-0.993 respectively with HDTMA. The values of K_{des} , n_{des} and R^2 values ranged from 0.895-1.289, 0.494-0.818, and 0.889-0.999 for desorption process respectively by anionic surfactant SDS, the values of K_{des} , n_{des} and R^2 ranged from 0.953-1.270, 0.429-0.650, and 0.888-0.995 respectively for non-ionic surfactant Tween-80.

Index Terms — Adsorption - desorption kinetics, Adsorption isotherms, HPLC, Picloram, Surfactant.

1 INTRODUCTION

The use of kinetic models in the study of adsorption and desorption processes in heterogenous system is important. Three reasons for the use of kinetic or time-dependent models in soils have been suggested. First, many reactions in soil are slow; yet, they proceed at measurable rates. Second, non-equilibrium conditions can exist as a result of the physical transport of gases and solutes. Third, information about reaction mechanisms and processes occurring may be obtained from such data [1], [2]. The sorption pattern indicates an initial fast sorption that occurs within the first 24h till it attained the equilibrium within 48h. This was followed by slow reactions that appear to be the dominant processes i.e desorption of picloram if compared to the amount of picloram still sorbed on the soil. Picloram; is anionic herbicide is used to control unwanted woody plants and to prepare sites for planting trees and used to control broad-leaf plants and trees [3], [4]. Its adsorption involved ionic interaction with positive charges in soil and also the less energetic Van der Waals forces and charge transfer [5], [6]. A two step adsorption-desorption mechanism was used to model the observed behavior that can be described in terms of external and internal sorption sites. Desorption from ex-

ternal sites is relatively fast, taking place in about 5h and is characterized by a first-order rate constant. Many studies have indicated that the sorption and desorption of the organic chemicals in soils are not rapid, reversible process, despite past assumption to the contrary [7], [8]. A study of picloram desorption isotherms show positive hysteresis coefficients H in the six selected soil samples [9], [10]. Hysteresis coefficients H_1 , where N_a / N_{des} ratio for 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, indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases [8].

2 METHODOLOGY

2.1 Soils

Fresh soil samples were taken from plough layer (0-15 cm depth), after removal of stones and debris, air dried under shade, ground then sieved through 2mm sieve and stored in black plastic container in dark [11], [12]. The six soil samples were collected from six main agricultural, representing a range of physico-chemical properties. Sub-samples of homogenized soils were analyzed for moisture content, organic matter content, particle size distribution, texture, pH, loss on ignition and exchangeable basic cations were listed in Table 1 a & b.

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2.2 Pesticide and Surfactant

Analytical grade substituted picloram herbicide was purchased from Riedal-de Haen, Sigma-Aldrich company Ltd. With following purities expressed in weight percent picloram >97.4% [CAS-No.1918-02-1] respectively. The three different surfactants employed in this study comprised; the cationic Hexadecyltrimethylammonium bromide (HDTMA), the anionic sodium dodecyl sulphate (SDS) and nonionic polyoxyethylene sorbitanmonooleate (Tween-80). These compounds were purchased at reagent grade purity from BDH, and were used without further treatments. The critical micelles concentration cmc of the three surfactants are shown in Table 2. The three surfactants were studied at three concentrations: the critical micelles concentration (cmc), twenty-fold higher than cmc (20cmc), and 10-fold lower than cmc (cmc/10). 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 picloram from aqueous solution was determined at laboratory temperature (25 ± 1 C°) employing a standard batch equilibrium method [13], [14]. Duplicate air-dried soil samples were equilibrated with different pesticide concentrations (2, 5, 10, and 15 $\mu\text{g ml}^{-1}$) were for the pesticide at the soil solution ratios 4:8, 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, 24, 48h. The tubes were centrifuged for 20 min. at 3500 rpm. One ml of the clear supernatant was removed and analyzed for the pesticide concentration [15]. Pesticide identification was done by PerkinElmer series 200 USA family high performance liquid chromatography (HPLC) equipped with a changed loop (20 μl), C_{18} reversed phase column, flow rate 1.0 ml min^{-1} , and a variable wave length UV detector at wavelength 220 nm. Separation of picloram in aqueous phase was achieved with a mobile phase of 40% acetonitrile and 60% water (acidified with 0.1% phosphoric acid). 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. The same procedure is repeated in presence of surfactants.

