

AN ABSTRACT OF THE THESIS OF

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Title: DIFFUSION AND SURFACE REACTION PROCESSES OF
ADSORPTION ON SURFACES OF SOIL PARTICLES IN
UNSATURATED SOILS

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At present the adsorption kinetic of ions by soil particles is considered to be a surface reaction. When the transport of solutes in soils is described using the one-dimensional flow equation, it becomes a serious problem that lateral diffusion of ions from the bulk solution towards the soil surfaces is not considered. The objectives of this study were to re-examine the adsorption process on theoretical and experimental bases in an attempt to develop more appropriate descriptions.

We considered the adsorption process to be a three-step mechanism, namely, diffusion of ions from the bulk solution to the "subsurface" layer around soil particles, diffusion across the "subsurface" layer, and a surface reaction. Diffusion across the subsurface layer is assumed to be at a constant rate and may be the rate limiting process under certain conditions. Ions from the subsurface

layer are adsorbed onto the surfaces of soil particles. This process is described by a surface kinetic reaction which is regarded as another rate limiting process.

A new procedure for measurement of adsorption isotherms was proposed and tested. The new procedure employs a soil sample packed in a short column so that the structure of the soil can be maintained. In our studies solution was added to bring the soil water potential to -0.05 bars. Other water contents could be used. After equilibration, solution was extracted using a pressure membrane apparatus.

The resulting isotherms conformed to the Freundlich-type isotherm. For both iodide and cadmium ions, the soil column and the currently used shaking batch procedures produced isotherms that differed significantly from each other, with the magnitude of adsorption being much greater in the soil column.

It was hypothesized that the arrangement of soil particles influences the attractive force fields and restricts the transitional freedom of ions to a greater extent than occurs in the shaking batch. It was concluded that the soil column procedure more realistically represents conditions as they exist in soil and therefore is preferable over the shaking batch method.

The activation energies for adsorption and desorption were assumed to be logarithmic function of the amounts adsorbed. When

the lateral diffusion process is also considered, the equation describing the adsorption kinetics for one-dimensional solute transfer in soil is

$$\frac{\partial S}{\partial t} = \left[\frac{1}{1/K_d + 1/(k_1 \zeta^{-b})} \right] (\theta / \rho_b) C - \left[\frac{1}{(k_1 \zeta^{-2b} / k_2)(1/K_d) + 1/(k_2 \zeta^b)} \right] S,$$

where K_d (sec^{-1}) is the diffusive conductance of the subsurface layer, k_1 and k_2 (sec^{-1}) are surface reaction constants, b is a constant associated with the change of energy of adsorption as a function of surface coverage, $(\theta / \rho_b)C$ ($\mu\text{g/g soil}$) is the amount of ions in the liquid phase and ζ is the nondimensional representation of S .

The kinetic adsorption equation was evaluated for cadmium for four pore water velocities, \bar{v} , ranging from 0 to 2.7 cm/hr. The soil water potential was maintained at about -0.126 bars. The calculated values of K_d showed an increase with increasing \bar{v} implying that the thickness of the subsurface layer decreased with increasing velocity. The magnitudes of K_d of about 0.07 to $0.4 \times 10^{-3} \text{ sec}^{-1}$ are very important. They are sufficiently low to indicate a rate limiting process especially when the system is far from equilibrium. The studies thus confirm our argument that lateral diffusion cannot be ignored in studies of adsorption kinetics. The ratio of the rate constants, k_1/k_2 , also increased with \bar{v} which led us to conclude

that the rate of adsorption proceeds faster when there is solute flow in the soil system. This is attributed to the higher rates of lateral diffusion and rapid removal of ions originally present at the adsorption sites.

Diffusion and Surface Reaction Processes of
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DIFFUSION AND SURFACE REACTION PROCESSES OF
ADSORPTION ON SURFACES OF SOIL PARTICLES
IN UNSATURATED SOILS

INTRODUCTION

With the development of numerical analysis and computer technology, it has become possible to simulate the movement of water and chemicals through soil under a wide range of initial and boundary conditions. There exist now many programs which describe the movement of water. However, in soil physics most programs remain restricted to one dimensional flow. The experimental techniques for the determination of the parameters needed to solve the flow equations, such as the soil water characteristic curves and the hydraulic conductivity and diffusivity coefficients, though not perfect, are fairly well established. Few of the computer programs, however, allow the hysteretic nature of most of these parameters to be considered. Complete success of numerically describing water and solute flow cannot be expected until soil physical properties such as pore size distributions and active and inactive pore channels can be properly characterized, in addition to the soil water content.

Consideration of chemical movement adds additional complications. Solute transfer is governed by dispersion-diffusion and by convection processes, as well as by chemical reactions in the soil. These reactions include dissociation/association, degradation, and,

most important of all, adsorption by the soil components. The chemical reactions are rather specific for a particular chemical being examined and must be treated individually.

Numerical simulation of water and chemical transport in soil has received much attention only in recent years. It is not unexpected to find that the results of research done on soil systems in the past, though undeniably useful, rendered data inappropriate for use in numerical simulation. This observation is one of the major reasons for the investigation of adsorption processes in soils reported in this study. Most previous studies of adsorption in the field of soil chemistry, had as their main purpose the study of the nature of the soil surface and the associated diffuse double layer. With its emphasis on surface reactions, these studies generally ignored the process of diffusion of ions from the bulk solution to the soil surface, especially as it is affected by the water film around the soil particles. Ward and Tordai (1946) were the first to mention the presence of what they called the "subsurface layer." In a soil system, this is a layer of water near the surface of a soil particle across which ions must pass by diffusion to reach the soil surface.

The study of transverse diffusion processes is not new. The problem has been treated by chemical engineers in their studies of mass flow through adsorbing columns (Smith, 1970). Their studies tend to emphasize equilibrium conditions and simplify the adsorption

process to equilibrium or simple linear adsorption kinetics. Unfortunately, the application of principles used by chemical engineers to the field of soil science has been slow to develop.

Apart from de-emphasizing the diffusion process near the surfaces of the soil particles, there are also problems with the experimental procedures used at the present time for the evaluation of the surface reaction processes. The procedures used to acquire soil water characteristic curves, hydraulic conductivity and diffusivity functions, and the solute dispersion-diffusion coefficients employ soil columns. However, the adsorption parameters are evaluated by using shaking batch or stirred tank procedures (Smith, 1970) which do not preserve or simulate the pore channels of the soil in its natural state. The implied assumption for this procedure, namely that adsorption is solely a surface reaction, is not valid. The procedure does not allow for lateral diffusion. Yet this diffusion resistance is an important parameter in the one dimensional analysis of the process of water and solute transport through soils. More importantly this procedure is limited to the study of saturated conditions and cannot yield data applicable to the simulation of flow through a soil in its natural state which is not saturated.

The purpose of this study is to develop a theoretical and experimental analyses of the adsorption processes in soil in its natural state. The primary objective is to examine the bulk behavior

of the adsorption process to obtain proper mathematical formulations to form the basis for the numerical simulation of chemical transport. It is not intended to deal with the molecular aspects or mechanism of this process. This would require a more sophisticated study.

This report is divided into two parts. The first part describes procedures used for the measurement of the equilibrium adsorption isotherms. The adsorption isotherms will be used for the evaluation of parameters which describe the surface reaction process. The second part describes studies of the adsorption process under dynamic conditions where both surface reactions and lateral diffusion processes take place concurrently. These studies consist of the measurement of adsorption in soil columns under unsaturated condition with water and solute flowing through them at several pore-water velocities.

EQUILIBRIUM ISOTHERMS

Introduction

In a general form, the net rate of adsorption of chemicals by soil surfaces is described by

$$\frac{\partial S}{\partial t} = r_a - r_d , \quad (1-1)$$

where S ($\mu\text{g/g}$ soil) is the amount of the ion of interest adsorbed per unit weight of soil, t (sec) is time and r_a and r_d ($\mu\text{g/g}$ soil/sec) are the forward (adsorption) and backward (desorption) rates of sorption, respectively. In this study it will be assumed that the forward and backward rates account for both the surface reactions and the lateral diffusion processes. This assumption will be evaluated in more detail in the discussion of the dynamic studies. However, as equilibrium is approached, diffusion is completed and the adsorption process is determined only by the surface parameters, so that,

$$\frac{\partial S}{\partial t} \rightarrow 0 \quad \text{and} \quad r_a = r_d . \quad (1-2)$$

Equation (1-2) can be expressed in more detail as

$$k'_a e^{-E_a/RT} f(C,S) = k'_d e^{-E_d/RT} g(S), \quad (1-3)$$

where the rate constant k' (1/sec) is a function of temperature, E (kcal/mole) is the activation energy, the subscripts a and d denote the adsorption and desorption reactions, respectively, R (kcal/mole/°K) is the universal gas constant, and T (°K) is the absolute temperature. The forward rate, r_a , is assumed to be a function of both the concentration C ($\mu\text{g}/\text{ml}$) of ions in the bulk solution and the amount of ions, S , already adsorbed on the surface. The backward rate, r_d , is assumed to be a function solely of S .

Rearranging Equation (1-3) yields

$$g(S) = \left(\frac{k'_a}{k'_d}\right)e^{-(E_a - E_d)/RT} f(C, S). \quad (1-4. a)$$

Adsorption is an exothermic reaction and the difference, $q = (E_d - E_a)$ is the heat of adsorption. The energy levels of E_a , E_d , and q are shown schematically in Figure 1-1. Rewriting Equation (1-4. a) yields

$$g(S) = \left(\frac{k'_a}{k'_d}\right)e^{q/RT} f(C, S). \quad (1-4. b)$$

Equation (1-4. b) shows that the adsorption equilibrium involves only the net difference between the two activation energies, namely, the heat of adsorption.

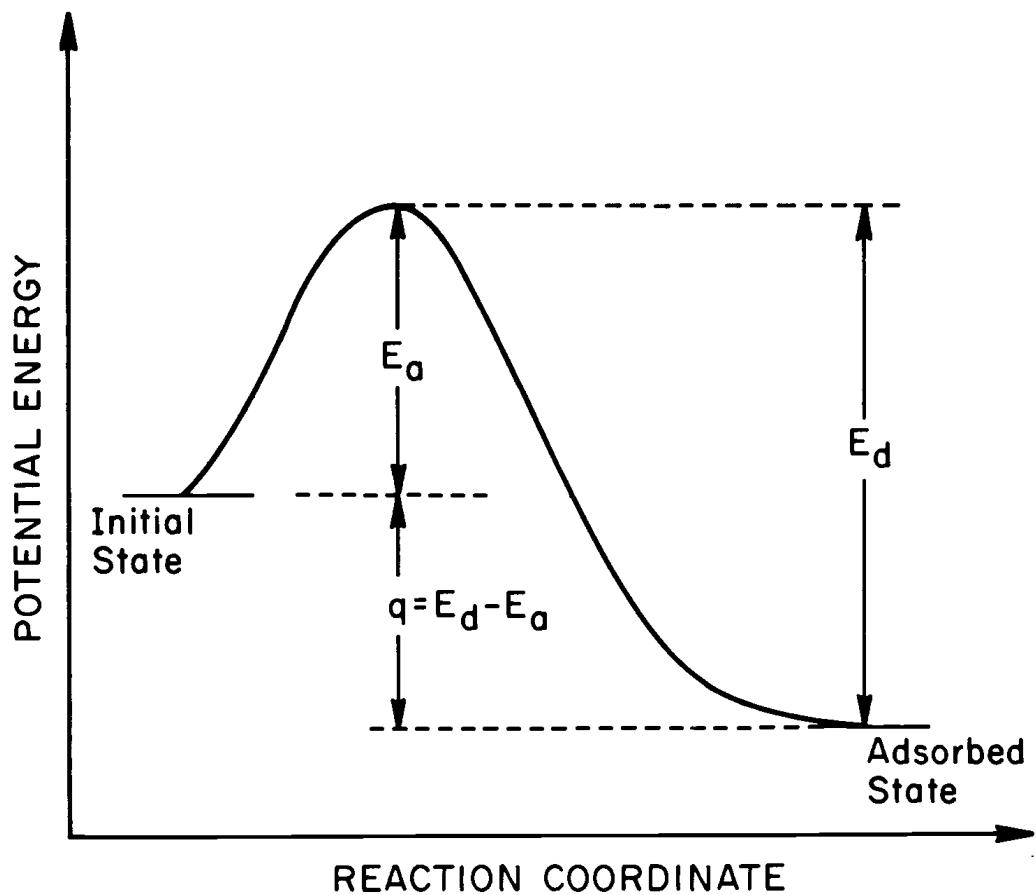


Figure 1-1. Diagrammatic representation of the change in the potential energy of the adsorbed molecule during adsorption.

Several models have been proposed for adsorption isotherms which relate the amounts adsorbed on a surface to the concentrations of molecules in equilibrium with the surface at a particular temperature. Good reviews of the principles of these models can be found quite readily (Hayward and Trapnell, 1964; Ross and Olivier, 1964; Ponec, Knor and Cerny, 1974). For this study, we will bypass the models for homogeneous surfaces and only consider the models for heterogeneous surfaces which are presently at the center of interest in the study of surface chemistry. The term "heterogeneous" surface implies heterogeneity with respect to the heat of adsorption of different regions of the surface. Present models can only deal with surfaces having simple distributions of energy, e.g., a unimodal distribution. It is obvious that the surfaces for adsorption of soil which are composed of many diversified components must have a very high degree of heterogeneity with respect to adsorption energy. Our goal is to find workable models that can describe the bulk behavior of the adsorption processes in soils without complete prior understanding of the actual mechanisms underlying all these models.

The adsorption isotherm for heterogeneous surfaces with non-interacting sites and for non-dissociated ions can be represented in an integral form as

$$\phi(p) = \int_{\Omega} \phi(p, q) \chi(q) dq, \quad (1-5)$$

where ϕ is the fraction of surface covered, $\phi(p)$ represents the isotherm of the combined adsorption at all individual patches at pressure p , $\phi(p, q)$ is the local isotherm for the adsorption on a surface patch which has an adsorption energy equal to q . Each of these patches is called "homotactic." Sanford and Ross (1954) defined a homotactic surface as the surface of a patch or region, usually a part of a larger surface, that acts as though its structure were uniform and homogeneous with respect to adsorption. The energy distribution function, $\chi(q)$, describes how heat of adsorption changes with the extent of surface coverage. The expression for $\chi(q)$ is

$$\chi(q) = - \frac{d\phi}{dq}. \quad (1-6)$$

The integration limit of Equation (1-5), Ω , is the range of variation of the values of energy q . Rudzinski and Wojciechowski (1977) discussed the problem of the physically permissible domain of q . Defining this domain is not without difficulty. The physical domain of Ω was initially proposed by Sips (1948) to be $(-\infty, +\infty)$. Later the more acceptable range $(0, +\infty)$ was used by Hill (1949). Recently the consensus that there must be some relatively low maximum energy of adsorption, q_{max} , on every heterogeneous surface has become

more widely accepted. This is because the non-physical part of the integral from q_{\max} to infinity leads to physically meaningless results for $\chi(q)$, e.g., negative values of $\chi(q)$.

One important point should be made. Most of the adsorption theories apply to studies of adsorption of gases on solid surfaces. This problem is much easier to describe in as much as two well established theories exist which can be used in the evaluation of the equations. These are the Gas Law and the kinetic theory of gases. However, these equations can also be applied to the problem of adsorption from a dilute liquid solution onto a solid surface.

Glasstone et al. (1941) pointed out that

the treatment of physicochemical reactions (in solution) should, in principle, be the same as for gas reactions with the modification that the partition functions should contain terms which allow for the influence of the liquid phase environment. The molecules in the liquid are still considered to be mass points which must pass an energy barrier when they move from the bulk phase of solution to the surface or vice versa. The difference with respect to the gas phase is that the solvent molecules are treated as having an external potential effect which modifies the configurational potential energy and the free space of motion of each of the solute molecules.

Accordingly, the adsorption of ions from solution onto solid surfaces is in general satisfactorily described by the basic equations derived originally for the adsorption of gases onto solid surfaces.

One of the basic problems with the experimental investigation of heterogeneous adsorbents is to solve Equation (1-5) to determine the

energy distribution function $\chi(q)$ when the overall adsorption isotherm, $\phi(p)$ is known and a particular analytic form of the local adsorption isotherm, $\phi(p, q)$ is assumed. The knowledge of $\chi(q)$ is normally used in an attempt to link the adsorption energies to the adsorbent surface properties which in turn leads to information on activation energies, E_a and E_d , of the surface. At present, even though the common concern is to consider the importance of both of the functions of the local isotherm and the energy distribution, most studies still are based on the opinion (Adamson et al., 1966) that the interaction energy distribution is the dominant one for most surfaces and the most uniquely characteristic, so that emphasis on it rather than on the adsorption model should have preference.

As a consequence, the local adsorption isotherm is usually assumed to have Langmuir behavior. This is expressed by

$$\phi(p, q) = \left[1 + \frac{K e^{-(q/RT)}}{p} \right]^{-1}, \quad (1-7)$$

where K is the characteristic constant of the Langmuir isotherm.

Substitution of Equation (1-7) into Equation (1-5) gives

$$\phi(p) = \int_{\Omega} \frac{p}{\{p + K e^{-(q/RT)}\}} \chi(q) dq. \quad (1-8)$$

It is not difficult in principle to calculate $\chi(q)$ through the inversion of Equation (1-8). Many attempts have been made to solve

this equation analytically. Sips (1950) and Misra (1970) solved the integral Equation (1-8) explicitly for the Freundlich isotherm and Misra (1969) also solved Equation (1-8) for the Dubinin-Radushkevich (D-R) isotherm using the method of Stieltjes transform and obtained the corresponding energy distribution function, $\chi(q)$ which characterized energetic heterogeneity of the surface.

Another widely used method is based on the principle of "Condensation Approximation" (Harris, 1968). The essence of this method is to replace the true kernel $\phi(p, q)$ by a step-function, $\phi_c(p, q)$, as follows,

$$\phi_c(p, q) = \begin{cases} 0, & p < p_c(q, T) \\ 1, & p \geq p_c(q, T) \end{cases} \quad (1-9.a)$$

which can be rewritten in the form of the heat of adsorption as

$$\phi_c(p, q) = \begin{cases} 0, & q < q_c(p, T) \\ 1, & q \geq q_c(p, T) \end{cases} \quad (1-9.b)$$

where p_c and q_c are defined as the pressure and energy at which the discontinuity, or condensation, in filling up the adsorption sites, occurs.

Then the solution for $\chi(q)$ is

$$\chi(q) = - \frac{\partial[\phi(p)]}{\partial q} \Big|_{p=p_c(q)} \quad (1-10)$$

The Condensation Approximation simplifies the mathematical procedure and the approximation gives satisfactory results.

Cerofolini (1972) obtained the energy distribution function $\chi(q)$ for the D-R isotherm using this approximation. The final solution is similar whether using this method or the Stieltjes transform.

Table 1-1 shows the resulting overall adsorption isotherms and the corresponding energy distribution functions. These energy distributions are now widely used. However, the next step of relating these energy functions to the adsorbing characteristics of sorbing surfaces has not been quite as successful. Cerofolini (1975) proposed models which explain the properties of surfaces for which adsorption follows the D-R or Freundlich isotherms. Ionescu (1976) extended and modified these concepts to explain the behavior of Henry and Temkin isotherms. Hsu et al. (1976), however, argued that the explanations are in fact merely post facto rationalizations and cannot be considered to constitute a rigorous proof. The point is that there has not been as yet a well established explanation for the behavior of the adsorption processes represented by the commonly used isotherms.

For this study, we plan to use accepted concepts about the energy distribution function. The first objective of the study is to determine the adsorption isotherm for a Pope Ridge soil of which the physical and chemical properties were listed in the Appendix, and to

Table 1-1. Adsorption isotherms and the corresponding energy distribution functions.

Isotherms	Expressions	Energy Distribution Functions
Dubinin-Radushkevich ^{1/} (D-R)	$\theta(p) = \begin{cases} e^{-B(RT \ln p/p_m)^2} \\ 1 \end{cases}$	$\chi(q) = \begin{cases} 2B(q-q_m)e^{-B(q-q_m)^2}, & p \leq p_m \text{ or} \\ 0, & q \geq q_m \\ & p > p_m \text{ or} \\ & q < q_m \end{cases}$
Freundlich ^{2/}	$\theta(p) = Ap^c$	$\chi(q) = (c/RT)e^{-c(q-q_m^F)/RT}$
Temkin ^{3/}	$\theta(p) = C + D \ln p$	$\chi(q) = 1/q_{\max} = \text{constant}$

^{1/} B and p_m are two characteristic constants of the D-R isotherm. $q = -RT \ln(p/K)$ and the minimal adsorption energy, $q_m = RT \ln(K/p_m) = \text{a constant}$, where K is the Langmuir constant in Equation (1-7) associated with the molecular partition function of molecules in the monolayer.