2.4 Desorption Experiments

Desorption processes were done as each test tube was placed in a thermostated shaker at 25°C after equilibration for 48 h with different pesticide concentrations (2, 5, 10 and 15 $\mu\text{g ml}^{-1}$) the samples were centrifuged, 5ml of supernatant was removed from the adsorption equilibrium solution and immediately replaced by 5ml of water and was this repeated for four times. The resuspended samples were shaken for 0.5, 1, 3, 6, 9, 12, 24, and 48h for the kinetic study. Desorption of picloram was studied in

the six selected soil samples, initially treated with different concentrations alone (2, 5, 10 and 15) μgml^{-1} in presence of surfactant, after equilibrium had been reached for 24h, 5ml were removed from the solution and immediately replaced by 5ml of the surfactant suspension used in the study. The resuspended samples were shaken for 24h, after sufficient time, were centrifuged and the desorbed picloram was measured as reported previously, this desorption procedure was repeated two times for each soil. The amount of picloram at each desorption stage was calculated as the difference between the initial amount adsorbed and the amount desorbed, all determinations were carried out in duplicate. Competitive picloram adsorption-desorption between soil and surfactant in the soil-picloram-water-surfactant system, in the presence HDTMA, SDS, and Tween-80 at concentrations of cmc/10, cmc, and cmc*20 were conducted adsorption-desorption isotherms [16].

3 DATA ANALYSIS

3.1 Adsorption Isotherms

During adsorption studies, equilibrium concentration of pesticide in solution (C_e) was determined by direct analysis of the solution and amount of pesticide adsorbed on soil (C_s) was computed by the difference between the initial and the equilibrium concentration in the aqueous phase. Analysis of control samples showed that, in the absent of soil, pesticide concentration remained constant during the course of the batch experiments [17].

3.2 Freundlich Adsorption-Desorption Isotherms

Adsorption isotherm parameters were calculated using the linearized form of Freundlich equation [18]. 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 $\log C_e$ shown in Fig-1. The values of K_F and $1/n$ calculated, from the regression equation showed that Freundlich adsorption model effectively describes isotherms for the pesticides in all cases were listed in Table 3.

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

Desorption isotherms of picloram were fitted to the linearized form of the Freundlich equation [19], [20].

$$\log C_s = \log K_{Fdes} + \frac{1}{n_{des}} \log C_e \quad (2)$$

The values of K_{Fdes} is Freundlich desorption coefficients, and $1/n_{des}$ is a linearity factor, it is also known as desorp-

tion intensity and from the regression equation showed that Freundlich desorption model effectively describes isotherms for the pesticides in all cases, [21], [22] were listed in Table 4. To investigate the effect of different types of surfactants on adsorption behavior of pesticides [23], [24]. The Freundlich adsorption equation in the presence of surfactant used to determined follows as [8], [25].

$$\log C_s = \log K_s + \frac{1}{n_s} \log C_e \quad (3)$$

Where C_s is the amount of adsorbed herbicide equation in the presence of surfactant ($\mu\text{g ml}^{-1}$), C_e is the equilibrium concentration of herbicide in solution of herbicides in solution equation in the presence of surfactant ($\mu\text{g ml}^{-1}$), and K_s and n_s are the Freundlich affinity and nonlinearity coefficients respectively in the presence of surfactant. The Freundlich equation for desorption in the presence of surfactant, values of K_{sdes} for all experiments were calculated using the following equations

$$\log C_s = \log K_{sdes} + \frac{1}{n_{sdes}} \log C_e \quad (4)$$

Where C_s is the amount of picloram still adsorbed ($\mu\text{g g}^{-1}$), C_e is the equilibrium concentration of picloram in solution after desorption equation in the presence of surfactant ($\mu\text{g mL}^{-1}$), and K_{Fdes} ($\mu\text{g g}^{1-n_{Fdes}} / \text{ml}^{n_{Fdes}} \text{g}^{-1}$) and n_{fd} are the Freundlich desorption affinity and nonlinearity coefficients, respectively equation, for all the three surfactant at the three different concentrations.

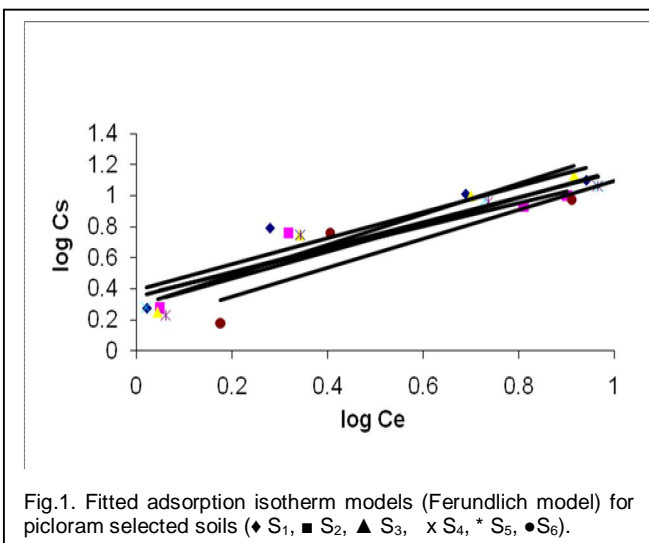


Fig.1. Fitted adsorption isotherm models (Ferundlich model) for picloram selected soils (♦ S₁, ■ S₂, ▲ S₃, x S₄, * S₅, ● S₆).

3.3 Hysteresis coefficient

A study of picloram desorption isotherms show positive hysteresis coefficients H in the six selected soil samples [8], [10]. Hysteresis coefficients H_1 , can be determined by using the following equation.

$$H_1 = \frac{N_a}{N_{des}} \quad (5)$$

Where N_a / N_{des} ratio for 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 picloram from the selected soil samples in the range from 0.223-0.553 for desorption process, indicating an increase in the irreversibility of the adsorption of herbicide as the clay content increases [8].

4 RESULT AND DISCUSSION

2.1 Adsorption – Desorption Isotherms

Previously work indicated that the linear model not fitted properly most experimental data with the pesticides [12]. The non-linear adsorption isotherms might be expected for the compounds for which competition for a limited number of cation exchange sites contributes significantly to adsorption process. Data from batch equilibrium method revealed that the adsorption of herbicides on the selected soil samples followed the first order rate law. To investigate the effect of different types of surfactants on adsorption behavior of pesticides [26], [27]. The K_s values for picloram adsorption in the presences of cationic surfactant (HDTMA) The K_s values of picloram range between 0.940-1.344, 0.943-1.407, and 0.952-1.434 ml/g, for cmc/10, cmc, and cmc*20 respectively. Freundlich adsorption coefficients of picloram in the presence of anionic surfactant (SDS) was determined and summarized in table 3, the K_s values obtained were in the range 0.761-1.151, 0.654-1.141, and 0.631-1.099 ml/g, for cmc/10, cmc, and cmc*20 respectively. Batch equilibrium experiments performed for tween-80, picloram soil –water system and K_s values were determined and summarized in table 3. The K_s values were in the range 0.971 -1.229, 1.104-1.303, and 1.189-1.404 ml/g, for cmc/10, cmc, and cmc*20 respectively. The values of K_F , n and R^2 ranged from 1.078-1.211, 0.344-0.966, and 0.882-0.993 respectively for adsorption picloram without surfactant, while the values of K_{Fdes} , n and R^2 ranged from 1.045-1.586, 0.718-1.947, and 0.987-0.999 respectively for desorption of picloram without surfactant. The desorption isotherms of picloram with HDTMA treatment was lower. Data demonstrated in table 4 represents the values of K_{sdes} , n_{sdes} and R^2 for desorption of picloram from the selected soil samples. The values of K_{sdes} , n_{sdes} and R^2 ranged from 0.839-1.286, 0.267-0.619, and 0.889-0.993 respectively. However sorption of anionic herbicides picloram was almost unaffected by anionic surfactant SDS, slightly decrease in adsorption, with slightly increased in desorption of picloram was detected. Data demonstrated in table 4. K_{sdes} , n_{sdes} and R^2 for desorption of picloram from the selected soil samples.