^{2/} A and c are two characteristic constants of the Freundlich isotherm. The minimal adsorption energy $q_m^F = -RT \ln(A^{1/c}) = \text{a constant}$.

^{3/} C and D are two characteristic constants of the Temkin isotherm. q_{\max} is the upper limit of the adsorption energy of the surface.

deduce from the isotherm the relationship between the heat of adsorption and the amount adsorbed. The equilibrium isotherms such as those shown in Table 1-1 are derived for systems consisting of clean adsorbing surfaces and one species of adsorbed molecule. This is not the condition found in the soil system. The surfaces of soil particles are always occupied by various kinds of cations which are bound in two layers, namely, tightly bound onto the soil surface (Stern layer) and loosely bound in the diffuse (Gouy) layer (Van Olphen, 1977). Our study of the equilibrium isotherm is expected to verify any discrepancies which might exist in the application of the simple theoretical models to the complex system of the soil.

A second objective is to evaluate new experimental procedures proposed here for the study of adsorption, in order to obtain information which may be used in the numerical simulation of chemical transport through soil. We propose to measure adsorption in a soil of which the structure and pore size distribution remains intact in contrast to the conventional method of using the shaking batch procedure. We wish to evaluate the differences, if any, between the results of these two methods and examine the cause for such differences.

Materials and Methods

Two isotherms were to be determined, namely one for a cation and another one for an anion. Cadmium and iodide were chosen as the

representative cation and anion, respectively. These were chosen because they do not undergo microbial transformations and are relatively easy to prepare and analyze. In the evaluation of the isotherms, two experimental procedures were to be compared. One procedure is the currently used shaking batch method. The other is a method proposed by the author. It uses a soil column, which allows the structure of the soil to be maintained, to obtain the adsorption isotherm.

The soil used in this study was the Pope Ridge soil obtained from the 0-15 cm depth. This soil is developed from volcanic ash deposits. Physical and chemical properties were obtained (Appendix I and II).

The Shaking Batch Procedure

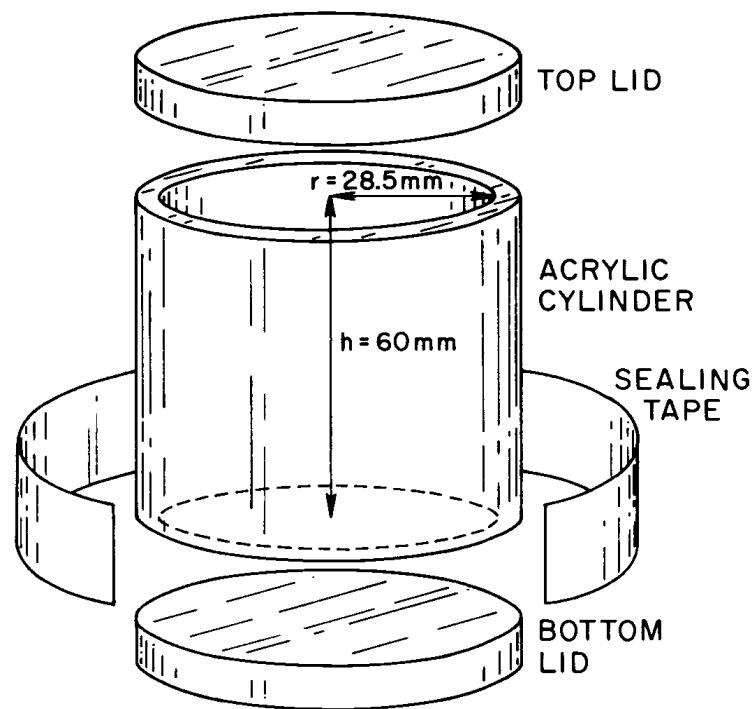
The shaking batch procedure is a method which is widely used in the study of adsorption. In this study 10 g of air dried soil were weighed and put in 250 ml plastic bottles. Fifty ml of solution containing both Cd and I ions prepared from CdI_2 were added to each sample. The bottles were sealed and secured on a shaking tray in a constant temperature bath set at $22.5 \pm 0.5^\circ\text{C}$. The shaking continued for 48 hours. Preliminary studies of a time series showed that 48 hours is a sufficient length of time for the system to attain equilibrium. The bottles were centrifuged at the speed of $2500 \times g$ for ten minutes. The supernatant was filtered, collected, and analyzed for

the concentrations of Cd and I.

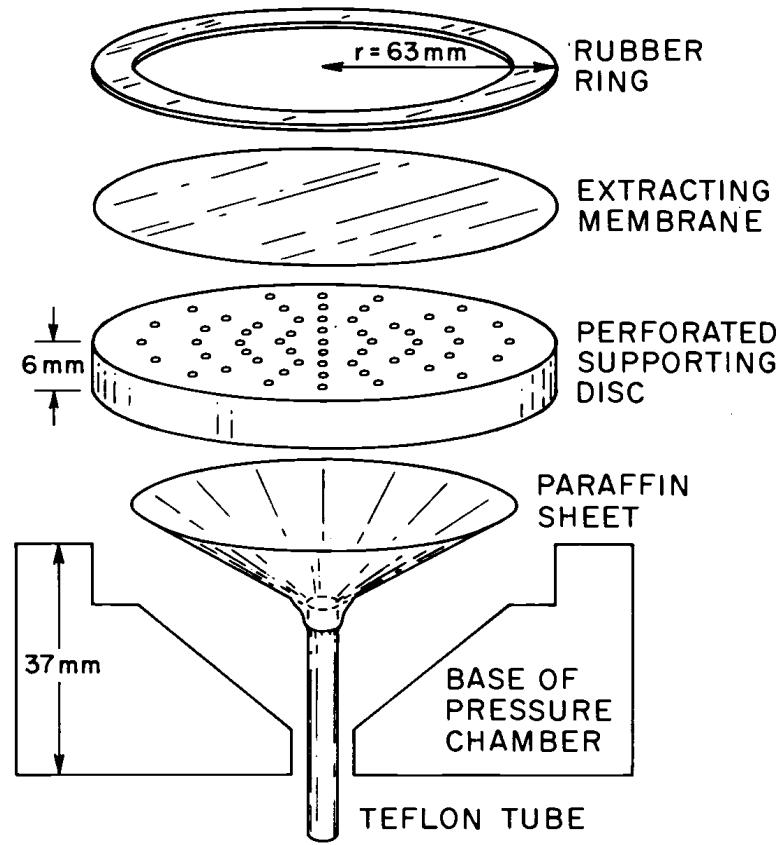
The Short Soil Column Procedure

Instead of equilibrating the soil with excessive solution by shaking it over a period of time, the solution is added to a soil sample packed in a short column up to a predetermined water content. The soil column, is then incubated until adsorption equilibrium is reached. This procedure allows the measurement of adsorption isotherms in soils which are not completely saturated. There are certain limitations at low degrees of saturation. One serious problem is to obtain a uniform distribution of the solution to every part of the soil. Another problem is the increasing difficulty encountered in extracting pressures and longer periods of extraction are required as the water content is lower.

In our study 100 g of air dried soil were packed into a short plastic cylinder to a bulk density of 1.12 g/cm^3 . The cylinder was an acrylic tube with an I.D. = 57 mm and a height of about 60 mm. The top and bottom of the cylinder were sealed by discs also made of acrylic material with the same O.D. as the cylinder itself (Figure 1-2a). The bottom disc must be sealed tightly to prevent leaking when solution is added, yet in such a manner that it can be removed easily later. Adhesive "Scotch" tape was found to serve the purpose quite satisfactorily (Figure 1-2a). The packing



a.



b.

Figure 1-2. a. Schematic diagram of an acrylic cylinder with lids on top and bottom.
b. The arrangement of the extracting chamber.

of soil was done manually by adding about 10-20 g of soil at a time which was packed with a plunger made of a thick acrylic disc. The packing was found to be fairly uniform since the soil used was sandy loam which is quite well graded (Appendix I).

Forty-one ml of CdI₂ solution was added to each core from a burette. The delivery rate of solution must be gradual. Because the bottom part is sealed, the surface cannot be allowed to be ponded. Should that occur, air would not have a way to leave the soil as the solution enters the soil pores. The entrapment of air would cause ruptures in the soil mass. The amount of solution added brought the soil water content to 44% by weight on the oven dried mass basis and the corresponding water potential was -0.05 bars.

The purpose for measuring the adsorption isotherm is to obtain values of the parameters which describe the surface reaction step of the adsorption process. Additional details of the calculations are given in a later chapter. The measurements were therefore done at high levels of saturation. This ensured that the soil solution formed a continuous body such that complete diffusion of ions could take place throughout the soil system. According to the soil water characteristics of the Pope Ridge soil (Figure 3-1 in Appendix I), the water content at -0.05 bars may be considered equivalent to saturation because it is within the so-called "capillary fringe" region. Therefore the amount of solution added was nearly sufficient to bring the

soil to saturation. Additional solution tends to seep from the bottom of the column.

After addition of the solution, the column was sealed at the top with adhesive tape and incubated in a glass jar, placed in a temperature controlled room at $22.5 \pm 0.5^{\circ}\text{C}$ for 48 hours.

When adsorption equilibrium was reached, the top and bottom discs were removed and the column was placed in the extracting chamber, shown in Figure 1-3. The extracting membrane is made of nylon material and is a product of the Millipore Corp. (Brand name: Duralon with a pore size of $1.0 \mu\text{m}$ and a bubbling pressure of 0.517 bars (7.5 psi).) The supporting disc (Figure 1-2b) is made of acrylic. The solution was collected by a funnel covered with paraffin paper and penetrated by a short teflon tube to allow the solution to flow into the collecting bottle. These special precautions were necessary to avoid loss of ions during extraction, due to contact with sorbing surfaces such as metal surfaces. Metals are considered to be active surfaces with respect to adsorption. After placing the soil column on the membrane, the acrylic column was raised up a few millimeters by gently pressing on the soil surface while pulling up on the cylinder. As a result, the acrylic column was not in contact with the membrane. This ensured that the bottom surface of the soil was in good contact with the membrane.

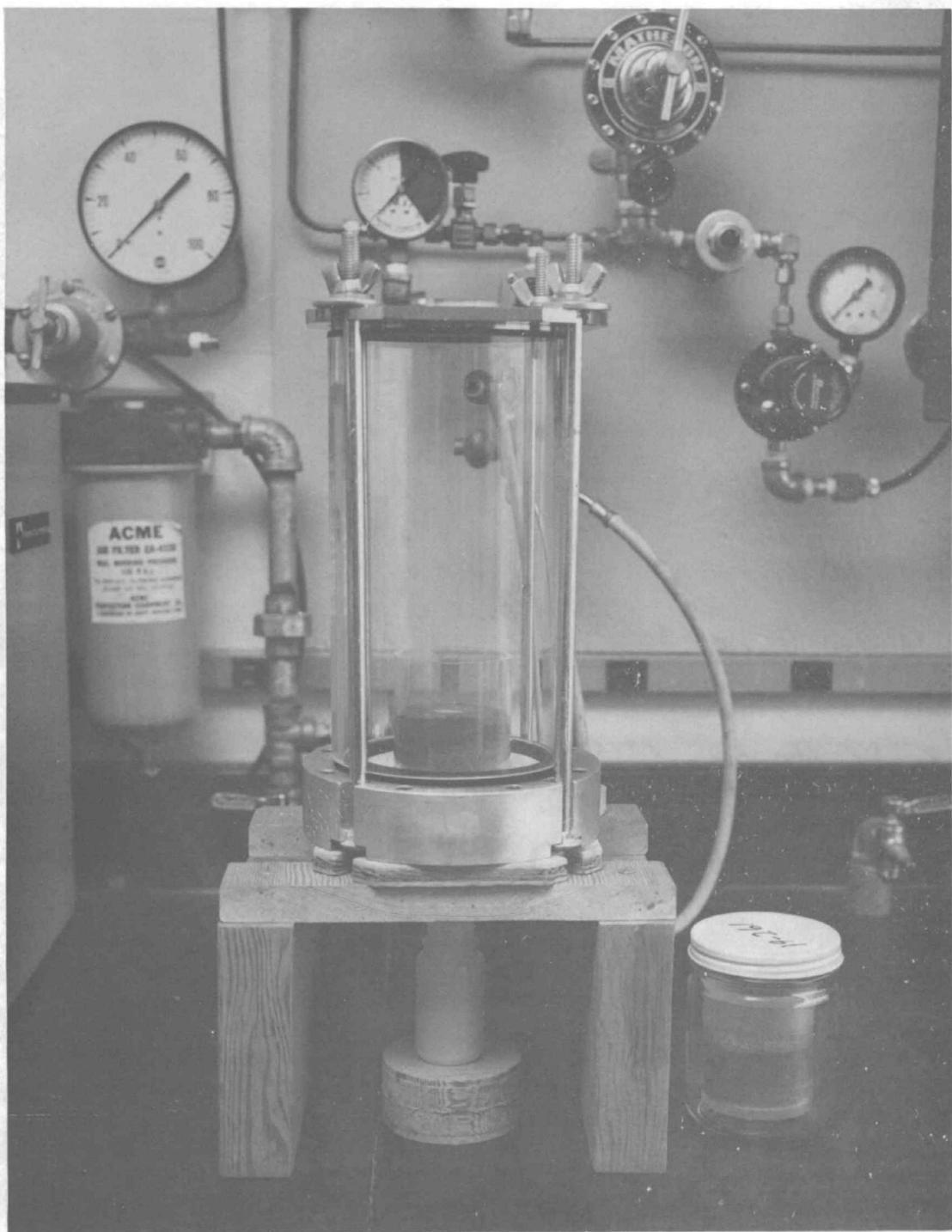


Figure 1-3. Photograph of the extracting chamber and the soil column incubating in a sealed glass jar.

The extracting chamber was sealed and a pressure of 0.34 bars (5 psi) was applied for a fixed period of time. The length of the extraction time depends on the amount of solution needed for analysis. Once the time period is set, it should be kept constant for all samples. In our case, the time period used was 30 minutes. The effluent was collected and analyzed for the concentrations of cadmium and iodide.

According to the soil-water characteristics of the soil (Appendix I), most of the solution is withdrawn at 0.34 bars. Increasing the pressure will not yield much additional solution. On the other hand, higher pressures would require the use of a pressure membrane with a higher bubbling pressure and much lower conductivity. The time required for extraction would be much longer.

Using the relationship between pore water pressure and pore radius of

$$P = \frac{2\sigma \cos \alpha}{r} , \quad (1-11)$$

where P (dyne/cm²) is the potential of soil water, σ (dyne/cm) is the value for the surface tension of water, α is the contact angle and r (cm) is the radius of the soil pore, we obtain the corresponding radius of pore at -0.34 bars of 4.26 μm , assuming $\sigma = 72$ dyne/cm and $\alpha = 0$ for complete wetting. Consequently, using the extracting pressure of 0.34 bars obtains solution from pores with radii of 4.26 μm and larger. As discussed earlier, the soil

sample is wetted to a high degree of saturation where the solution may be considered to be a continuous medium through which the diffusion process of ions can attain complete equilibrium. Therefore, the concentration of the solution extracted from the large pores is assumed to be the equilibrium concentration. In the smaller pores and dead-end pores, the concentrations may be higher. However, we perceive that for ions to accumulate in these smaller pores, they must be within some kind of force field exerted by soil particles which retain them against concentration gradients.

Preparation and Analysis of Cadmium and Iodide Solutions

The Cd and I ions were supplied by adding CdI_2 . This procedure was used to maintain a constant cation-anion ratio. The range of concentration of the cadmium ions used in the shaking batch experiments was 0.1 to 2000 $\mu\text{g Cd/ml}$ and the range used for the short soil column studies was 400 to 1500 $\mu\text{g Cd/ml}$. The range of concentration of iodide was 0.2 to 11,000 $\mu\text{g I/ml}$ for the shaking batch experiments and 0.2 to 23,000 $\mu\text{g I/ml}$ for the short soil column experiments. Wide ranges of concentration were used to cover the entire range of the adsorption process. Most isotherms are known to be applicable to certain ranges of concentration only and not valid in other ranges. Using a wide range of concentrations assured us of obtaining data in all possible ranges of applicability. The degrees of adsorption for

cadmium and iodide are different. Therefore, there is only a range of concentrations where adsorptions of cadmium and iodide can be determined simultaneously using the same sample. For most concentrations the experiments had to be carried out separately for the two ions as the concentration of Cd would be too low to be detectable.

The CdI_2 compound was diluted in a calcium acetate-acetic acid $[\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}(\text{C}_2\text{H}_3\text{O}_2)]$ buffer solution. The solution contains 0.01 N of calcium and has a pH of 5.9 ± 0.1 . To prepare two litres of buffer solution, set the pH of distilled water to 7.00 with 0.1 N NaOH and add 1.2 ml of 1N $\text{H}(\text{C}_2\text{H}_3\text{O}_2)$ and 1.72 g of $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{XH}_2\text{O}$ (Mallinckrodt AR grade).

The analysis of Cd was done by atomic absorption spectrophotometry in the range of 0-2 $\mu\text{g Cd/ml}$ (Perkin-Elmer Model 306). The measurement of iodide was done with a specific ion electrode (Orion Research Incorp. Model 94-53). Resolution and reproduction of the iodide determinations were improved significantly by using the procedure of Hoover et al. (1971). Since a magnetic stirrer was used instead of a stirrer driven by water or air flow, a modification was necessary to minimize temperature changes of the analyzed solution. This was accomplished by placing the 100 ml beaker containing solution to be measured in a larger beaker (250 ml) filled with water. Periodically, the water in the larger beaker was changed to maintain a constant temperature throughout the period of measurement. To

further improve accuracy, all samples should be measured using the same sample container, which was rinsed thoroughly with distilled water and blotted dry between samples, and using the same stirring speed, and with the electrodes being immersed into the solution to the same depth. At low concentrations ($\leq 1 \mu\text{g I/ml}$), the readings tend to drift and a 3 to 4 minute period is recommended before readings are recorded. At higher concentrations a one to two minute waiting period is sufficient.

Calculations

The computations of the amount of ions adsorbed is to account for the amount of ions added to the soil and the amount present in the equilibrium solution. Let C_{in} and C_f ($\mu\text{g}/\text{ml}$) be the concentrations of the bulk solution before applying it to the soil and at the end when equilibrium is reached, respectively. Then the amount adsorbed is

$$S = \frac{V}{M_s} (C_{in} - C_f) , \quad (1-12)$$

where S ($\mu\text{g/g}$ soil) is the amount of ion adsorbed per unit weight (air-dried basis) of soil, V (ml) is the volume of the solution added to the soil and M_s (g soil) is the weight of the soil sample.

Results

The value of C_{in} in Equation (1-12) is the concentration of the solution applied to the soil sample. The value of C_f , the concentration at equilibrium, is the concentration of the solution obtained from the soil sample by centrifugation in the experiments with the shaking batch samples and that of the solution extracted from the soil column in the short column experiments. The values of V and M_s were changed during the progress of the experiments. For the experiments with the short soil columns, initially 165 g of air-dried soil were used and 68 ml of solution were added so that $V/M_s = 68/165$ ml/g soil. Later on, it was found that a sample of 100 g soil with 41 ml solution added, which maintained the same ratio of V/M_s , yielded sufficient solution for analysis. The latter values were then used so that the time of sample preparation was decreased. For the shaking batch experiments initially 3 g of soil in 25 ml of solution were used. Subsequently, 10 g of soil were used in 50 ml of solution in order to incorporate more soil into the measurement. Therefore, the ratio V/M_s was 0.41 ml/g soil for the soil column experiments and 5.0 ml/g soil for the shaking batch experiments. The amount of ions adsorbed is expressed on the basis of the air-dried weight of the soil. Air-dried soil has a water content of 0.021 g/g soil.

The results of the experiments showing concentrations at equilibrium and the amount adsorbed for the Cd cation and the I anion are tabulated in Tables 1-2 and 1-3 and are shown graphically in Figures 1-4 and 1-5. Both the Cd and I isotherms are of the Freundlich type which are described by the general equation $S = a(C_{eq})^c$. Straight lines representing the relationship between the logarithm of S and the logarithm of the concentration at equilibrium, (VC/M_s) , were determined using the least square error analysis. Each point represents the measurement of one soil sample. All the correlation coefficients, r , have levels of significance at 0.001. Values of r^2 are shown in Figures 1-4 and 1-5.

In our analysis we used the values of (VC/M_s) which indicate the amount of ions in the equilibrium solution per unit weight of soil instead of the concentration based on the volume of soil solution, as used in conventional plots. On the log-log plot, this difference in expression simply raises the intercept of the lines by an amount equal to $\log(V/M_s)$, since

$$\log(VC/M_s) = \log(V/M_s) + \log C. \quad (1-13)$$

This procedure serves to normalize the system which is very useful since the amount of solution and the amount of soil used in this kind of study is quite arbitrary. Moreover, this procedure helps

Table 1-2. The initial concentration and the concentration of iodide at equilibrium, the amount adsorbed and the amount adsorbed as percentage of the initial concentration.

Sam- ple No.	Concentration of Iodide		Amount of I Adsorbed	I Adsorbed as % of Initial Amount
	Initial <u>μg I/ml</u>	At Equilibrium <u>μg I/ml</u>		
<u>Short Soil Column^{1/}</u>				
1	.228	.038	.016	.078 83.17
2	.610	.121	.050	.201 80.10
3	1.16	.264	.109	.370 77.30
4	5.98	2.65	1.09	1.37 55.68
5	10.18	4.31	1.78	2.41 57.59
6	34.52	21.94	9.04	5.18 36.44
7	57.64	38.10	15.70	8.05 33.90
8	172.32	121.41	50.03	20.98 29.50
9	163.55	124.42	51.28	16.12 23.92
10	216.89	149.75	61.71	27.67 30.96
11	161.73	109.90	45.29	21.36 32.05
12	552.26	375.36	154.69	72.90 32.03
13	792.52	563.56	232.25	94.36 28.89
14	619.65	449.67	185.32	70.05 27.43
15	938.73	651.16	268.36	118.51 30.63
16	2,193.67	1,402.95	578.18	325.88 36.05
17	3,316.14	1,933.34	796.77	569.88 41.70
18	4,367.59	2,604.50	1,073.37	726.61 40.38
19	7,891.41	2,802.45	1,979.19	1,273.02 39.14
20	11,270.82	7,423.00	3,059.18	1,585.77 34.14
21	18,312.25	10,994.36	4,531.01	3,015.86 39.96
22	23,053.81	17,113.11	7,052.67	2,448.29 25.77
23	.195	.087	.037	.046 55.37
24	1.21	.429	.182	.330 64.49
25	.871	.297	.126	.243 65.86
26	2.24	.873	.370	.579 61.00
27	4.65	2.07	.879	1.09 55.46
28	11.41	6.52	2.76	2.08 42.90
29	22.90	14.34	6.08	3.63 37.39
30	53.87	37.99	16.12	6.74 29.48
31	108.47	78.16	33.16	12.86 27.94
32	10.09	5.29	2.17	1.92 46.99

Table 1-2. Continued.

Sam- ple No.	Concentration of Iodide		Amount of I Adsorbed	I Adsorbed as % of Initial Amount	
	Initial	At Equilibrium		$\mu\text{g I/g soil}$	%
<u>2 /</u> <u>Shaking Batch</u>					
1	.213	.123	.617	.447	42.04
2	1.23	1.00	5.02	1.14	18.52
3	.930	.733	3.66	.987	21.22
4	2.26	1.95	9.73	1.55	13.78
5	4.68	4.25	21.25	2.15	9.20
6	11.44	10.92	54.60	2.60	4.54
7	23.23	22.12	110.61	5.55	4.78
8	54.27	52.91	264.53	6.84	2.52
9	110.80	108.41	542.03	11.99	2.16
10	.228	.169	.847	.292	25.64
11	.610	.498	2.49	.557	18.27
12	1.16	.968	4.84	.973	16.74
13	1.83	1.56	7.82	1.31	14.36
14	2.40	2.10	10.51	1.51	12.56
15	3.56	3.14	15.70	2.13	11.93
16	5.98	5.53	27.63	2.28	7.62
17	10.18	9.97	49.85	1.03	2.02
18	19.06	17.81	89.05	6.25	6.56
19	22.99	22.48	112.39	2.57	2.24
20	34.52	33.30	166.49	6.13	3.55
21	172.32	168.10	840.48	21.14	2.45
22	163.55	154.57	772.86	44.88	5.49
23	216.89	209.67	1,048.35	36.11	3.33
24	552.26	532.67	2,663.33	97.96	3.55
25	619.65	590.96	2,954.78	143.46	4.63
26	938.73	893.24	4,466.22	227.42	4.84
27	2,193.68	2,111.08	10,555.41	412.96	3.76
28	4,367.59	4,270.10	21,350.51	487.46	2.23
29	11,270.82	10,895.56	54,477.81	1,876.31	3.33
30	.833	.727	6.06	.889	12.80
31	1.76	1.60	13.30	1.37	9.34

Table 1-2. Continued.

Sam- ple No.	Concentration of Iodide		Amount of I Adsorbed	I Adsorbed as % of Initial Amount	
	Initial	At Equilibrium			
	$\mu\text{g I/ml}$	$\mu\text{g I/ml}$	$\mu\text{g I/g soil}$	$\mu\text{g I/g soil}$	$\%$
32	3.57	3.27	27.28	2.47	8.30
33	7.22	6.70	55.80	4.36	7.25
34	9.09	8.37	69.77	5.97	7.88
35	14.64	13.76	114.68	7.28	5.97
36	18.55	17.44	145.37	9.23	5.97
37	98.87	95.33	794.42	29.51	3.58

1/ For samples no. 1-22, $V/M_s = 68 \text{ ml}/165 \text{ g soil}$; no. 23-31, $V/M_s = 70 \text{ ml}/165 \text{ g soil}$; no. 32, $V/M_s = 41 \text{ ml}/100 \text{ g soil}$.

2/ For samples no. 1-29, $V/M_s = 50 \text{ ml}/10 \text{ g soil}$; no. 30-37, $V/M_s = 25 \text{ ml}/3 \text{ g soil}$.

Table 1-3. The initial concentration and the concentration of cadmium at equilibrium, the amount adsorbed and the amount adsorbed as percentage of the initial concentration.

Sam- ple No.	Concentration of Cadmium		Amount of Cd Adsorbed	Cd Adsorbed as % of Initial Amount	
	Initial $\mu\text{g Cd/ml}$	At Equilibrium $\mu\text{g Cd/ml}$	$\mu\text{g Cd/g soil}$	%	
<u>Short Soil Column^{1/}</u>					
1	383.50	.05	.0205	157.21	99.987
2	422.50	.08	.0328	173.19	99.981
3	487.50	.10	.0410	199.83	99.979
4	533.00	.20	.0820	218.45	99.962
5	578.00	.49	.2009	236.78	99.915
6	620.50	1.00	.4100	253.99	99.839
7	675.75	2.40	.9840	276.07	99.645
8	722.50	7.93	3.2513	292.97	98.902
9	790.02	11.13	4.5633	319.34	98.591
10	831.60	13.53	5.5473	335.41	98.373
11	893.97	29.93	12.2713	354.26	96.652
12	935.55	30.34	12.4394	371.14	96.751
13	1,006.50	59.86	24.5426	388.12	94.053
14	1,072.50	60.68	24.8788	414.85	94.342
15	1,187.01	91.00	37.3100	449.36	92.334
16	1,295.91	141.40	57.9740	473.35	89.089
17	1,383.03	193.60	79.3760	487.67	86.002
18	1,205.82	135.52	55.5632	438.82	88.761
19	346.38	.03	.0124	142.74	99.991
<u>Shaking Batch^{2/}</u>					
1	.50	.03	.15	2.35	94.000
2	1.08	.16	.80	4.60	85.185
3	1.80	.36	1.80	7.20	80.000
4	4.80	1.02	5.10	18.90	78.750
5	10.50	2.86	14.30	38.20	72.762
6	24.80	8.78	43.90	80.10	64.597
7	48.00	21.19	105.95	134.05	55.854
8	.54	.03	.15	2.55	94.444
9	.85	.09	.45	3.80	89.412
10	1.01	.21	1.05	4.00	79.208

Table 1-3. Continued.

Sam- ple No.	Concentration of Cadmium		Amount of Cd Adsorbed	Cd Adsorbed as % of Initial Amount
	Initial	At Equilibrium	$\mu\text{g Cd/g soil}$	%
	$\mu\text{g Cd/ml}$	$\mu\text{g Cd/ml}$	$\mu\text{g Cd/g soil}$	
11	1. 64	. 26	1. 30	84. 146
12	2. 60	. 49	2. 45	81. 154
13	4. 80	. 95	4. 75	80. 208
14	8. 64	2. 21	11. 05	74. 421
15	10. 32	2. 87	14. 35	37. 25
16	14. 52	3. 95	19. 75	52. 85
17	24. 78	7. 13	35. 65	72. 796
18	71. 75	38. 53	192. 65	46. 300
19	76. 50	37. 22	186. 10	51. 346
20	92. 92	45. 44	227. 20	51. 098
21	258. 53	175. 70	878. 50	32. 039
22	264. 60	176. 39	881. 95	441. 05
23	409. 20	289. 84	1, 449. 20	596. 80
24	1, 884. 96	1, 670. 74	8, 353. 70	1, 071. 10
25	88. 98	47. 00	391. 67	349. 83
26	193. 22	134. 00	1, 116. 67	493. 50
27	396. 61	322. 00	2, 683. 33	621. 75
28	508. 47	405. 00	3, 375. 00	862. 25
29	813. 56	700. 00	5, 833. 33	946. 33
30	1, 016. 95	905. 00	7, 541. 67	932. 92

^{1/} Only sample no. 19 has $V/M_s = 68 \text{ ml}/165 \text{ g soil}$, all other samples have $V/M_s = 41 \text{ ml}/100 \text{ g soil}$.

^{2/} For samples no. 1-24, $V/M_s = 50 \text{ ml}/10 \text{ g soil}$; no. 25-30, $V/M_s = 25 \text{ ml}/3 \text{ g soil}$.

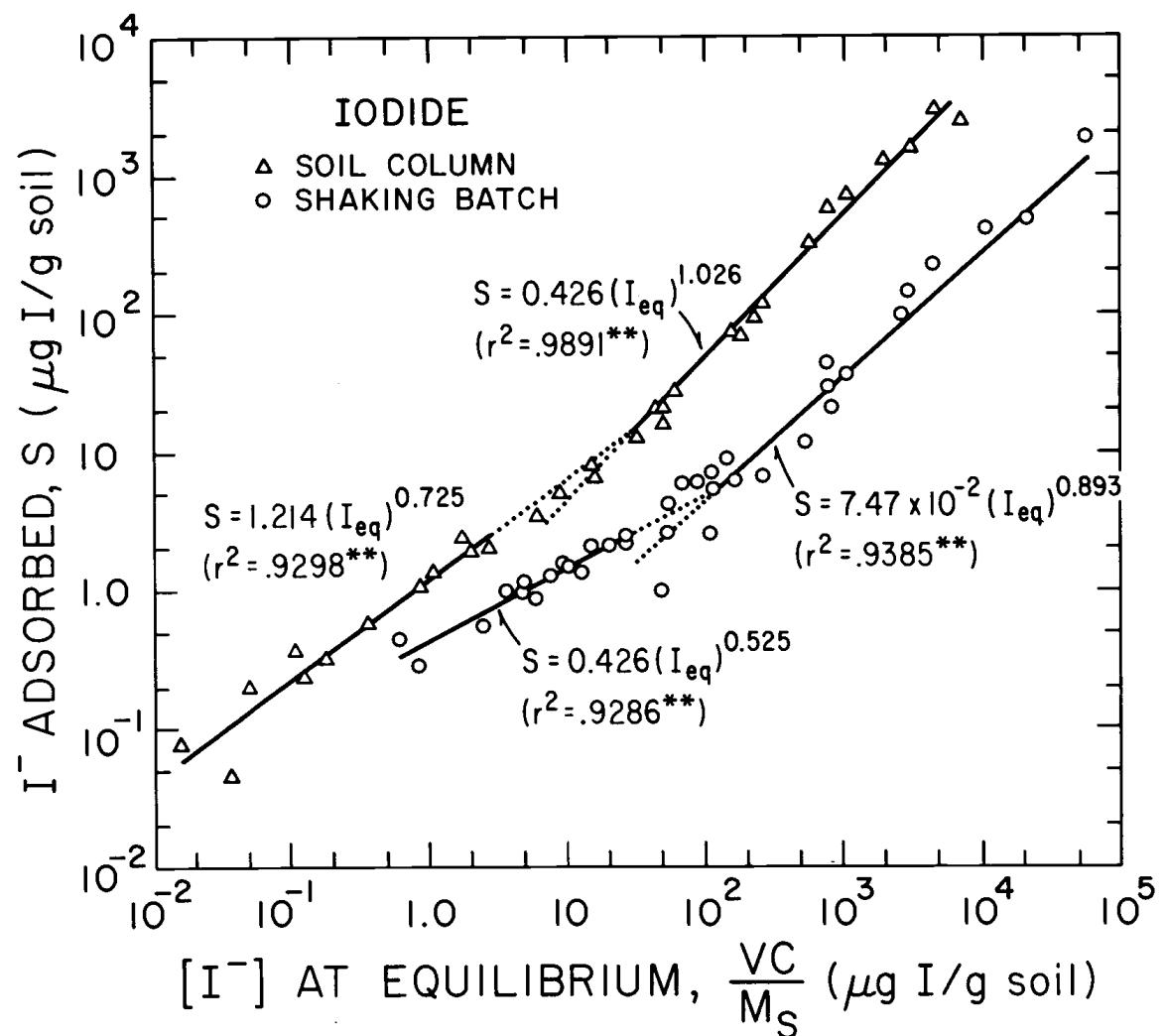


Figure 1-4. Adsorption isotherms of iodide for the Pope Ridge soil. Temperature was 22.5 ± 0.5 C.

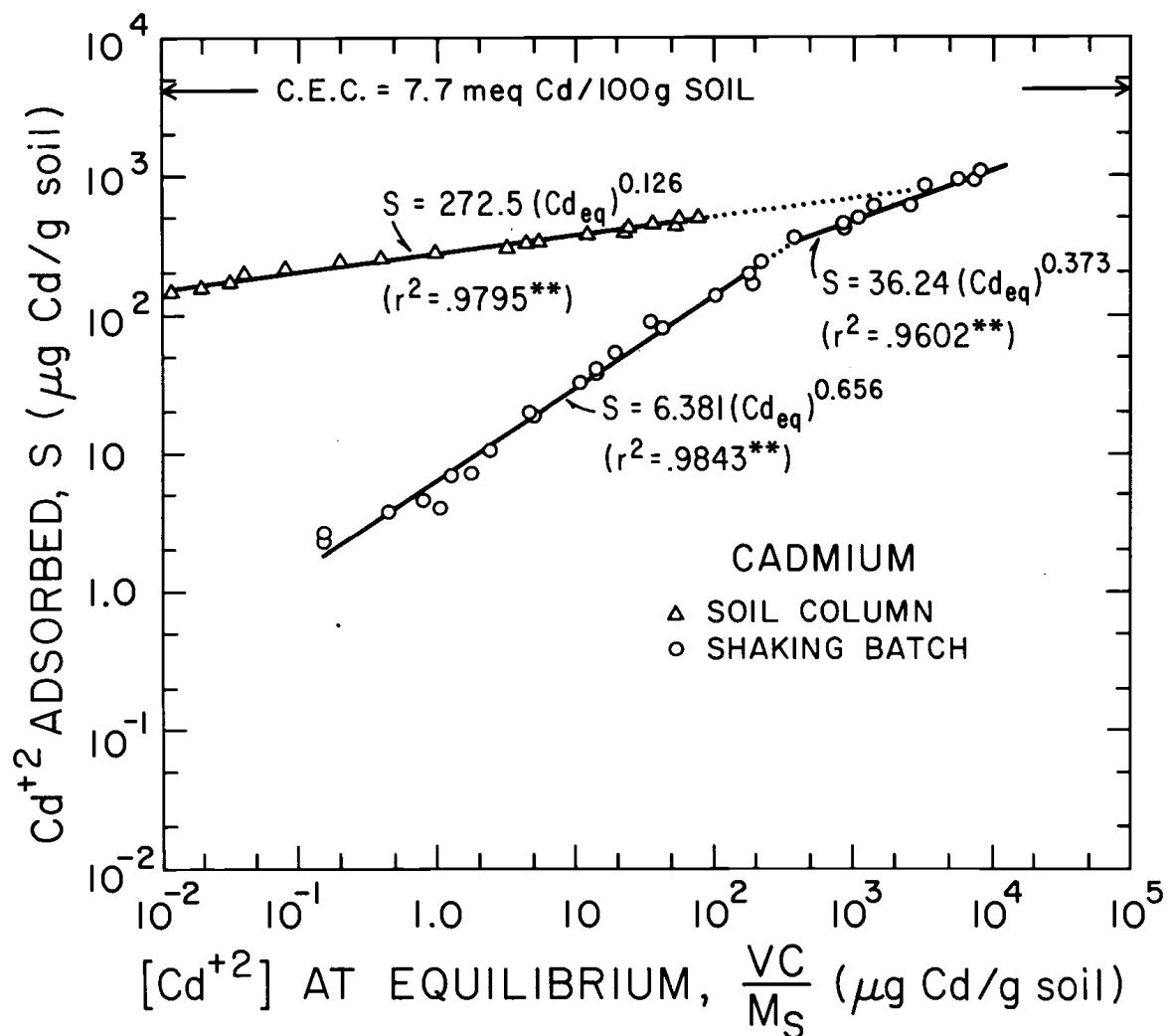


Figure 1-5. Adsorption isotherms of cadmium for the Pope Ridge soil. Temperature was 22.5 ± 0.5 C.

separate the curves of isotherms evaluated by the two different procedures so that the slopes which remain constant through this manipulation become more apparent.

For consideration of the physical units, the isotherms will be

$$S = a(\gamma)^c , \quad (1-14)$$

where S ($\mu\text{g/g soil}$) is the amount adsorbed, a ($\mu\text{g/g soil}$) and c are the characteristic constants of the Freundlich isotherm, and γ is the non-dimensional quantity (VC/M_s) . The rationale for Equation (1-14) is that, since

$$S = a(VC/M_s)^c , \quad (1-15.a)$$

or

$$\log S = \log a + c \log(VC/M_s) , \quad (1-15.b)$$

the amount adsorbed, $S = a$ when $(VC/M_s) = 1 \mu\text{g/g soil}$, so that

$$\left(\frac{S \mu\text{g/g soil}}{a \mu\text{g/g soil}}\right) = \left\{ \frac{(VC/M_s) \mu\text{g/g soil}}{1 \mu\text{g/g soil}} \right\}^c . \quad (1-16)$$

Therefore, if we rewrite the normalized concentration, the right hand side of Equation (1-16) as γ , then γ has the same magnitude as (VC/M_s) but will be non-dimensional.

The heat of adsorption is determined from the energy distribution function. Table 1-1 showed that for the Freundlich isotherm the

energy function is of the form

$$\chi(q) = (c/RT)e^{-(c/RT)(q-q_m)} \quad (1-17.a)$$

Since c , RT and q_m are constants, they can be grouped together as

$$\chi(q) = \{(c/RT)e^{cq_m/RT}\}e^{-(c/RT)q} \quad (1-17.b)$$

According to Equation (1-6), $\chi(q)$ is defined as

$$\chi(q) = -\frac{d\phi}{dq},$$

so that

$$\chi(q) = -\frac{1}{S_{max}} \frac{dS}{dq}$$

where S_{max} is the maximum amount that the surface can adsorb.

This value is considered to be constant for each system. Equating Equation (1-17.b) to (1-17.c) yields

$$\frac{dS}{dq} = -\{S_{max}(c/RT)e^{cq_m/RT}\}e^{-(c/RT)q} \quad (1-18)$$

Integration of Equation (1-18), yields

$$S = (S_{max}e^{cq_m/RT})e^{-(c/RT)q} \quad (1-19)$$

Taking logarithms of both sides gives

$$\ln S = \ln(S_{\max} e^{\frac{cq_m}{RT}}) - (c/RT)q, \quad (1-20.a)$$

or

$$q = (RT/c) \ln(S_{\max} e^{\frac{cq_m}{RT}}) - (RT/c) \ln S, \quad (1-20.b)$$

or

$$q = m_1 - b_1 \ln S, \quad (1-20.c)$$

where m_1 is a constant representing the first term of the right hand side of Equation (1-20.b) and $b_1 = (RT/c)$. Equations (1-20.b, c) show that theoretically the heat of adsorption is a function of the logarithm of the amount adsorbed, S . Differentiating Equation (1-20.c) such that

$$\frac{dq}{dS} = - \frac{b_1}{S} \quad (1-20.d)$$

clearly shows that the energy change with respect to S drops rapidly in an inverse proportion to S .