K_{sdes} , n_{sdes} and R^2 values ranged from 0.895-1.289, 0.494-0.818, and 0.889-0.999 for the desorption process respectively. The non-ionic surfactant Tween-80 at different concentrations enhanced desorption of herbicides from soils. All desorption isotherms showed that hysteresis coefficients were decreased. These variations were dependent on surfactant concentration and soil OM and the clay contents. The effect of tween-80 on desorption of the picloram was very low in soil with a high clay content. The results indicate the potential use of tween-80 to facilitate desorption of these herbicides from soil to the water-surfactant system. Values of K_{sdes} , n_{sdes} and R^2 for desorption of picloram from the selected soil samples. Data in Table 4 listed the values of K_{sdes} , n_{sdes} and R^2 ranged from 0.953-1.270, 0.429-0.650, and 0.888-0.995 respectively. Important aspect to be considered is the interaction of surfactant with soil, since it may, on one hand, alter the surfactant concentration in solution, thereby decreasing its efficiency for desorption, and on the other, alter the soil surface, where surfactant molecules may be adsorbed in the form of monomer or forming hemicelles or admicelles. Thus surfactant adsorption increases the organic content of the soil and increased hydrophobic surfaces, which may contribute to decrease in the organic compound desorption. Of all the above processes, the study of surfactant-enhanced desorption for organic pollutants adsorbed on soil has been addressed by many investigators in recent years although such information can only be considered a beneficial effect in the context of major engineered remediation processes. In the study of surfactant-enhanced desorption it is necessary to take into account the characteristics of the surfactant (e.g., chemical structure, hydrophilic-lipophilic balance [HLB], or cmc), its concentration in the soil-water system, the solubility and hydrophobicity of the characteristics of soil (e.g., OM, clay content). Enhanced solubility of pollutants has been clearly indicated by several authors at surfactant concentrations higher than the cmc. However, at surfactant concentrations below the cmc competitive adsorption of organic compound by soil and/or by a surfactant in solution may occur, and hence an increase or decrease in desorption of compound from soil, depending on the characteristics of soil and organic compound [28], [29].

4.2 Hysteresis Coefficients

Desorption isotherms of picloram show a positive hysteresis coefficients H_1 . Values of hysteresis coefficient for adsorption-desorption of picloram on the selected soil samples in the presence of HDTMA, SDS and tween-80 were summarized in Table 5. The results of present study, which show the decrease in H_1 values indicated higher hysteresis at lower pesticide concentration in presence of HDTMA, exhibited a higher sorption affinity and higher resistance for desorption [30]. Data in Table 5 demonstrated that H_1 for desorption of picloram from the selected soil samples in the presence of HDTMA were in the range $S_3 > S_6 > S_5 > S_4 > S_1 > S_2$, values of H_1 ranged from 0.693-

2.594. The increase or decrease in hysteresis of the adsorption-desorption isotherms in the presence of SDS solutions depend on the SDS concentration and on OM content of the soils. Below the cmc, SDS only increase the desorption of picloram in the highest OM content (3.196%). However, above the cmc*20 desorption of picloram increases in all soils while the efficiency of desorption increasing with OM content of the Soil [31], [32]. Data in Table 4 demonstrated the value of H_1 for desorption of picloram from the selected soil samples in the presence of SDS were in the range $S_5 > S_4 > S_6 > S_1 > S_2 > S_3$, and values of H_1 ranged from 0.493-1.667. Consistent with the previous study [33], [34]. The H_1 values for tween-80 decrease indicated higher hysteresis at lower picloram concentration. OM considered as the primary soil component responsible for the adsorption of non-ionic pesticides. Desorption of the neutral form was completely reversible, however, the charged species exhibited desorption-resistance fraction. The difference in sorption and desorption between the neutral and charged species is attributed to the fact that the neutral form partition by the hydrophobic binding to the soil, while anionic sorbs by a more specific exothermic adsorption reaction [35], [36]. Data in Table 4 demonstrated that H_1 for adsorption-desorption of picloram from the selected soil samples in the presence of tween-80 were in the range $S_2 > S_1 > S_5 > S_4 > S_6 > S_3$, and values of H_1 ranged from 0.331-2.741. Desorption of soil-associated pesticides, hysteresis, and possible mechanisms have received considerable attention in literature [37], [38]. Desorption rates of pesticides can be characterized by three types of processes, rapid desorption, rate-limited desorption, and a fraction that does not desorb over experimental time scale. Many factors affect the adsorption-desorption of pesticides such as pesticide type; soil properties, organic matter, clay content, soil pH and environmental conditions [39], [40]. Equation 5 shows the main effect of surfactant at concentrations close to cmc is to increase the affinity of picloram for the soil with, except for soils high in clay content where the surfactant effect is to enhance the affinity of picloram for aqueous phase [41].