The value of b_1 is of interest since it indicates how fast the heat of adsorption decreases with an increasing amount of ions adsorbed. Its value is obtained once the Freundlich isotherm and the characteristic constant c are determined.

The above derivation was based on theoretical considerations. In practice, due to the complexity of the adsorbing surfaces, we might

not be able to express the constants $b_1 = RT/c$ and m_1 as the first term of the R.H.S. of Equation (1-20.b). In general, we let

$q_m = 0$ and write q with generalized constants, though the form of q is maintained. So we obtain q as

$$q = b_2 \ln S_{\max} - b_2 \ln S \quad (1-21.a)$$

or

$$q = m_2 - b_2 \ln S \quad (1-21.b)$$

where the constant m_2 is still associated with both the characteristic constant c of the Freundlich isotherm and S_{\max} , b_2 is associated with the c value only.

To obtain b_2 from data points, we need to apply the equilibrium equation for adsorption as written in Equation (1-4.b), namely,

$$g(S) = (k_a'/k_d') e^{q/RT} f(C, S) \quad (1-4.b)$$

Substitute q from (1-21.a) into the above equation to yield

$$g(S) = (k_a'/k_d') e^{\{(b_2/RT) \ln S_{\max} - (b_2/RT) \ln S\}} f(C, S) \quad (1-22.a)$$

or

$$g(S) = (k_a'/k_d') S_{\max}^{b_3} S^{-b_3} f(C, S) \quad (1-22.b)$$

where $b_3 = b_2/RT$ still indicates the rate of change in the energy

function, and k_a and k_d are the corresponding rate constants which incorporate any approximation due to generalization of the heat of adsorption function when Equation (1-21.b) is used instead of Equation (1.20.c).

According to the kinetic theory of gases, functions $g(S)$ and $f(C, S)$ include the sticking probability functions to account for the fraction of the molecules that strike the surface and are actually adsorbed on it. The problem discussed here can be approximated by assuming a constant probability value for both functions. This probability need not be unity, but must be constant. In other words, we assume that the effect on adsorption of the change in the heat of adsorption, i.e., the exponential term is dominant and greater than the probability function. Normally, this function is considered to be a function of surface coverage. By our approximation, we express $q(S)$ and $f(C, S)$ as

$$q(S) = S \quad (1-23.a)$$

and

$$f(C, S) = C \quad \text{in general} \quad (1-23.b)$$

and

$$f(C, S) = (VC / M_s) \quad \text{for our purpose} \quad (1-23.c)$$

Combining Equations (1-23.a), (1-23.c) and (1-22.b) gives

$$S = \left(\frac{k_a}{k_d} \right) S_{\max}^{b_3} S^{-b_3} (VC/M_s) \quad (1-24.a)$$

or

$$\left(\frac{SM_s}{VC} \right) = \left(\frac{k_a}{k_d} \right) S_{\max}^{b_3} S^{-b_3} \quad (1-24.b)$$

Taking logarithms on both sides yields,

$$\ln \left(\frac{SM_s}{VC} \right) = \ln \left(\frac{k_a}{k_d} S_{\max}^{b_3} \right) - b_3 \ln S \quad (1-24.c)$$

Consequently, a plot of $\ln(SM_s/VC)$ versus $\ln S$ should give a straight line with a slope of b_3 . These plots are shown in Figure 1-6 for iodide and in Figure 1-7 for cadmium.

In summary, Freundlich isotherms for the adsorption of cadmium and iodide on Pope Ridge soil were obtained. The data were used to calculate for the rate of change of heat of adsorption with respect to the amount adsorbed, namely, the b_3 values. The summary of these parameters are shown in Table 1-4.

Discussion

Our first objective was to compare results obtained by the procedures employing the shaking batch and the short soil column. There are two important observations to be made about the results of the isotherms as shown in Figures 1-4 and 1-5.

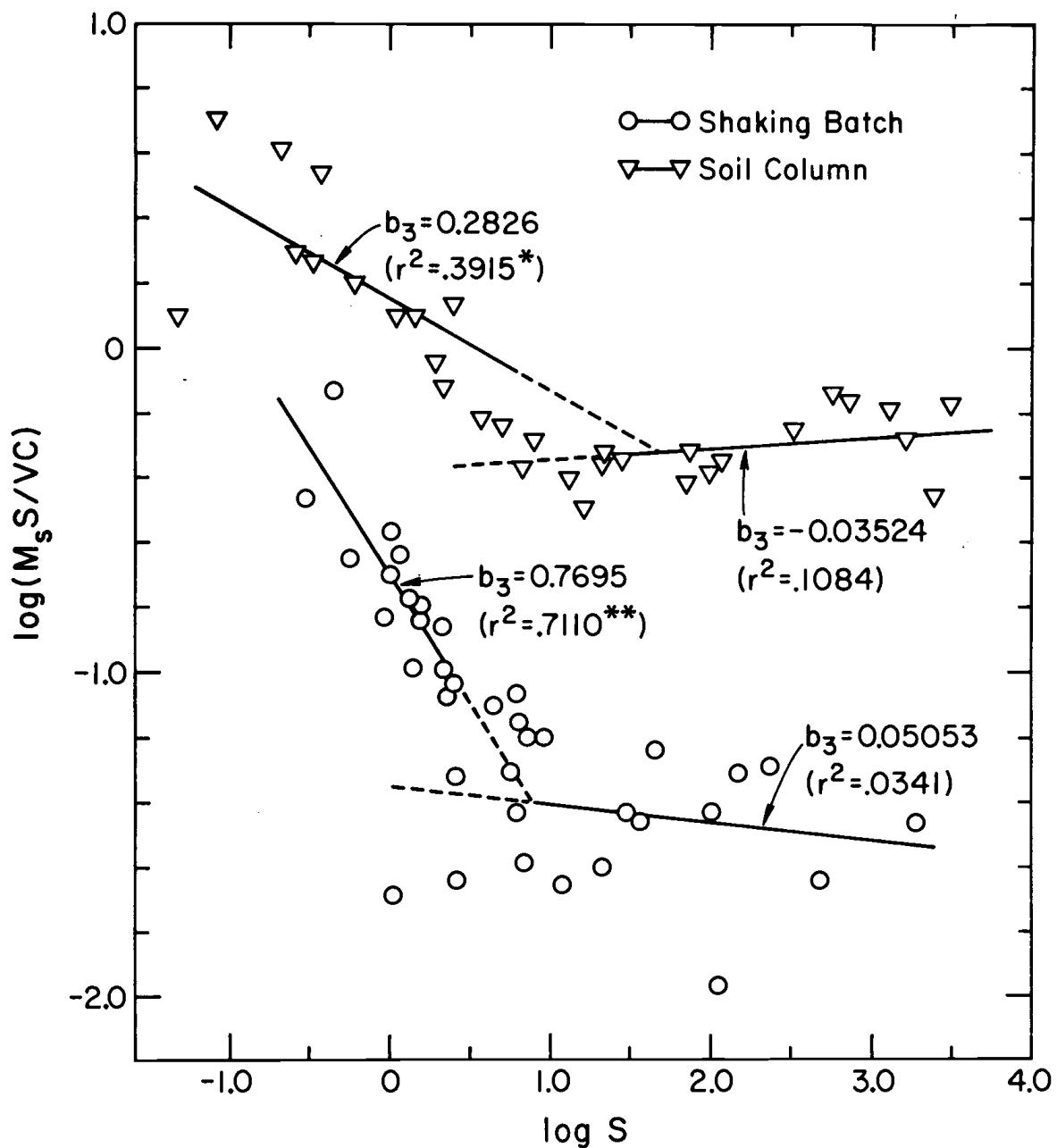


Figure 1-6. Representations of Equation (1-24.c) for iodide using data obtained by the shaking batch method and by the soil column method.

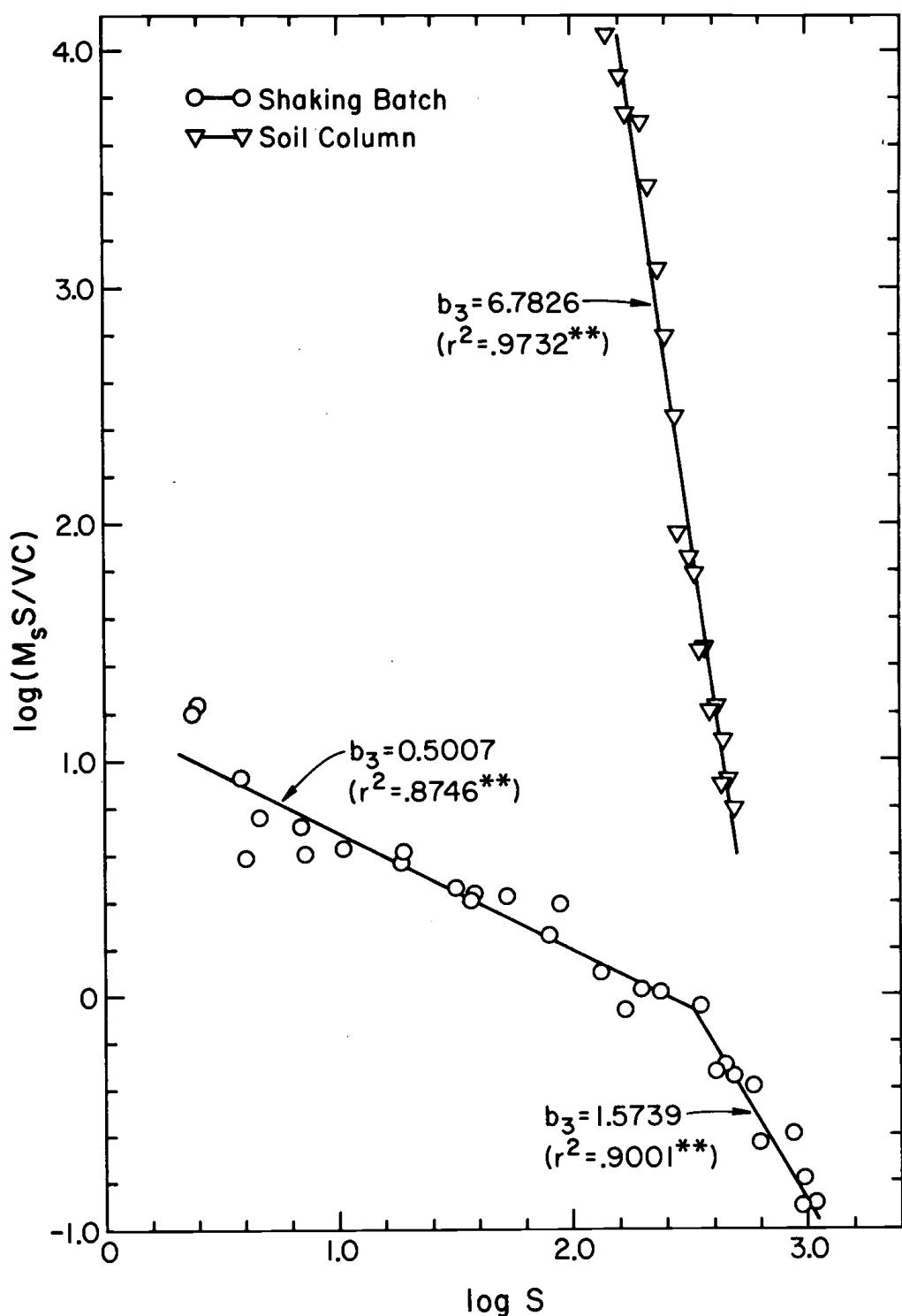


Figure 1-7. Representations of Equation (1-24.c) for cadmium using data obtained by the shaking batch method and by the soil column method.

Table 1-4. Summary of the characteristic constants of the Freundlich isotherm, the ratio of the forward and backward rate constants, b_3 values, and the amount adsorbed as percentage of the amount initially added for different ranges of amount adsorbed.

Freundlich Isotherm $S = a(\gamma)^c$			Equation (1-24. c)		Range of Amount Adsorbed, S		% Adsorbed as of Initial
	a	c	$k_a S_{\max} / k_d$	b_3			
<u>$\mu\text{g/g soil}$</u>					<u>$\mu\text{g/g soil}$</u>		<u>%</u>
Iodide							
Soil column	1.214 .426	.725 1.026	1.379 .975	1.4007 .4155	.2826 -.0352	.04 < S < 2.5 3 < S < 310	83-43 42-20
Shaking batch	.426 .075	.525 .893	1.906 1.119	.1934 .0445	.7695 .0505	.2 < S < 2.5 1.0 < S < 1900	42-7 7-2
Cadmium							
Soil column	272.5	.126	7.945	8.88×10^{18}	6.7826	140 < S < 490	99.99-86
Shaking batch	6.381 36.24	.656 .373	1.525 2.681	1.566×10 7.589×10^3	.5007 1.5739	2 < S < 240 340 < S < 1100	94-51 47-10

The first is that as the concentration of the bulk solution at equilibrium increases, the slopes of the isotherms change. The discontinuities of the lines imply that the mechanisms of adsorption at low concentration and high concentration are different.

The second observation is that when soil is exposed to the same amount of ions in the bulk solution, the amount of ions adsorbed by soil particles is higher when the structure of the pores is maintained as it is in the short column than when the sample is shaken as it is in the batch procedure. This result seems to be contrary to expectations. If adsorption depends on the area of exposed surfaces of the soil particles, the breaking up of the aggregates by the shaking procedure should result in more adsorption. Obviously, the surface area is not the only important parameter of the adsorption process. Other factors must also play a role and these become more important when the soil is maintained in its natural structure.

The Mechanisms of Adsorption

It was pointed out in the introduction that we do not have a specific theory to describe the mechanism of adsorption of ions as far as the structure of the ions and the adsorbing surfaces are concerned. However, adsorption mechanisms are reflected collectively through the value of ' b_3' ' which is associated with the change in the heat of adsorption as a function of surface coverage. We will therefore

discuss the mechanism by examining the values of b_3 .

For the iodide anion, Figure 1-4 showed the discontinuities in the isotherm lines while Figure 1-6 showed the corresponding change in the values of b_3 . For both the shaking batch and the soil column procedures, the discontinuity occurred at about the same concentration range, namely, at $S \sim 2-10 \mu\text{g/g}$ soil. The values of the slope, i. e., the characteristic constant 'c', were 0.725 for the soil column and 0.525 for the shaking batch at $S < 2 \mu\text{g/g}$ soil. At higher S , the slope values increased to 1.025 and 0.893 respectively. These values of the slope were not greatly different between the two procedures. On the other hand, the value of b_3 at $S < 2 \mu\text{g/g}$ soil was 0.2826 for the soil column which was only one-third of the value of 0.7695 for the shaking batch. At $S > 3 \mu\text{g/g}$ soil, the values of b_3 decreased to -0.0352 and 0.0505, respectively. The correlation analysis showed that the r^2 values for this range of S were not significant statistically. It is possible that at $S \geq 3$ to 10 $\mu\text{g/g}$ soil, anion is retained by other mechanisms which do not involve the heat of adsorption function.

The results with the cadmium cation were more complicated than with the iodide anion. This should be expected since Cd is a cation in the negative potential field of the soil particles. The interacting forces between ion and surface may be expected to be more pronounced than with the anion. The slope and the b_3 values for the

soil column procedure were 0.126 and 6.7826, respectively. For the shaking batch, the slope was 0.656 and b_3 was 0.5007 for $S < 240 \mu\text{g/g}$ soil. When S was greater than $340 \mu\text{g/g}$ soil, these values became 0.373 and 1.5739 respectively. The slopes of the isotherms and the b_3 values for the cadmium isotherm were distinctly different between the two procedures. When the shaking batch procedure was used, the isotherm and the b_3 value showed discontinuities with the value of b_3 increasing when S was greater than $300 \mu\text{g/g}$ soil. For iodide, the b_3 value decreased as adsorbed ions accumulated.

Admittedly, the nature of the different mechanisms of adsorption cannot be resolved unequivocally by this experiment alone. The results only point out that ions are adsorbed onto the soil surfaces by two different mechanisms corresponding to two different functions of the heat of adsorption.

Hayward and Trapnell (1964, p. 171) were more specific in the interpretation of the slope value of the Freundlich isotherm. The Freundlich isotherm is expressed as $S = a(C_{\text{eq}})^c$. An equally popular alternative expression is $S = a(C_{\text{eq}})^{1/n}$ where $n = 1/c$. The characteristic value 'n' has been interpreted as a constant accounting for the mutual interaction of the adsorbed molecules. The forces between adsorbed molecules within the surface layer are attractive if n is less than unity and repulsive if n is greater than

unity. In most cases, n values are greater than unity indicating repulsive interaction.

The isotherms for the iodide anion (Table 1-4) showed that when $S \leq 3 \text{ } \mu\text{g/g}$ soil, the value of n was 1.906 for the shaking batch procedure and 1.379 for the short soil column. These values decreased as the adsorption process progressed, namely, n became 1.119 and 0.975 respectively. For the cadmium cation, the value of the characteristic constant n was 7.90 for the short soil column. This value is much greater than the normally reported values of about 1 to 2. It implies that the repulsive force between the adsorbed molecules is high. For the shaking batch experiment, the n value was 1.525 with $S < 300 \text{ } \mu\text{g/g}$ soil which is within the normal range. At higher S , the value of n increased to 2.75. The results indicate that if the ion is an anion, the repulsive force decreases as the density of adsorbed ions becomes higher, but if the ion is a cation, the repulsive force between the adsorbed ions becomes stronger.

The probable sequence of adsorption for the cation might be that the first amount of cations adsorbed is exchanged with other species of ions, originally present in the diffuse layer. Ions in this region are held with a lesser attracting force than ions adsorbed directly on the soil surface, i. e., in the Stern layer. As the concentration of ions in the bulk solution increases, more and more ions make their way into

the Stern layer where the heat of adsorption is higher. The change in the required heat of adsorption is then reflected in the change of the values of b_3 and n for adsorption of Cd in the shaking batch.

However, in the soil column experiment, no such transition was indicated but the values of b_3 and n were unusually high. It is conceivable that the close packing of the soil particles affect the configuration of the diffuse double layer in such a way that there is no sharp difference in the extent of adsorbing force throughout the region, i.e., the diffuse double layer may be a compressed one. A conceptual diagram was drawn (Figure 1-8) in an attempt to show the difference in the distributions of cations near the soil surfaces between the dispersed condition in the shaking batch and the closely packed condition in the soil column.

Anions, on the other hand, have received little attention by soil researchers so that at present we have no satisfactory explanation for the decreasing values of n which indicates that the repulsive force becomes smaller as more ions are adsorbed. For our soil samples which were developed from volcanic deposits, there is also the possibility that iodide formed complexes with amorphous materials. This mechanism would be completely different from the adsorption process. Likewise, we can offer no explanation for the observation that the repulsive forces between anions seemed to be lower when ions

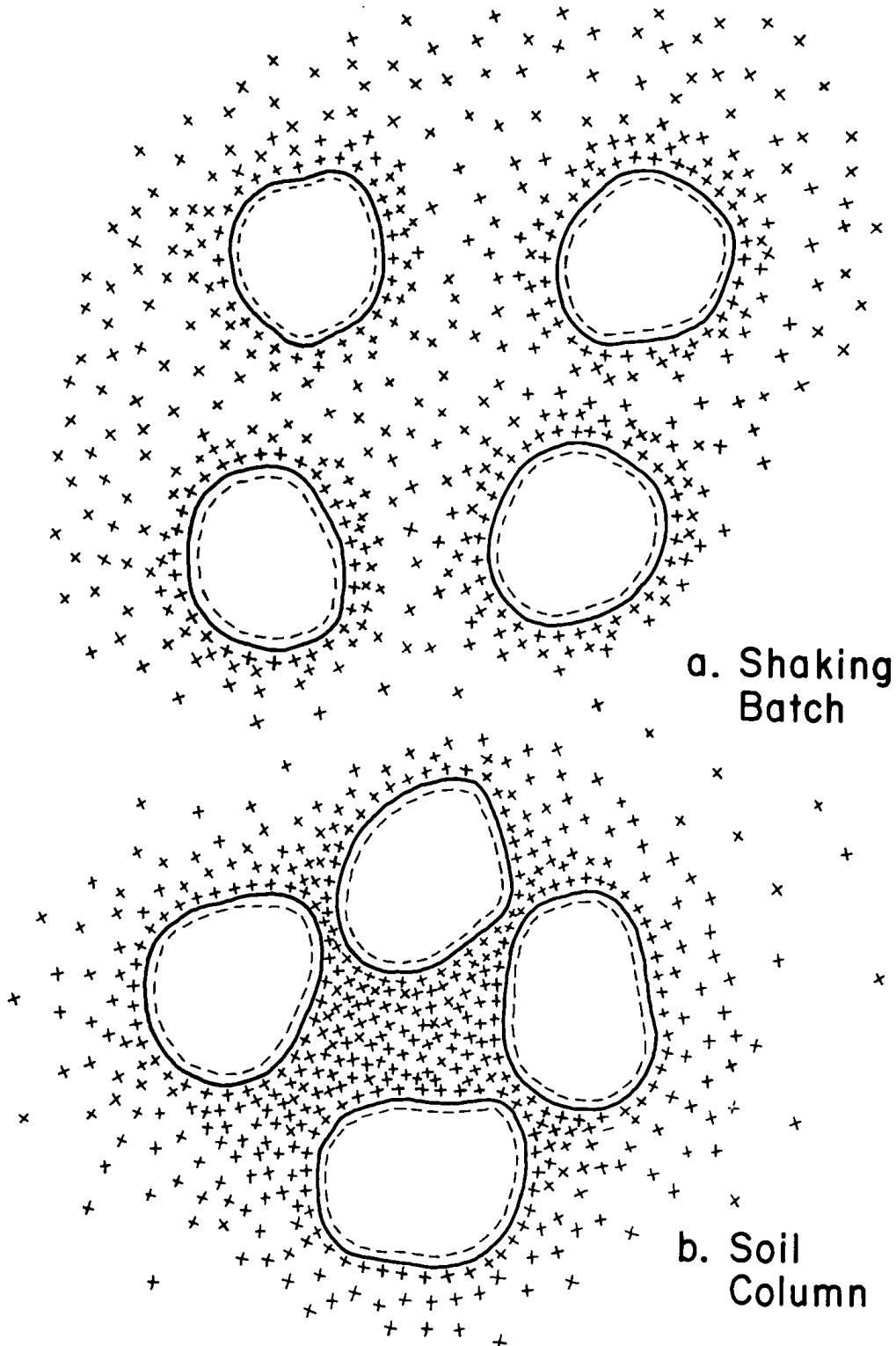


Figure 1-8. A conceptual diagram showing the difference in distributions of cations near the soil surfaces between a. the dispersed condition in the shaking batch and b. the closely packed condition in the soil column.

were adsorbed on the surface of soil particles in a core of which the structure was maintained.

However, it is obvious that under a natural condition, the electropotential fields of the soil particles interact with each other in a complex way. The interactions must have played a dominant role in causing the distribution of ions to deviate to a great extent from the simple concept for the diffuse double layer model. This simple theoretical model is based on the presence of a single or at most two surfaces facing one another where ions are distributed as a function of the exponential of the distance from the surface (van Olphen, 1977 and Mitchell, 1976).

The Magnitude of Adsorption

The differences in the amounts of ion adsorbed as measured by the shaking batch procedure and by the soil column procedure can be compared by examining the values of the Freundlich characteristic constant 'a', namely, the intercept of the log-log plot as shown in Table 1-4 and Figures 1-4 and 1-5. For the iodide anion, the magnitude of adsorption was about three to six times higher in the soil column than in the shaking batch. For the cadmium cation, the difference between the two procedures was conspicuously large especially at $S < 300 \mu\text{g/g}$ soil. The value of a was over 40 times larger for the adsorption in the soil column than in the shaking batch. As

shown in Figure 1-4, the difference in the magnitude of adsorption of iodide between the two procedures was smaller at low S and became larger at higher S. On the contrary, the difference in the adsorption of cadmium (Figure 1-5) was greatest at low amount adsorbed and then the isotherms approached each other as the amount adsorbed increased.

The amount of ions adsorbed as percentages of the amount added initially also differed. The degree of adsorption may be categorized qualitatively into three levels (Table 1-4), namely, high, medium and low. For iodide the region of high adsorption is the percentage range of 50 to 100%, the region of medium adsorption is from 40 to 10% and the region of low adsorption is below 10%. For cadmium, the corresponding three levels are high at > 95%, medium at 95-50% and low at < 50%. For both the anion and the cation, the soil column procedure obtained adsorption in the high percentage range, while the shaking batch procedure obtained adsorption in the medium and low intensity ranges for the same amount of ions added per gram of soil. This comparison reveals another difference between the two procedures, namely that they do not result in the same adsorption intensities.

We will now seek explanations for the differences between the shaking batch system and the short soil column. One obvious difference is in the physical configuration of the soil particles. In the soil

column, even though a disturbed sample is used, the pore channels configurations is simulated as would be found in the soil in its natural state. This places the soil solution in a different environment than it would be in the shaking batch (Figure 1-8). Ions in the pore solution will be in close proximity to the soil surfaces. With the shaking batch, ions are close to the soil surface on the one hand, but on the other hand they are relatively free to move in the large reservoir of the excess solution.

We suggest that ions in the pore solution are restricted in their movement due to two factors. First, there is the restriction due to Coulombic attractive forces caused by the negatively charged surfaces of the soil particles. These forces exist in both the soil column and the shaking batch system. The second factor is the decrease in entropy of the system due to the presence of the soil matrix. This factor is much more dominant in the soil column. Ions in the pore solution have a lower degree of translational freedom because they are close to the soil surface. This effect might be regarded as a physical restriction or the so-called "boundary effect." The difference in adsorptive capacity between the two systems, therefore, may be attributed as one factor to the existence of a stronger potential field exerted by the surface charges as well as by the entire soil mass due to the arrangement of the soil particles in the column.

In general, adsorption is considered to be a process involving the attractive force field of the surface charges. The question then arises: should the restriction of the physical movement of the ions due to the force field exerted by the soil mass be considered as part of the adsorption process formulations. A conditional second question is: if this is so, will we be able to distinguish the adsorbed ions held by the Coulombic force of the surface charges from those held by other possible short distance attractive forces exerted due to the packing of the soil particles. The distinction is not as simple as taking the difference in the amount adsorbed, S , corresponding to the same amount of ions present in the equilibrium solution, $(V/M_s)C$, obtained by the two procedures of shaking batch, where the adsorption is primarily due to surface charges, and of soil column where both potential fields of surface charges and of the soil mass exist. This is so because the boundary effect would very much depend on the structure and the soil water content of the soil system.

We are convinced by the results that use of the shaking batch method, which does not reflect the true nature of the adsorption process in the natural soil, should be discontinued, whether our speculation on the existence of the stronger potential field exerted by the entire soil mass which enables soil in a column to adsorb more ions than soil in the shaking batch is valid or not. This is particularly important when we need the adsorption data for simulation of solute

transport in the soil rather than for the study of the surface characteristics of soil minerals.

For the soil column procedure, we still have several concerns about its principle which need further verification. The first is the variations in the amount adsorbed, S and the amount in the solution, $(V/M_s)C$ as a function of soil depth. Since solution is applied on to the soil surface, the upper part of the soil will be exposed to and have longer time to adsorb more ions than the bottom part of the column, i.e., a chromatographic effect.

In our case, the height of soil column was 3.5 cm. The texture of the soil was sandy and the addition of the 41 ml of solution could be completed within 5 minutes during which the solution could reach the bottom part of the soil quite rapidly through large pores. Consequently, we feel that the bottom part would still be in contact with solution having initial concentration. We assume that the variation with depth for our soil is small and the obtained values of S and $(V/M_s)C$ are the averages for the whole column.

This problem may be aggravated when heavy-textured soil is studied. Smaller amounts of soil may be used to decrease the height of the soil column so long as a sufficient amount of solution can be extracted from the sample for analysis.

The second problem is about the effects of water content of the sample and the applied extracting pressure on the concentrations of

the solution extracted from the sample. We perceive that ions are most concentrated near the soil surface while the concentration is decreasing in the horizontal direction away from the surface. With this kind of distribution, it becomes critical as to which part of the free solution we extract the solution from.

Figure 1-9 was a conceptual diagram showing the concentration distribution of a cation along the distance from the surface of the soil. As low extracting pressure is applied, solution is extracted from large pores. For example, in Figure 1-9, the solution may be considered to come from region a to b. Then the analysis will give the concentration of the solution as the average value of this region. But when higher pressure is applied, solution now comes from region a' to b and the corresponding average concentration will be higher than before.

The matter is further complicated when water content is included in the treatment. The thickness of the water film around the soil particles decreases at lower water content which will affect the distribution of the ions as presumed in Figure 1-9.

We are not certain how and to what extent the water content and the extracting pressure will affect the outcome of the studies of the equilibrium isotherm. We hope that more studies will be set up to fully explore this subject. Our anticipation is that it would become necessary to redefine the equation of the isotherm so that it has more

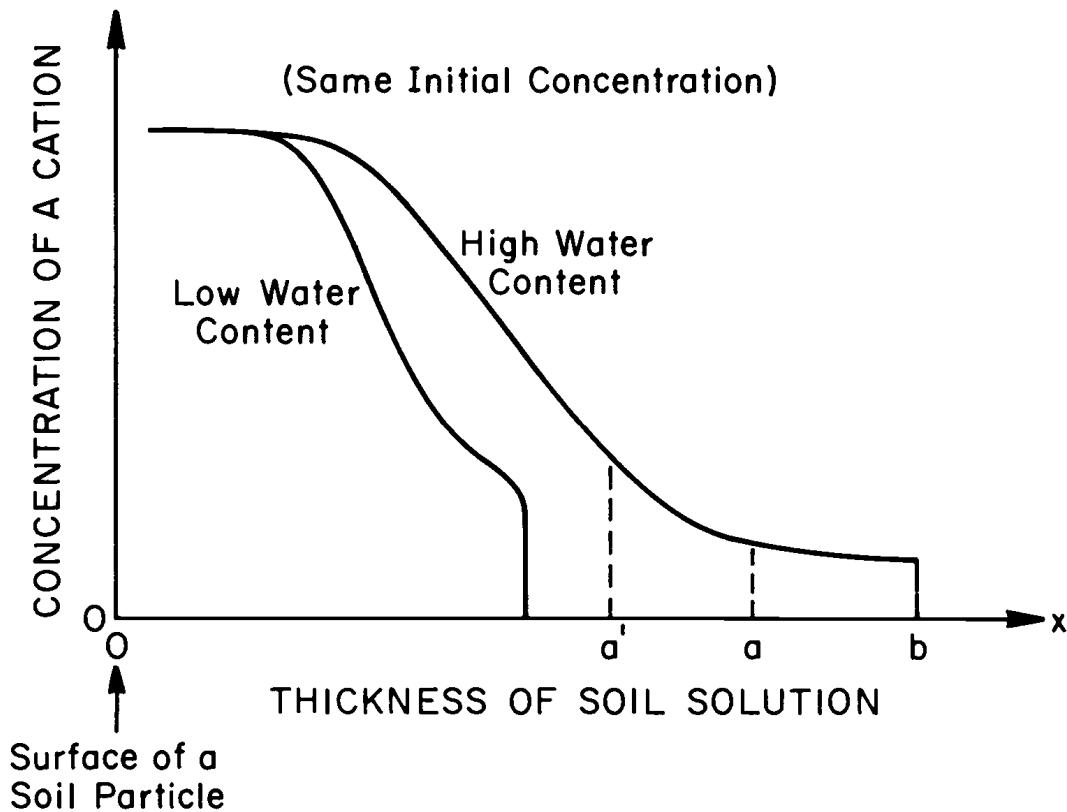


Figure 1-9. A conceptual diagram showing concentration distributions of a cation along the distance away from the surface of a soil particle as a function of water content of the soil sample.

specific meanings for the so-called concentration of the "bulk solution" at equilibrium, i.e., the C term and for the amount of ion adsorbed, S, namely, by what criteria, an ion is considered as adsorbed ion.

The third point of consideration is the way we use the amount of ion in the solution, $(V/M_s)C$ instead of the usual concentration, C in the construction of the isotherm graphs. We suggest that it could be one way of accounting for the variations in the amount of solution and soil used for the studies. Using the value of concentration, C by itself makes it necessary to examine the effect of the soil : water ratio. In our case, there appeared to be no effect of soil : water ratio for the shaking batch studies whereas for the soil column, we did not have sufficient samples to make the comparison.

Using the $(V/M_s)C$ values had increased the magnitude of the isotherm by a factor of (V/M_s) as shown in Equation (1-13). For iodide, plotting S vs. $(V/M_s)C$ did, in fact, raise the isotherm curve of the soil column above the shaking batch methods. If we plotted S vs. C, the two curves were inseparatable with the data points of the soil column slightly lower than the shaking batch in the region of low C. However, the magnitude of adsorption in the case of cadmium was distinctly higher for the soil column regardless of whether we plotted S vs. C or S vs. $(V/M_s)C$.

Finally, we realize that we have raised more questions than we have answered on the subjects of the adsorption process in the soil. However, we think that we have offered a new aspect to this process and given a better understanding if not on the mechanism of the adsorption itself, then at least on possible questions concerning this process as it may take place in the soil under natural condition.

DYNAMIC STUDY OF THE SORPTION PROCESS

Introduction

Studies of the adsorption kinetics of molecules onto a solid surface are divided into two groups--one group emphasizes surface reactions, i.e., transfer of the molecules between interface and boundary layer and the other considers the exchange process between the boundary layer and the bulk solution. The division is not arbitrary. The adsorption process is the final result of a diffusion process accompanied by a process which involves the crossing of an energy barrier. For molecules to be adsorbed onto a surface, they must have a certain level of energy which is higher than the ground state level of the free-moving molecules.

Ward and Tordai (1946) were the first investigators to consider the influence of diffusion in the adsorption process. They proposed a one-dimensional model with a non-flowing or closed boundary based on the assumption that equilibrium is established instantaneously between the subsurface and the adsorbed layers. Later studies by Hansen (1961), Baret (1968), and Petrov and Miller (1977) followed this same approach. Results are useful in static systems. Lapidus and Amunson (1952) introduced consideration of both longitudinal diffusion and ion exchange. Their approach has become the basic principle employed by chemical engineers in the treatment of mass transfer

through packed beds, and other adsorbing columns. Columns with spherical, porous, particles in which both inter- and intra-particle diffusion occurs have been investigated extensively by Smith and co-workers (Smith, 1968; Masamune and Smith, 1965; Furusawa and Smith, 1973).

Adsorption kinetics can be treated from a statistical or thermodynamic viewpoint. The more familiar way is to treat the kinetics of adsorption as a chemical reaction. Consequently, the rate of adsorption is deduced directly from the fundamental differential equation

$$\frac{\partial S}{\partial t} = r_a - r_d ,$$

which was shown as Equation (1-1). According to classical statistical mechanics, energies of molecules are distributed in different possible states characterized by the partition functions. The numbers of molecules distributed over the energy levels are described by the Maxwell-Boltzmann distribution law. Only molecules which possess energies at the level of and higher than the activation energy of adsorption, E_a can be adsorbed. Likewise, only molecules with energies equal to or greater than the activation energy of desorption, E_d can be desorbed. So the general form of adsorption kinetics is represented by

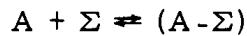
$$\frac{\partial S}{\partial t} = k'_a e^{-E_a/RT} (VC/M_s) - k'_d e^{-E_d/RT} S, \quad (2-1)$$

where all the terms are as described previously with Equation (1-3).

Basically, there are three theories which have been proposed as attempts to explain the mechanisms of the adsorption process according to Equation (2-1). Clark (1970) gave an excellent discussion of these theories. The three theories are: i) Activated-nonactivated chemisorption theory; ii) Electronic theory and iii) Absolute rate theory.

Activated-Nonactivated Chemisorption Theory

The adsorption and desorption process may be expressed by



where an atom or molecule of A is adsorbed on a vacant site Σ .

This theory considers a free molecule to proceed from a physically adsorbed state to a chemisorbed state. This complies with Lennard-Jones (1932) who showed that there exist two minima in the potential energy curve of a molecule as a function of its distance from a surface (Figure 2-1.a), namely,

- a) a shallow one due to physical forces and
- b) a deeper one closer to the surface resulting from chemical forces.

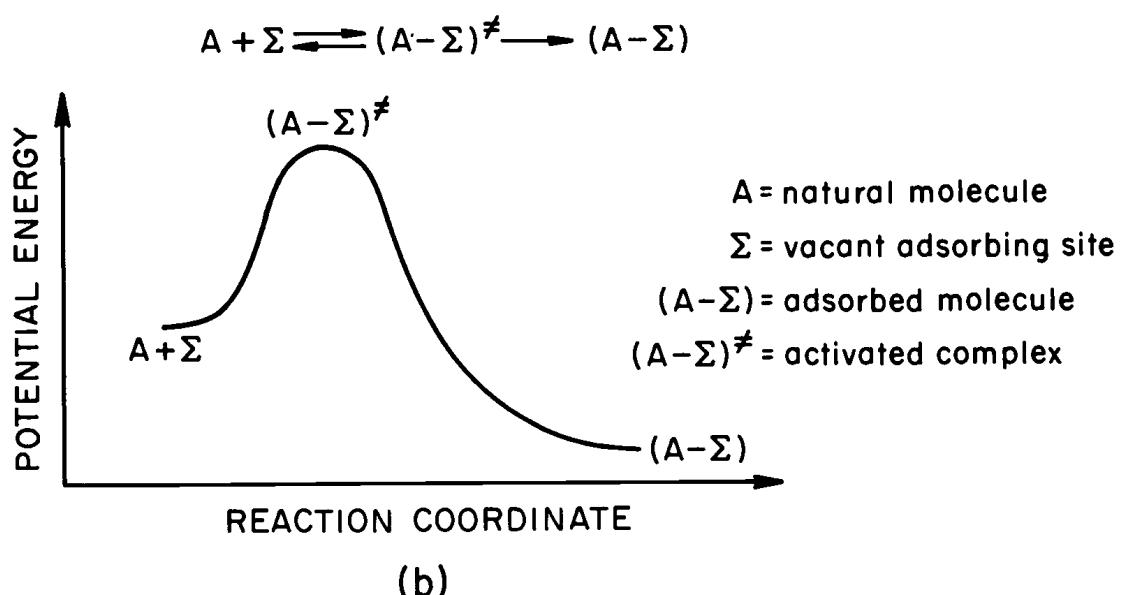
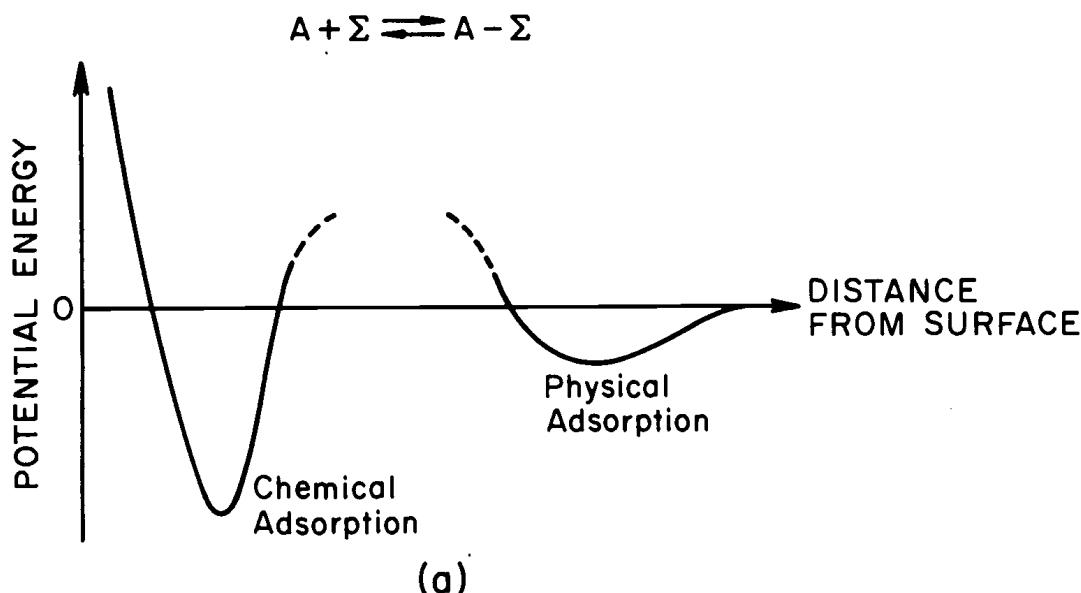


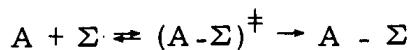
Figure 2-1. a. Potential energies of chemical and physical adsorption as considered in the activated-nonactivated chemisorption theory. b. Potential energies of the natural, adsorbed molecules and the intermediate "activated complex" as proposed by the absolute rate theory.