5 CONCLUSION

Desorption rates of pesticides can be characterized by three types of processes, rapid desorption, rate-limited desorption, and a fraction that does not desorb over experimental time scale. Many factors affect the adsorption-desorption of pesticides such as pesticide type; soil properties, organic matter, clay content, soil pH and environmental conditions. The batch kinetics experiments were used to differentiate the behavior of the pesticide in six agricultural soil samples. The desorption studies demonstrated that picloram has stronger affinity to all the selected soil samples than adsorption, and the soils varied widely in their adsorption capacities for picloram. We have further found that soil OC and clay content and the

chemical nature of the constituents determined the adsorption affinity of the soil. Soil characteristics as solubility and hydrophobicity (e.g., OM, clay content). Enhanced solubility of pollutants has been clearly indicated by several authors at surfactant concentrations higher than the cmc.

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TABLE 1A
SOME PHYSICO-CHEMICAL PROPERTIES OF THE SELECTED SOIL SAMPLES

| Soil | OM % | Moisture % | Loss On ignition % | C meq100g ⁻¹ EC | E.C*10 ² sm ⁻¹ in D.W | pH | |
|----------------|-------|------------|--------------------|----------------------------------|--|--------|----------------------|
| | | | | | | In D.W | in CaCl ₂ |
| S ₁ | 2.799 | 2.544 | 7.864 | 47.760 | 0.414 | 7.516 | 7.501 |
| S ₂ | 1.039 | 1.864 | 3.445 | 54.276 | 0.431 | 6.825 | 6.805 |
| S ₃ | 3.196 | 2.633 | 6.160 | 26.780 | 0.572 | 6.981 | 6.906 |
| S ₄ | 2.356 | 2.604 | 4.058 | 41.133 | 0.388 | 7.651 | 7.621 |
| S ₅ | 1.914 | 2.012 | 5.442 | 32.488 | 0.492 | 6.395 | 6.305 |
| S ₆ | 1.509 | 3.417 | 2.926 | 55.121 | 0.545 | 6.940 | 6.900 |

TABLE 1B
PARTICALE SIZE DISTRIBUTION AND THE TEXTURE OF THE SELECTED SOIL SAMPLES

| No. | Soil | X (m) | Y (m) | Sand % | Silt % | Clay % | Texture |
|-----|---------------|-----------|------------|--------|--------|--------|-----------------|
| S1 | Ha-labjh | 45+58.905 | 35+101.166 | 4.4 | 39.4 | 56.2 | Clay |
| S2 | Darb-nidikhan | 45+42.31 | 35+06.39 | 37.4 | 46.1 | 20.2 | Loam |
| S3 | Jam-jamal | 44+50.026 | 35+31.355 | 11.7 | 52.2 | 36.1 | Silty Clay Loam |
| S4 | Ha-labjh | 45+58.786 | 45+10.338 | 20.2 | 48.0 | 31.8 | Clay loam |
| S5 | Kir-kuk | 44+21.825 | 35+34.940 | 17.6 | 61.8 | 20.6 | Silt Loam |
| S6 | Duhok | 42+53.944 | 36+51.185 | 11.6 | 45.7 | 42.7 | Silty Clay |

TABLE 2
 SELECTED PROPERTIES OF THE SURFACTANTS (M=6 TO 13, N=7 TO 13)

| Surfactant | Type | Formula | cmc gL ⁻¹ |
|------------|----------|---|----------------------|
| HDTMA | Cationic | C ₁₆ H ₃₃ N(CH ₃) ₃ Br | 0.3 |
| SDS | anionic | C ₁₈ H ₂₉ SO ₄ Na | 2.38 |
| Tween-80 | nonionic | CH ₃ (CH ₂) _m CH ₂ O(CH ₂ CH ₂ O) _n H | 0.04 |

TABLE 3
 FREUNDLICH ADSORPTION COEFFICIENT FOR THE ADSORPTION OF PICLORAM IN THE PRESENCE OF HDTMA, SDS AND TWEEN-80 OF THREE DIFFERENT CONCENTRATIONS ON THE SELECTED SOIL SAMPLES

| IloS | K _F (ml/g) Without surfac. /n /R ² | K _s (ml/g) HDTMA /n _s /R ² | | | K _s (ml/g) SDS /n _s /R ² | | | K _s (ml/g) Tween-80/ n _s /R ² | | |
|----------------|--|---|-------|---------|---|-------|---------|--|-------|---------|
| | | cmc/10 | cmc | cmc* 20 | cmc/10 | cmc | cmc* 20 | cmc/10 | cmc | cmc* 20 |
| S ₁ | 1.171 | 1.006 | 1.092 | 1.177 | 1.061 | 1.035 | 0.865 | 1.054 | 1.277 | 1.327 |
| | 0.397 | 0.558 | 0.519 | 0.472 | 0.431 | 0.516 | 0.547 | 0.945 | 0.881 | 1.211 |
| | 0.933 | 0.970 | 0.957 | 0.994 | 0.973 | 0.951 | 0.903 | 0.973 | 0.881 | 0.901 |
| S ₂ | 1.085 | 0.940 | 0.943 | 0.952 | 0.984 | 0.974 | 0.814 | 1.199 | 1.218 | 1.221 |
| | 0.435 | 0.423 | 0.398 | 0.605 | 0.456 | 0.655 | 0.824 | 0.671 | 0.884 | 0.797 |
| | 0.973 | 0.991 | 0.990 | 0.980 | 0.977 | 0.989 | 0.939 | 0.960 | 0.939 | 0.937 |
| S ₃ | 1.211 | 1.344 | 1.374 | 1.397 | 0.761 | 0.654 | 0.631 | 1.021 | 1.104 | 1.211 |
| | 0.497 | 0.785 | 0.943 | 1.063 | 0.337 | 0.872 | 0.557 | 0.301 | 0.645 | 0.839 |
| | 0.997 | 0.985 | 0.975 | 0.974 | 0.811 | 0.852 | 0.704 | 0.971 | 0.974 | 0.974 |
| S ₄ | 1.078 | 1.142 | 1.153 | 1.195 | 0.963 | 0.936 | 0.852 | 0.971 | 1.117 | 1.189 |
| | 0.344 | 0.652 | 0.647 | 0.885 | 0.707 | 0.782 | 0.763 | 0.290 | 0.926 | 1.395 |
| | 0.999 | 0.965 | 0.976 | 0.938 | 0.929 | 0.914 | 0.901 | 0.997 | 0.923 | 0.893 |
| S ₅ | 1.168 | 1.198 | 1.199 | 1.211 | 1.151 | 1.141 | 1.099 | 1.229 | 1.303 | 1.404 |
| | 0.559 | 0.751 | 0.796 | 0.919 | 0.657 | 0.548 | 0.853 | 0.508 | 0.808 | 1.124 |
| | 0.978 | 0.950 | 0.948 | 0.949 | 0.920 | 0.928 | 0.971 | 0.989 | 0.963 | 0.936 |
| S ₆ | 1.189 | 1.328 | 1.407 | 1.434 | 0.816 | 0.794 | 0.675 | 1.003 | 1.198 | 1.211 |
| | 0.966 | 1.046 | 1.269 | 1.398 | 0.706 | 0.886 | 0.970 | 0.204 | 0.802 | 0.692 |
| | 0.882 | 0.871 | 0.865 | 0.884 | 0.788 | 0.762 | 0.752 | 0.926 | 0.987 | 0.990 |

TABLE 4
FREUNDLICH DESORPTION COEFFICIENT FOR THE DESORPTION OF PICLORAM IN THE PRESENCE OF HDTMA, SDS AND TWEEN-80 OF THREE DIFFERENT CONCENTRATIONS ON THE SELECTED SOIL SAMPLES