Electronic Theory

This theory was first developed based on the boundary-layer theory (Hauffe, 1955) assuming that the rate determining step is electron transfer between adsorbent and adsorbate while the free electrons or holes on the surface were regarded as centers of adsorption. Wolkenstein and Peshev (1965) later applied this theory to the kinetics of chemisorption on semiconductors. They assumed that the chemisorbed particles are of the acceptor type such that they can exist on the surface in an electrically neutral or negatively charged state and can be converted from one state to the other whereas only particles in the neutral state can be desorbed from the surface. According to this theory chemisorption is a process which involves a change in the surface charge and hence a flow of current in the semiconductor. In other words, both adsorption and desorption cause disturbance of the electron equilibrium in the body of the semiconductor. The activation energy of adsorption is calculated as a function of the parameters characterizing the electronic state (Fermi level) of the adsorbent surface. Consequently, there is a unique relation between the activation energy of the adsorption and the electrical conductivity of the semiconductors.

Absolute Rate Theory

According to this theory, the free-moving molecules are treated as reactants and the adsorbed molecules as products in analogy to a chemical reaction. For adsorption to take place, there exists an intermediate activated state between the free and the adsorbed molecules. This activated state is described as an "activated complex," and the adsorption process is expressed by



where $(A - \Sigma)^{\ddagger}$ represents the intermediate activated complex and equilibrium exists between the free molecules and the activated complex. This activated complex is considered to be at the top of an energy barrier lying between the normal states of reactants and products (Figure 2-1.b). The rate of reaction is controlled by the rate at which molecules in the activated complex pass over the top of the barrier. This basic theory was first applied by Eyring (1935a, 1935b, 1938) to chemical reactions and was later applied to adsorption processes by Laidler (1954) allowing the formulation of a method for the calculation of the rates of reaction. Additional details are discussed by Fava and Eyring (1956) and Baret (1969).

All these theories, though providing different points of view of the adsorption mechanisms, give similar final expressions for the

rate of adsorption and desorption. This makes it difficult to design the proper experiment for verification of each theory separately. For the first theory, solid evidence needs to be obtained for the presence of a physically adsorbed precursor state. The electronic theory is purely theoretical. It contains several parameters, required in the derivation, which cannot be evaluated experimentally. The widely used absolute rate theory, on the other hand, contains the concept of the activated complex which is so general that physical interpretation is often difficult when experimental results deviate from the theory. An example of one of its difficulties is that the theory contains no surface parameters except as they operate collectively through the activation energy. Though mathematical agreement with experimental data can be attained, the desired information about surface mechanism is lacking. As a consequence, we arrive at the same conclusion we reached earlier in the discussion of equilibrium, namely that there exists an equation (Equation 2-1) to describe adsorption kinetics as a whole but that the equation does not provide a good understanding of the actual mechanisms underlying the equation.

The purpose of this part of the study is to formulate a theoretical basis for the surface kinetic reactions by elaborating on the functions of activation energies of adsorption and desorption based on information obtained earlier from equilibrium isotherm studies. In addition, a transverse diffusion-controlled process will be

incorporated into the overall adsorption kinetic equation. To evaluate parameters for this proposed model, experiments will be set up to determine kinetic adsorption rates for a soil system with solute flow proceeding under conditions where the soil is not saturated with water.

Proposal for a Kinetic Model

For one dimensional analysis of solute transport in soil, diffusion and dispersion along the direction of flow are usually appropriately accounted for but diffusion perpendicular to the direction of flow is ignored. This omission might not be valid when adsorption occurs. The purpose of proposing the model presented here is to incorporate the horizontal diffusion process into the sorption function. Consider adsorption to be a process described by a three-step mechanism namely (Figure 2-2):

- i) diffusion of the ion from the bulk solution to the subsurface layer of the soil particle.
- ii) diffusion of the ion across the subsurface layer.
- iii) adsorption of the ion by surface reaction onto the surface of the soil particle or incorporation into the diffuse double layer.

The surface reaction takes place in the region closest to the surface of the soil particle. Ions have to overcome an activation energy barrier to be bound onto the surface by electrical forces. This process

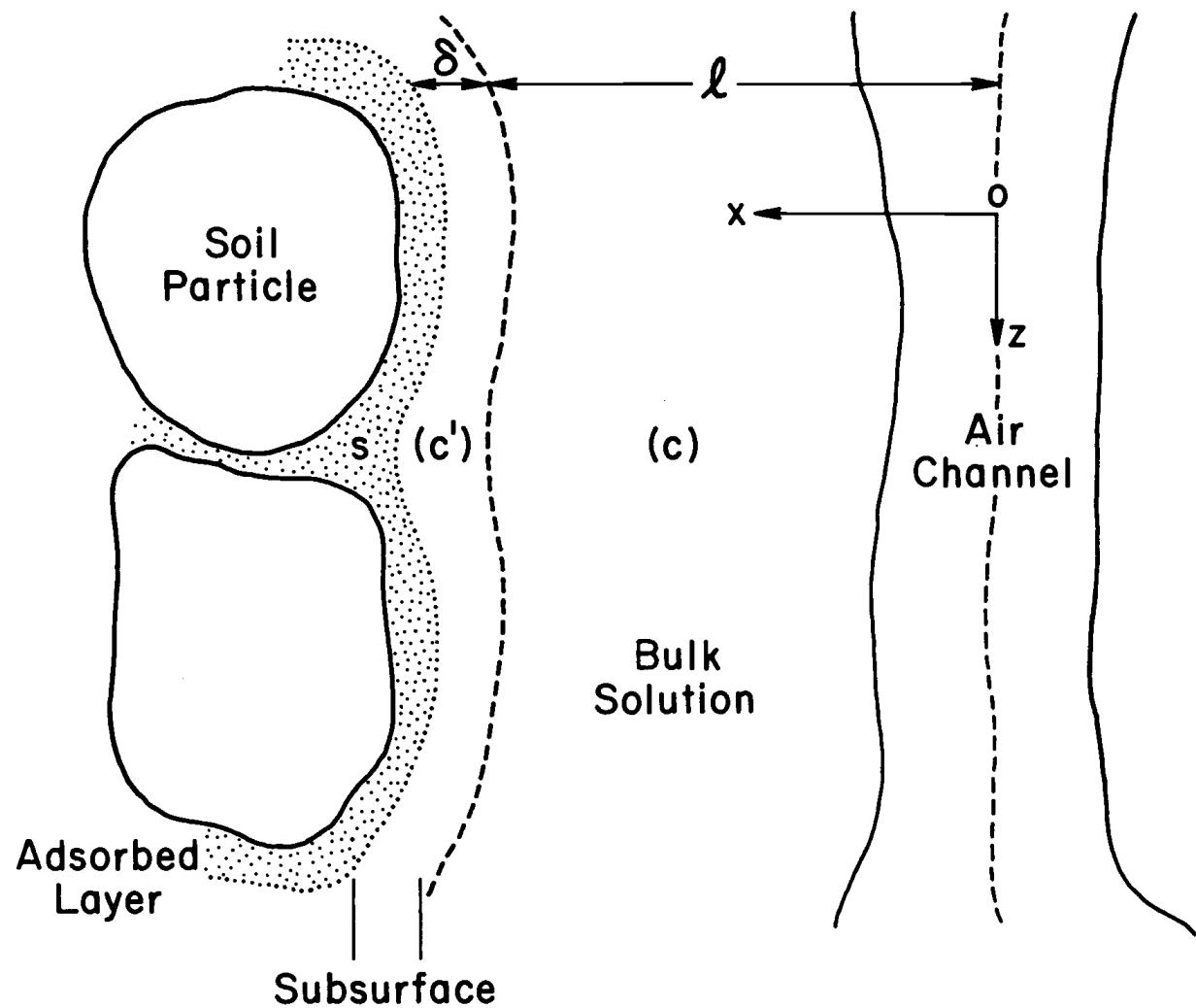


Figure 2-2. Diagram showing the adsorbed layer, subsurface layer and bulk solution region of the soil system.

leads to the formation of a diffuse double layer, a zone in which ions distribute themselves under the influence of two opposing forces, namely, an attraction force towards the surface due to surface charges and dispersion due to concentration gradients towards the bulk solution. The subsurface layer is the region in which ions have transitional freedom from the surface binding force but horizontal movement is controlled by diffusion. The concentration of the ions in this region is the actual concentration to which the soil surface is exposed. The thickness of this boundary layer and therefore the magnitude of the mass diffusive conductance is a function of pore-water velocity. The outer-most region is the so-called bulk solution where ions are distributed by being carried along with the water stream lines (convection) as well as by mixing caused by mechanical dispersion due to uneven velocity distribution and molecular diffusion as water moves along tortuous pores in the soil.

A mass transport equation can be derived for each step.

The Mass Balance for Ions in the Bulk Solution

In a two-dimensional analysis, the movement of ions is described by

$$\frac{\partial \theta C}{\partial t} + \frac{\partial qC}{\partial z} = \frac{\partial}{\partial z} (\theta D_z \frac{\partial C}{\partial z}) + \frac{\partial}{\partial x} (\theta D_x \frac{\partial C}{\partial x}), \quad (2-2)$$

where q ($\text{ml}/\text{cm}^2/\text{sec}$) is the Darcian flux and is present in z -direction only. D_x and D_z (cm^2/sec) are dispersion-diffusion coefficients in the horizontal, x , direction and vertical, z , direction, respectively. The lateral boundary conditions are

$$\frac{\partial C}{\partial x}(0, z, t) = 0 \quad (2-3.a)$$

and

$$-\theta D_x \frac{\partial C}{\partial x}(\ell, z, t) = k(\theta C - \theta' C'), \quad (2-3.b)$$

where ℓ (cm) is the thickness of the bulk solution region and $x = 0$ is the midpoint of a pore. k (cm/sec) is the horizontal mass transfer coefficient and $\theta' C'$ is the amount of ions in the subsurface layer.

Upon integration into a one-dimensional equation by taking the average in the x -direction, Equation (2-2) becomes

$$\frac{\partial \bar{\theta} \bar{C}}{\partial t} + \frac{\partial \bar{q} \bar{C}}{\partial z} = \frac{\partial}{\partial z} (\bar{\theta} D_z \frac{\partial \bar{C}}{\partial z}) - \frac{1}{\ell} \theta D_x \frac{\partial C}{\partial x} \Big|_0^\ell, \quad (2-4)$$

where the bar indicates that the terms are average values in the x -direction. For convenience, we will hereafter omit the bar with the implication that

$$\theta = \theta(z) \quad \text{and} \quad C = C(z) \quad \text{only.} \quad (2-5)$$

Applying boundary conditions, Equations (2-3.a and b), the resulting equation is

$$\frac{\partial \theta C}{\partial t} + \frac{\partial qC}{\partial z} = \frac{\partial}{\partial z} (\theta D_z \frac{\partial C}{\partial z}) - \frac{k}{l} (\theta C - \theta' C'). \quad (2-6)$$

The Mass Balance for the Ions in the Subsurface Layer

The subsurface layer is perceived to be sufficiently immobile such that there is no bulk flow in the vertical direction in this region. Only horizontal diffusion of ions occurs. The concentration distribution is described by

$$\frac{\partial \theta' C'}{\partial t} = \frac{\partial}{\partial x} (\theta' D_x \frac{\partial C'}{\partial x}), \quad (2-7)$$

with the boundary conditions of

$$k(\theta C - \theta' C') = -\theta' D_x \frac{\partial C'}{\partial x} \Big|_{x=l}, \quad (2-8.a)$$

and

$$-\theta' D_x \frac{\partial C'}{\partial x} \Big|_{x=l+\delta} = \ell \rho_b \frac{\partial S}{\partial t}, \quad (2-8.b)$$

where δ (cm) is the assumed thickness of the subsurface layer.

The Surface Rate of Reaction

The general kinetic equation for the surface reaction is, as written earlier (Equation 2-1)

$$\frac{\partial S}{\partial t} = k'_a e^{-E_a^a / RT} \left(\frac{VC}{M_s} \right) - k'_d e^{-E_d^d / RT} S.$$

The activation energy functions can now be determined since we learned from the study of the equilibrium isotherms that the system can be described by Freundlich isotherm. The heat of adsorption is a function of surface coverage and is expressed (Equation 1-21.a) by:

$$q = b_2 \ln(S/S_{max})$$

Cerofolini (1975) and Ionescu (1976) proposed that surfaces to which the Freundlich isotherm is applicable should have an activation energy which relates in a linear fashion to the heat of adsorption. Using this assumption here leads to the following relationships,

$$E_a = E_0^a - \beta q, \quad (2-9.a)$$

and

$$E_d = E_0^d + \beta q, \quad (2-9.b)$$

where E_0^a and E_0^d are the basal activation energies for adsorption and desorption. These are the energies of the adsorbing surface when adsorption of the ion being considered is completed, namely, at $S/S_{max} = 1.0$. β is a proportionality constant.

Equation (1-21.a) indicates that the heat of adsorption has its maximum value when adsorption is initiated and then decreases exponentially with the amount of ions adsorbed until it is zero at $S/S_{\max} = 1.0$ (Figure 2-3). The activation energy for desorption, E_d , follows this same pattern (Figure 2-3) with a minimum energy at $S/S_{\max} = 1.0$ equal to E_0^d . The activation energy for adsorption, E_a , on the other hand, operates in an opposite direction. The value of E_a is initially low and increases to the maximum value E_0^a at $S/S_{\max} = 1.0$. The behavior of E_a and E_d are more clearly expressed by substitution of q into Equations (2-9.a and b) which gives

$$E_a = E_0^a + \beta b_2 \ln(S/S_{\max}), \quad (2-9.c)$$

and

$$E_d = E_0^d - \beta b_2 \ln(S/S_{\max}). \quad (2-9.d)$$

Because E_a is smallest at low surface coverage, free-moving ions with sufficiently high energies will overcome the activation energy of adsorption and are adsorbed readily. Since the corresponding heat of adsorption is highest at low surface coverage, the adsorbed molecules release a high level of energy upon being adsorbed which means that the first number of ions adsorbed are bound tightly by the surface such that they are difficult to be desorbed. Consequently, the resulting

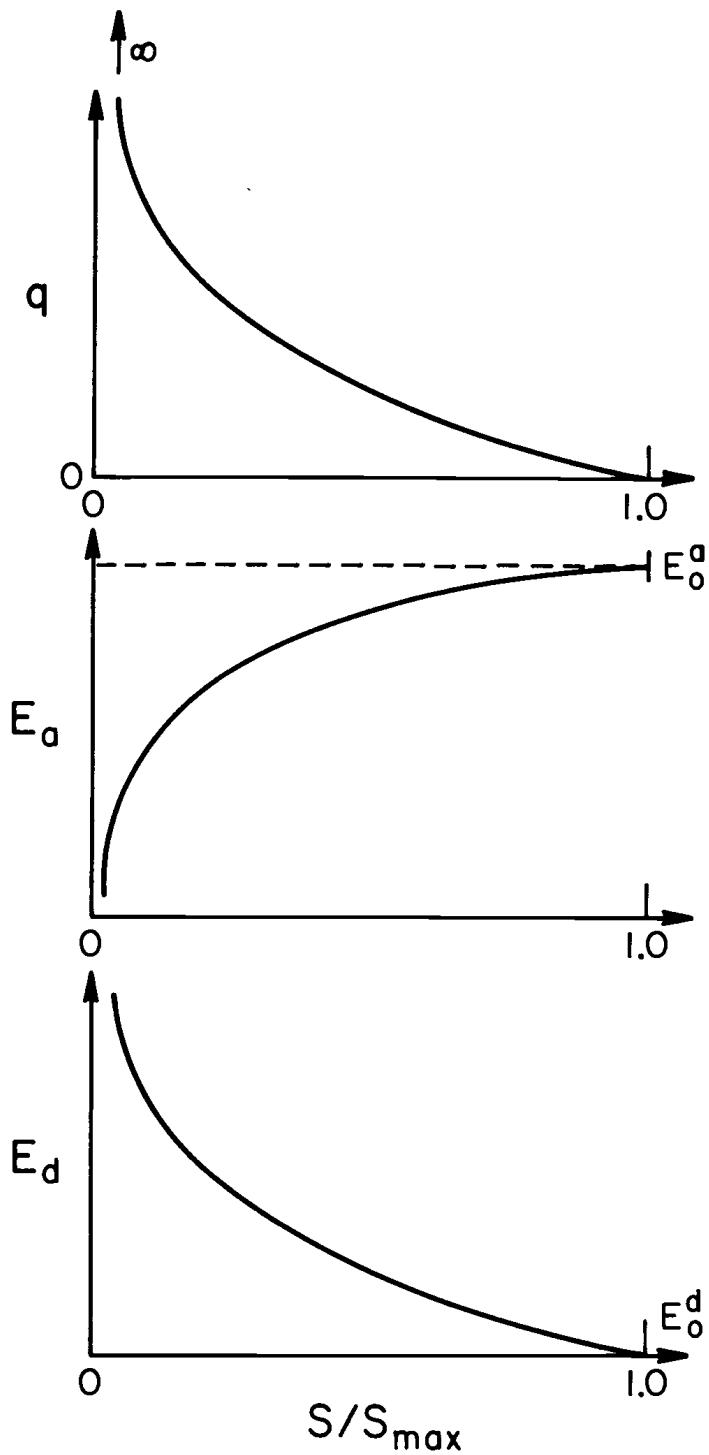


Figure 2-3. Diagrammatic representations of the functions of heat of adsorption, q and activation energies of adsorption, E_a and desorption, E_d , as functions of surface coverage S/S_{\max} .

equations for the forward and backward rate reactions are the following:

$$r_a = k'_a e^{-E_a^0 / RT} (VC / M_s) . \quad (2-10.a)$$

Substitution of E_a from Equation (2-9.c) yields

$$r_a = k'_a e^{-E_a^0 / RT} e^{-(\beta b_2 / RT) \ln(S / S_{max})} (VC / M_s) . \quad (2-10.b)$$

Rewriting $k'_a = k'_a e^{-E_a^0 / RT}$ and $b_3 = b_2 / RT$, then Equation (2-10.b) becomes

$$r_a = k'_a (S / S_{max})^{-\beta b_3} (VC / M_s) . \quad (2-10.c)$$

Likewise,

$$r_d = k'_d e^{-E_d^0 / RT} S , \quad (2-11.a)$$

$$r_d = k'_d e^{-E_d^0 / RT} e^{(\beta b_2 / RT) \ln(S / S_{max})} S , \quad (2-11.b)$$

$$r_d = k'_d (S / S_{max})^{\beta b_3} S , \quad (2-11.c)$$

where the subscripts a and d denote the forward (adsorption) and backward (desorption) rate of adsorption, k' is a rate constant which is considered to be a function of temperature, whereas

$k = k'e^{-E_0/RT}$ now includes the constant term of the activation energy into k' . Since S_{max} is considered to be constant, it is useful to incorporate it into the rate constant term. Before doing this however, it is convenient to first normalize the S/S_{max} term.

Normalize S/S_{max} such that

$$\frac{S(\mu\text{g/g soil})}{S_{max}(\mu\text{g/g soil})} = \frac{(S(\mu\text{g/g soil}))/(1(\mu\text{g/g soil}))}{(S_{max}(\mu\text{g/g soil}))/(1(\mu\text{g/g soil}))} = \frac{\zeta}{\zeta_{max}},$$

where ζ and ζ_{max} have magnitudes identical to S and S_{max} respectively, but are physically dimensionless. Rewrite Equations (2-10.c) and (2-11.c) as

$$r_a = k_a (\zeta_{max})^{\beta b_3} \zeta^{-\beta b_3} (VC/M_s) \quad (2-12)$$

and

$$r_d = k_d (\zeta_{max})^{-\beta b_3} \zeta^{\beta b_3} S. \quad (2-13)$$

The resulting net rate of adsorption becomes

$$\frac{\partial S}{\partial t} = k_a (\zeta_{max})^{\beta b_3} \zeta^{-\beta b_3} \left(\frac{VC}{M_s} \right) - k_d (\zeta_{max})^{-\beta b_3} \zeta^{\beta b_3} S. \quad (2-14)$$

Consider the condition at equilibrium, $\partial S/\partial t = 0$, so that

$$(k_a/k_d) \zeta_{max}^{2\beta b_3} \zeta^{-2\beta b_3} = (SM_s/VC). \quad (2-15)$$

Comparison of Equation (2-15) to Equation (1-24.b) shows that in order for Equation (2-15) to satisfy the previously obtained equilibrium condition, β must be equal to 1/2. Therefore, we shall use $\beta = 1/2$ for the analyses of our kinetic sorption studies.