| Soil | K _{Fdes} (ml/g) Without surfac. /n /R ² | K _{sdes} (ml/g) HDTMA /n _{sdes} /R ² | | | K _{sdes} (ml/g) SDS/n _{sdes} /R ² | | | K _{sdes} (ml/g) Tween-80/ n _{sdes} /R ² | | |
|----------------|---|---|-------|---------|--|-------|---------|--|-------|---------|
| | | cmc/10 | cmc | cmc* 20 | cmc/10 | cmc | cmc* 20 | cmc/10 | cmc | cmc* 20 |
| S ₁ | 1.045 | 0.839 | 1.211 | 1.237 | 0.895 | 0.964 | 1.219 | 1.174 | 1.199 | 1.256 |
| | 0.718 | 0.408 | 0.617 | 0.619 | 0.558 | 0.658 | 0.494 | 0.650 | 0.561 | 0.542 |
| | 0.999 | 0.985 | 0.991 | 0.993 | 0.901 | 0.889 | 0.949 | 0.995 | 0.919 | 0.992 |
| S ₂ | 1.586 | 1.286 | 1.270 | 1.273 | 1.014 | 1.161 | 1.184 | 0.953 | 1.152 | 1.175 |
| | 1.947 | 0.553 | 0.574 | 0.555 | 0.599 | 0.671 | 0.537 | 0.429 | 0.520 | 0.523 |
| | 0.987 | 0.979 | 0.988 | 0.989 | 0.939 | 0.981 | 0.996 | 0.888 | 0.938 | 0.94 |
| S ₃ | 1.066 | 1.136 | 1.217 | 1.223 | 1.156 | 1.198 | 1.202 | 1.018 | 1.167 | 1.270 |
| | 1.189 | 0.267 | 0.543 | 0.519 | 0.683 | 0.614 | 0.641 | 0.909 | 0.599 | 0.499 |
| | 0.999 | 0.961 | 0.948 | 0.979 | 0.999 | 0.961 | 0.963 | 0.999 | 0.974 | 0.970 |
| S ₄ | 1.277 | 1.004 | 1.199 | 1.208 | 1.058 | 1.164 | 1.189 | 1.189 | 1.197 | 1.212 |
| | 1.425 | 0.429 | 0.545 | 0.535 | 0.738 | 0.617 | 0.659 | 0.564 | 0.518 | 0.509 |
| | 0.992 | 0.932 | 0.957 | 0.959 | 0.912 | 0.966 | 0.999 | 0.977 | 0.971 | 0.974 |
| S ₅ | 1.398 | 1.038 | 1.196 | 1.212 | 1.009 | 1.082 | 1.241 | 1.097 | 1.146 | 1.158 |
| | 1.733 | 0.479 | 0.563 | 0.566 | 0.621 | 0.631 | 0.577 | 0.495 | 0.512 | 0.501 |
| | 0.998 | 0.896 | 0.926 | 0.938 | 0.981 | 0.975 | 0.995 | 0.952 | 0.961 | 0.965 |
| S ₆ | 1.493 | 1.162 | 1.177 | 1.197 | 1.105 | 1.211 | 1.289 | 1.183 | 1.196 | 1.206 |
| | 1.867 | 0.539 | 0.536 | 0.539 | 0.818 | 0.714 | 0.582 | 0.561 | 0.540 | 0.545 |
| | 0.995 | 0.889 | 0.911 | 0.934 | 0.998 | 0.923 | 0.974 | 0.982 | 0.968 | 0.975 |

TABLE 5
HYSTERSIS COEFFICIENT FOR ADSORPTION- DESORPTION OF PICLORAM ON THE SELECTED D SOIL SAMPLES

| Soil | H _i (HDTAM) | | | H _i (SDS) | | | H _i (Tween-80) | | |
|----------------|------------------------|-------|---------|----------------------|-------|--------|---------------------------|-------|--------|
| | cmc/10 | cmc | cmc* 20 | cmc/10 | cmc | cmc*20 | cmc/10 | cmc | cmc*20 |
| S ₁ | 1.368 | 0.841 | 0.763 | 0.772 | 0.784 | 1.107 | 1.454 | 1.570 | 2.234 |
| S ₂ | 0.765 | 0.693 | 1.090 | 0.761 | 0.976 | 1.534 | 1.564 | 1.700 | 1.524 |
| S ₃ | 2.940 | 1.737 | 2.048 | 0.493 | 1.420 | 0.869 | 0.331 | 1.077 | 1.681 |
| S ₄ | 1.519 | 1.187 | 1.654 | 0.958 | 1.267 | 1.158 | 0.514 | 1.788 | 2.741 |
| S ₅ | 1.568 | 1.413 | 1.624 | 1.058 | 0.868 | 1.478 | 1.026 | 1.578 | 2.243 |
| S ₆ | 1.941 | 2.367 | 2.594 | 0.863 | 1.241 | 1.667 | 0.364 | 1.485 | 1.269 |