Equation (2-14) with $\beta = 1/2$ can be rewritten as

$$\frac{\partial S}{\partial t} = k_a (\zeta_{max})^{b_3/2} \zeta^{-b_3/2} \left(\frac{VC}{M_s} \right) - k_d (\zeta_{max})^{-b_3/2} \zeta^{b_3/2} S. \quad (2-16)$$

Define

$$k_1 = k_a \zeta_{max}^{b_3/2},$$

$$k_2 = k_d \zeta_{max}^{-b_3/2},$$

and

$$b = b_3/2,$$

so that

$$\frac{\partial S}{\partial t} = k_1 \zeta^{-b} \left(\frac{VC}{M_s} \right) - k_2 \zeta^b S. \quad (2-17)$$

Note that mathematically we can multiply ζ by S , but physically, the two terms have different dimensions, namely, S has the unit of $\mu g/g$ soil while ζ is dimensionless. For a soil system the term (V/M_s) should be written as (θ/ρ_b) or θ_w . Experimental procedures will be based on the weight of air-dried soil so that θ_w will be expressed on this basis. Appropriate correction is needed if θ_w

is originally determined based on the weight of oven-dried soil. The correction is made by expressing $\theta_{w, \text{air}}$ by

$$\theta_{w, \text{air}} = \frac{\theta_{w, \text{oven}} - \theta_r}{1 + \theta_r}, \quad (2-18)$$

where $\theta_{w, \text{air}}$, expressed as a ratio, is the gravimetric water content based on an air-dried weight of the soil, $\theta_{w, \text{oven}}$ is the gravimetric water content based on an oven-dried weight of the soil and θ_r is the gravimetric water content based on an oven-dried weight of the soil at air-dried condition. For this study $\theta_r = 0.021$.

The surface reaction equation is

$$\frac{\partial S}{\partial t} = k_1 \zeta^{-b} \left(\frac{\theta' C'}{\rho_b} \right) - k_2 \zeta^b S, \quad (2-19)$$

where S ($\mu\text{g/g}$ soil) is the amount of ions adsorbed, ζ is the normalized form of S (dimensionless), C' ($\mu\text{g/ml}$) is the concentration of ions in the subsurface layer to which the soil surface is exposed, θ' (ratio) is the volumetric water content of the subsurface layer, ρ_b (g soil/cm^3) is the bulk density of the soil, t (sec) is time, k_1 and k_2 (sec^{-1}) are rate constants of the surface reaction, and b (dimensionless) is a constant associated with the rate of change in the heat of adsorption with the amount of ions adsorbed. Lindstrom et al. (1970, 1971) employed a similar approach

in obtaining equations for the kinetics of adsorption for a system with the equilibrium isotherm categorized as the Temkin isotherm, which states that the heat of adsorption is a linear function of the amount of ions adsorbed.

We now have equations for all three regions of the soil system, namely, Equations (2-6), (2-7) and (2-19). Solution of these equations requires the experimental evaluation of the parameters ℓ , k , D_x and D_z . The experimental and numerical work to be completed in order to accomplish this is very time consuming. The system can be simplified by assuming that one or more of the resistances are negligible. In this study it will be assumed that the subsurface layer is thin and that transverse diffusion is fast in comparison with the surface rate of reaction so that concentration gradients in this region are constant which implies a linear change in concentration with respect to distance. Therefore, we have

$$\frac{\partial C'}{\partial x} (x, t) = \text{constant}, \quad (2-20)$$

and the corresponding boundary conditions (Equations (2-8. a and b)) become

$$k(\theta C - \theta' C') = -\theta' D_x \frac{\partial C'}{\partial x} \Big|_{x=\ell} = \ell \rho_b \frac{\partial S}{\partial t} \quad (2-21)$$

Physically, the subsurface layer is similar to the "boundary layer" used in heat transfer problems. The diffusion of ions from the bulk solution toward the adsorbed layer is described collectively by the mass transfer coefficient, k . Since both Equation (2-19) and (2-21) contain the common term $\partial S / \partial t$, we can express $\theta' C'$ in terms of θC by equating the two equations and rearranging terms

$$\theta' C' = \left\{ \frac{(k/\ell)}{k_1 \zeta^{-b} + (k/\ell)} \right\} \theta C + \left\{ \frac{k_2 \zeta^b}{(k_1 \zeta^{-b}/\rho_b) + (k/\ell)} \right\} S. \quad (2-22)$$

Substituting the value of $\theta' C'$ in Equation (2-19) yields

$$\frac{\partial S}{\partial t} = \left[\frac{1}{(\ell/k) + 1/(k_1 \zeta^{-b})} \right] \frac{\theta C}{\rho_b} - \left[\frac{1}{(k_1 \zeta^{-2b}/k_2)(\ell/k) + 1/(k_2 \zeta^b)} \right] S. \quad (2-23)$$

Since both k and ℓ are unknown, it is useful to group them together and define the diffusive conductance, $K_d = k/\ell$ so that the resulting equation is

$$\frac{\partial S}{\partial t} = \left[\frac{1}{1/K_d + 1/(k_1 \zeta^{-b})} \right] \frac{\theta C}{\rho_b} - \left[\frac{1}{(k_1 \zeta^{-2b}/k_2)(1/K_d) + 1/(k_2 \zeta^b)} \right] S, \quad (2-24)$$

or

$$\frac{\partial S}{\partial t} = \frac{(k_1 \zeta^{-b} (\theta C / \rho_b) - k_2 \zeta^b S)}{(k_1 \zeta^{-b} / K_d) + 1} \quad (2-25)$$

In summary, the governing equations are

i) in the bulk solution

$$\frac{\partial \theta C}{\partial t} + \frac{\partial qC}{\partial z} = \frac{\partial}{\partial z} (\theta D_z \frac{\partial C}{\partial z}) - \rho_b \frac{\partial S}{\partial t} \quad (2-26)$$

ii) in the adsorbed layer

$$\rho_b \frac{\partial S}{\partial t} = \left[\frac{1}{1/K_d + 1/(k_1 \zeta^{-b})} \right] \theta C - \left[\frac{1}{(k_1 \zeta^{-2b}/k_2)(1/K_d) + 1/(k_2 \zeta^b)} \right] S. \quad (2-27)$$

The equation of interest in this study of the kinetics of adsorption for the adsorbed layer is Equation (2-27). In developing this equation, we consider the rate of diffusion across the subsurface layer to be steady so that the concentration of ions in this layer varies linearly with the thickness of the layer. Diffusion of the ion from the bulk solution across the subsurface layer is regarded as a rate limiting process. Adsorption of ions by surface kinetic reactions onto the surface of the soil particle also limits the rate of adsorption and is characterized by surface reaction parameters k_1 , k_2 and b .

Strictly speaking, the water content, θ of the soil sample as used in Equation (2-27) represents water of the "bulk solution" region which excludes the thin water film of the subsurface layer. In practice, however, we cannot determine water contents of the two regions separately. Therefore, θ would be approximated by water

content of the overall soil sample, namely, the water content, θ' of the subsurface layer is assumed to be negligible in comparison to the water content, θ of the bulk solution.

It must be emphasized at this point that the adsorption process considered in this study concerns solely with attraction forces between ions and soil particles. In this sense, the process excludes any other possible chemical reactions such as precipitation, dissociation / association, degradation and so forth. All chemical and biological reactions are described by a source/sink term which is added to Equation (2-26). The source/sink term is normally represented by a G function and must be considered separately from the $\partial S/\partial t$ function.

There have been several other expressions of the adsorption kinetic equations which contain similar concepts. One common approach is to assume that the rate of adsorption is governed mainly by the rate of diffusion of ions from the bulk solution to the subsurface layer. It is then assumed that diffusion across the subsurface layer and adsorption onto the soil surface are both steady. There is equilibrium between ions in the subsurface layer and adsorbed ions in the adsorbed layer. Consequently, the rate of adsorption is proportional to the lateral mass transfer coefficient and driven by the concentration difference between the initial concentration in the bulk solution and the final concentration of the bulk solution should equilibrium take

place. Kyte (1972) described the surface reaction for the above consideration by the Freundlich equilibrium isotherm. Hendricks (1972) and Garg and Ruthven (1975) described their systems with Langmuir isotherms. Shah et al. (1975) and Novak et al. (1975, 1975) applied the Langmuir approach to describe the movement of phosphorus in soils.

In this study, experiments will be described which were carried out to evaluate the parameters K_d , k_1 and k_2 in Equation (2-27) using the values of b obtained in the earlier equilibrium studies.

Materials and Methods

Experiments were carried out to measure the rate of adsorption in short soil columns under several flow rates. Included in the treatments was the measurement of the rate of adsorption for a static system, i.e., adsorption from a stationary solution. The soil water regime is kept constant, that is, a constant rate of flow is maintained at a given water content. Three pore water velocities ranging from 1.3 to 2.7 cm/hr were used to evaluate the relationship between the diffusive conductance, K_d , and the average pore water velocities. The experiments were carried out for periods of up to six hours. Dynamic equilibrium was not reached in any of the experiments. The concentration of ions in the soil column and the amount adsorbed was calculated by accounting for the mass balance which was possible

since the concentrations of the inflow and outflow solution were measured. The Pope Ridge soil was used in these experiments. The cation cadmium was chosen for this study.

Experimental Arrangement for Dynamic Studies

The critical parts of the experiment are the control of the water content of the soil sample and rate at which solution is applied. Water content is regulated by placing a soil sample in a pressure chamber. Solution is sprayed onto the soil surface through hypodermic needles. The pressure control system is shown schematically in Figure 2-4a. A photograph for an overview of the entire arrangement is shown in Figure 2-4b. Dry air was supplied from a cylinder of compressed air. The air was routed through two separate channels. One line went directly to the pressure chamber, which was used earlier in the equilibrium studies. Pressure regulators R_1 and R_2 were used to insure a constant pressure in the pressure chamber. The magnitude of the pressure was monitored with a mercury manometer. Regulator R_2 only allowed adjustment within the pressure range of 0-0.69 bars (0-10 psi). Bypass through 3-way ball valves, VT_1 and VT_2 , provided the opportunity to use pressure in excess of 0.69 bars. For pressure greater than 0.34 bars, the pressure was monitored with a pressure gauge operating in the range of 0-1 bar.

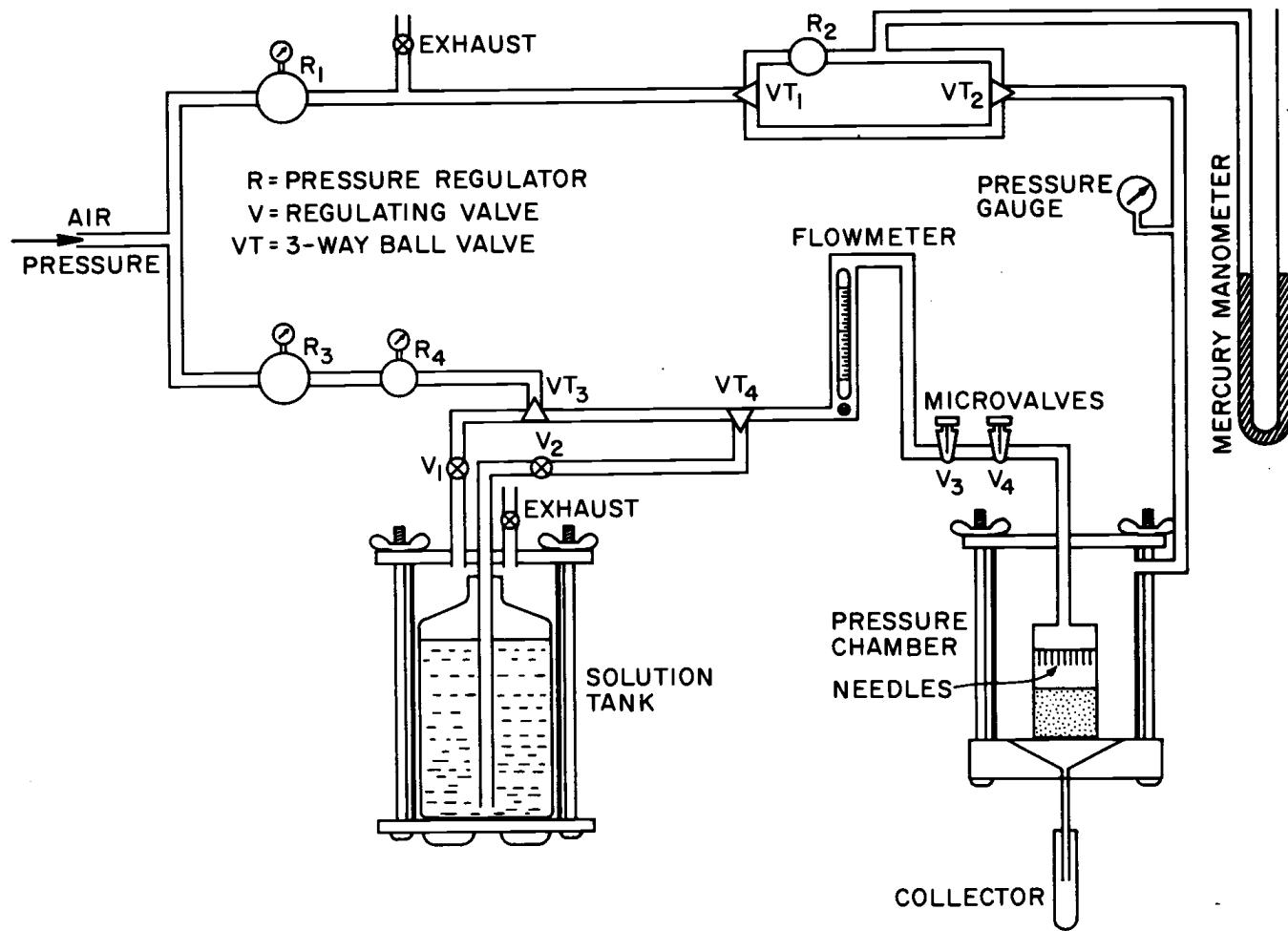


Figure 2-4a. Schematic diagram of the experimental arrangement used for the studies of adsorption kinetics in soil.

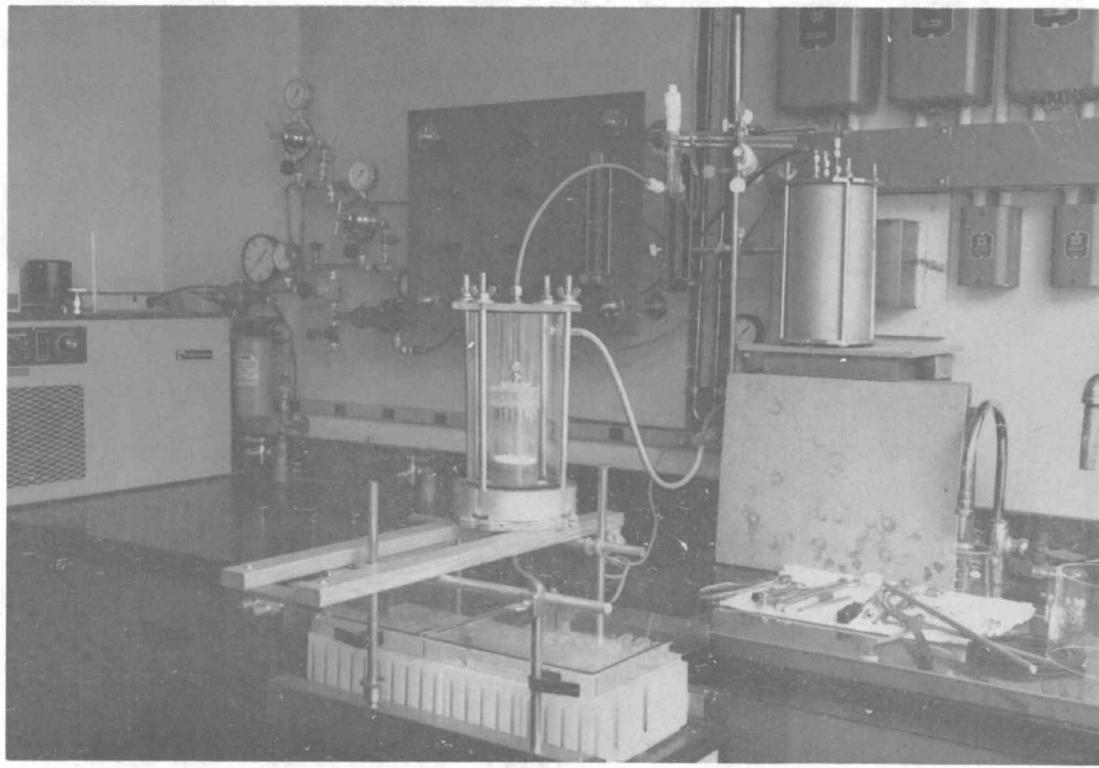


Figure 2-4b. Photograph of the experimental arrangement used for the studies of adsorption kinetics in soil.

Pressurized air on the second line served as the driving force for the distribution of solution through the hypodermic needles. Solution was stored in a 2-liter polyethylene bottle placed inside a stainless steel tank. The solution was routed through a flow meter. The flow rate was controlled by the regulator valves, V_3 and V_4 , which allowed adjustment of the flow rate to the desired range. The solution was distributed through a perforated disc made of an acrylic plate with holes of about 2 mm in diameter drilled through the plate and with hypodermic needles cemented to it (Figure 2-5). Through trial and error, it was found that the distributor disc with needles placed next to one another in three concentric circles gave the most uniform distribution of solution. The needles were removable as they were friction fitted onto the heads cut off from 1ml size disposable syringes which in turn were glued onto the disc. At low flow rates, the amount of solution was not sufficient to allow discharge from every needle simultaneously. However, it was found possible to prearrange which needles should discharge the solution. The needles are filled with solution flowing from the perforated disc through the applied pressure. The required pressure is inversely proportional to the radius of needle (Equation 1-11). The smaller the needle size, the easier it fills and forms a droplet. By arranging small size needles (gauge 27) intermittently with larger size needles (gauge 26), the distribution of the solution could be controlled through

the placement of the smaller size needles.

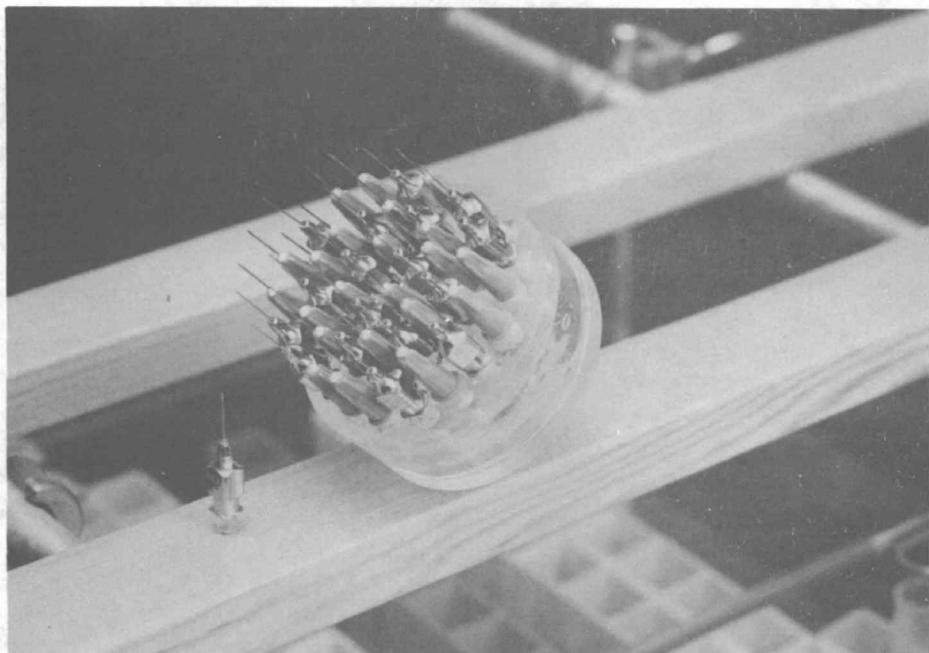


Figure 2-5. Solution distributor showing the arrangement of hypodermic needles.

Throughout the air pressure system, 0.635 mm O.D. (1/4 inch) copper and nylon tubings and gas tight, brass, Swagelock fittings were used. The solution was distributed through teflon coated tubings and stainless steel connectors to minimize loss of ions by adsorption on the wall of the conduits. Handling of the solution through the pressure chamber was carried out with the same precautions as described earlier to avoid direct contact of ions with metal surfaces. Effluent was collected in plastic test tubes using an automated fraction collector. A bypass through 3-way ball valves, VT₃ and VT₄, was used to allow direct air flow through the solution lines for the purpose

of cleaning out the solution after each experiment.

Experimental Procedure for Static Studies

Preparation of soil samples and the solution extraction method were as described earlier for the equilibrium studies. A series of soil columns was prepared and 41 ml of CdI₂ solution were added to the samples. Soil solution was extracted sequentially from each sample at an interval of an hour up to 18 hours. The first extraction was made two hours after the addition of cadmium solution.

This procedure used here for the static system is similar to that used for the kinetic adsorption studies by the shaking batch method where a small quantity of the bulk solution is drawn periodically for analysis. The difference is that the extraction method does not permit the use of the same sample throughout the time-series study.

Experimental Procedure for Dynamic Studies

Soil samples were packed in the container in the same manner as described for the equilibrium studies. The assembly was placed in the temperature-controlled room at least one day before the experimental run. Each experiment was initiated with the air pressure and solution flow rate at the specified levels. Solution of Cd was allowed to run through the system without the soil sample in it for a period of

one to two hours during which 200-300 ml of solution was expended.

During this period a steady state flow rate was established.

In order for every part of the soil to be wetted throughout, the sample was added up to saturation with 41 ml of solution first. This is the same amount as was used in the equilibrium studies. Time zero was when the solution was first added to the soil sample. Usually the 41 ml solution was added within five minutes. The sample was immediately placed in the extracting (pressure) chamber. Teflon balls with a diameter of 0.3 cm were packed on the soil surface to a thickness of about two layers to help increase the uniformity of the distribution of the solution over the soil surface. The chamber was then sealed and solution was applied. Total time elapsed from the first addition of 41 ml of solution until the flow started was ten minutes. Flow rates ranging from 0.55 to 1.15 cm/hr were used. The water potential of the soil sample was kept at about -0.126 bars corresponding to a gravimetric water content of about 0.41 on the oven-dried basis or about 87% of saturation. The cadmium solution was prepared using the CdI₂ compound and the concentration of inflow cadmium solution was about the same at 1000 µg/ml for all experimental runs. Effluent was collected every ten minutes during the first hour and every 15 minutes thereafter for a period of up to six hours. The preparation and analysis of cadmium ion were as described earlier.

Calculations

The amount adsorbed for the static studies was calculated using Equation (1-12).

The solute mass balance equation applicable to dynamic studies is

$$\theta \frac{\partial C}{\partial t} = -q \frac{\partial C}{\partial z} - \rho_b \frac{\partial S}{\partial t}, \quad (2-28)$$

where the assumption is made that the dispersion-diffusion process is negligible in comparison with the convective and adsorption process and that the water content and Darcian flux are held constant. Using a linear approximation method, the amount adsorbed during a period of time is calculated from

$$\Delta S^{k+1/2} = -\theta_w (C_i^{k+1} - C_i^k) - \frac{V}{M_s} \left\{ C_{in}^{k+1/2} - \frac{(C_{out}^{k+1} + C_{out}^k)}{2} \right\}, \quad (2-29)$$

where $\Delta S^{k+1/2}$ ($\mu\text{g Cd/g soil}$) is the amount adsorbed, based on the air-dried weight of the soil sample, during the time interval from t^k to t^{k+1} . The superscript k is the time index, θ_w (ratio) is the gravimetric water content, V (ml) is the volume of effluent collected during the time interval t^k to t^{k+1} and M_s (g soil) is the weight of the air-dried soil. C_{in} ($\mu\text{g Cd/ml}$) is the concentration of the inflow solution (a constant), C_{out} is the concentration of

outflow solution, and C_i is the average concentration of the bulk solution in the soil computed as

$$C_i^{k+1} = (C_{in}^{k+1} + C_{out}^{k+1})/2 \quad (2-30.a)$$

and

$$C_i^k = (C_{in}^k + C_{out}^k)/2. \quad (2-30.b)$$

The first twenty minutes, namely, ten minutes when 41 ml of solution was added and ten minutes for effluent collection, need special consideration since 41 ml of solution was initially added. The amount adsorbed was calculated from the mass balance such that

amount adsorbed = mass added

- (mass coming out

+ mass remaining in the bulk solution

in the soil sample)

or

$$\Delta S^{1/2=10\text{ min}} = (\theta_w + \frac{V}{M_s})C_{in} - (\frac{V}{M_s} C_{out} + \theta_w C_i^{k+1}) \quad (2-31)$$

and finally, the amount adsorbed at a certain time is the cumulative amount from $t = 0$ to $t = t$.

Results

For studies of adsorption in the static system, the concentration of the extracted solution was assumed to be the average concentration of the ions in the liquid phase and the amount adsorbed was calculated using Equation (1-12). This assumption must be carefully considered because it could introduce errors. Though the solution medium was continuous and ions could diffuse throughout the entire soil sample, the time elapsed might not have been sufficient for the ions to distributed themselves uniformly. The concentration of the extracted solution may not represent the concentration in the liquid phase in the soil pores especially not the solution in dead-end pores.

For studies of adsorption in the dynamic system, three pore water velocities were employed, i.e., $\bar{v} = 1.32, 2.29$ and 2.71 cm/hr. The experimental procedure allowed the monitoring of the concentrations of inflow and outflow solutions. The concentration of solution at the center point of the soil sample was calculated using Equation (2-30. a or b) and therefore is an average value.

The changes in the concentrations of cadmium with time in the soil solution and the corresponding amount adsorbed are shown in Table 2-1, Figures 2-6 and 2-8 for the static system and in Table 2-2 and Figures 2-7 and 2-9 for the dynamic flow system. The solid lines were determined from a curve fitting technique employing

polynomial degree two (2-spline) functions. Concentrations $C_i(t)$ and $S_i(t)$ were expressed as functions of time in the form of

$$\begin{aligned}
 S_i^{(1)}(t) &= \beta_0 + \beta_1 t + \beta_2 t^2 & 0 \leq t \leq T_1, \\
 S_i^{(2)}(t) &= S_i^{(1)}(t) + \beta_3(t-T_1)^2 & T_1 \leq t \leq T_2, \\
 S_i^{(3)}(t) &= S_i^{(2)}(t) + \beta_4(t-T_2)^2 & T_2 \leq t \leq T_3, \\
 S_i^{(4)}(t) &= S_i^{(3)}(t) + \beta_5(t-T_3)^2 & T_3 \leq t \leq T_{\max}.
 \end{aligned} \tag{2-32}$$

$C_i(t)$ was described by the same expression with C_i in place of S_i . The entire range of data was represented by four polynomial functions satisfying the condition that at the knot point of time (T_1 , T_2 and T_3), the functions and the first order derivatives exist and are continuous. The parameters β_i and T_i are listed in Table 2-3.

Table 2-1. Concentration of cadmium in the soil solution and the corresponding amount adsorbed as a function of time at $\bar{v} = 0.0 \text{ cm/hr}$.

Time <u>hr</u>	C_i <u>$\mu\text{g Cd/ml}$</u>	S_i <u>$\mu\text{g Cd/g soil}$</u>
2.26	204.49	410.55
3.26	171.82	423.94
4.26	163.35	428.46
5.26	150.05	432.87
6.26	148.83	433.37
7.26	176.66	421.96
8.26	169.40	424.90
9.26	170.61	424.44
10.26	102.85	452.22
11.26	105.27	451.23
12.26	93.17	456.19
18.26	121.00	444.78

Table 2-2. Concentration of cadmium in the soil solution and the corresponding amount adsorbed as a function of time at $\bar{v} = 1.32, 2.29$ and 2.71 cm/hr .

Time	$\bar{v} = 1.32 \text{ cm/hr}$		$\bar{v} = 2.29 \text{ cm/hr}$		$\bar{v} = 2.71 \text{ cm/hr}$	
	C_i	S_i	C_i	S_i	C_i	S_i
hr	$\mu\text{g Cd/ml}$	$\mu\text{g Cd/gsoil}$	$\mu\text{g Cd/ml}$	$\mu\text{g Cd/gsoil}$	$\mu\text{g Cd/ml}$	$\mu\text{g Cd/gsoil}$
.17	509.62	225.10	546.87	192.14	537.50	186.33
.42	509.87	246.39	531.25	223.07	521.87	228.56
.58	518.00	271.04	546.87	260.10	543.75	267.70
.75	540.62	287.27	596.87	272.65	584.37	287.64
.92	556.25	304.30	628.12	310.29	628.12	311.21
1.08	592.19	310.28	696.87	301.12	662.50	326.31
1.29	626.56	325.20	706.25	326.96	715.62	354.52
1.54	657.81	343.85	740.62	358.44	762.50	376.64
1.79	687.50	361.14	771.87	365.17	781.25	399.30
2.04	734.37	367.51	781.25	394.90	812.50	415.42
2.29	739.06	382.72	809.37	406.76	846.87	425.72
2.54	754.69	396.30	818.75	424.43	859.37	439.67
2.79	754.69	415.75	831.25	442.01	865.62	455.40
3.04	782.81	421.94	840.62	459.74	871.87	469.32
3.29	793.75	434.68	865.62	468.49	875.00	483.90
3.54	815.62	441.42	865.62	484.03	893.75	492.10
3.79	815.62	454.81	875.0	489.72	896.87	503.01
4.04	828.12	464.30	887.5	501.87	903.12	512.94
4.29	840.62	470.92	893.75	515.20	906.25	522.23
4.54	860.94	474.70	896.87	523.87	909.37	532.28
4.79	868.75	480.58	906.25	528.55	915.62	540.24
5.04	876.56	486.30	909.37	539.78	918.75	548.37
5.29	876.56	495.06	909.37	548.0	921.87	556.19
5.54	887.50	499.03			925.00	563.49
5.79	893.75	504.78			928.12	569.92
6.04	893.75	512.20			925.00	580.07
6.29	906.25	514.57			928.12	586.44
6.54	892.19	527.62				

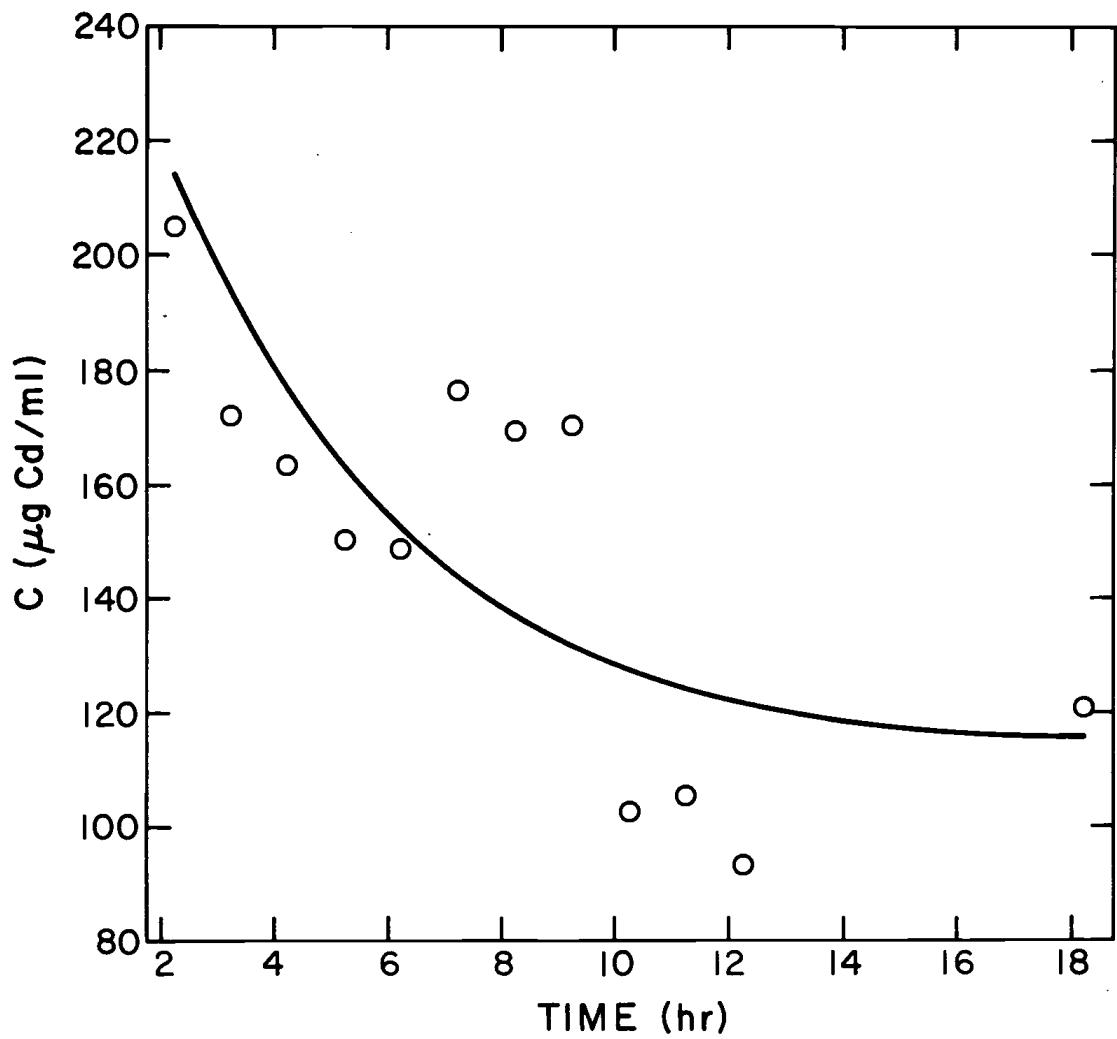


Figure 2-6. Concentration of cadmium in the soil solution, C_i , as a function of time at $\bar{v} = 0.0 \text{ cm/hr}$ for the static system.

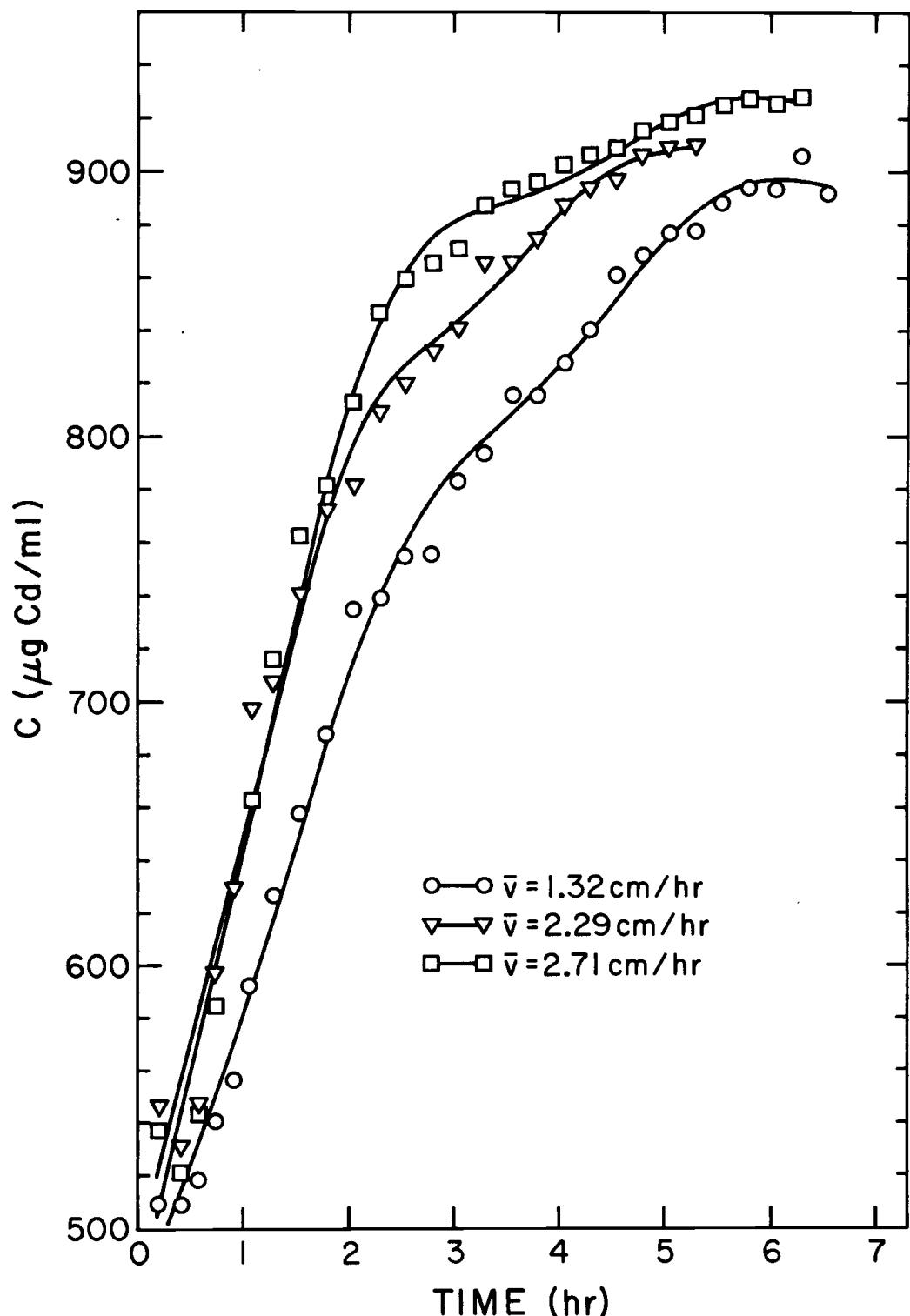


Figure 2-7. Concentration of cadmium in the soil solution, C_i , as a function of time at $\bar{v} = 1.32, 2.29$ and 2.71 cm/hr^{-1} .

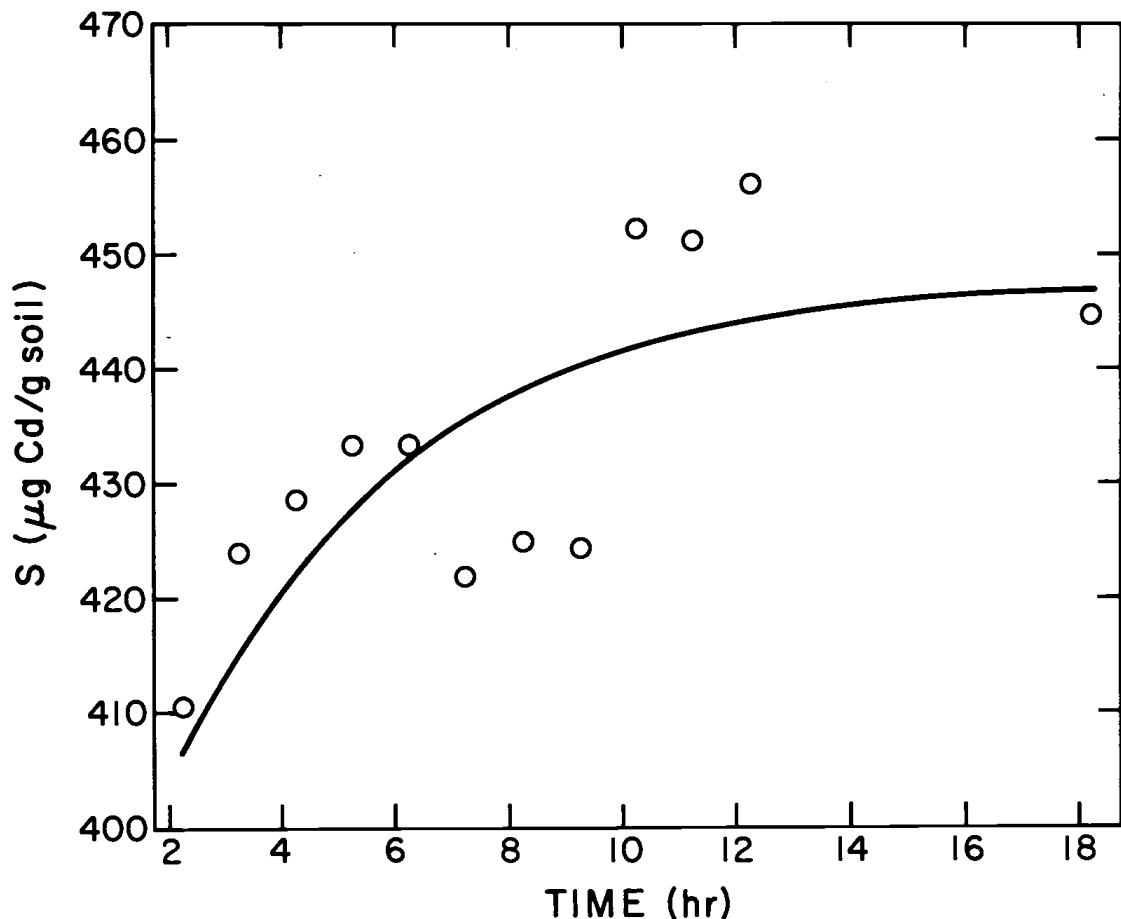


Figure 2-8. Amount of cadmium adsorbed per gram of soil, S_i , as a function of time at $\bar{v} = 0.0 \text{ cm/hr}$ for the static system.

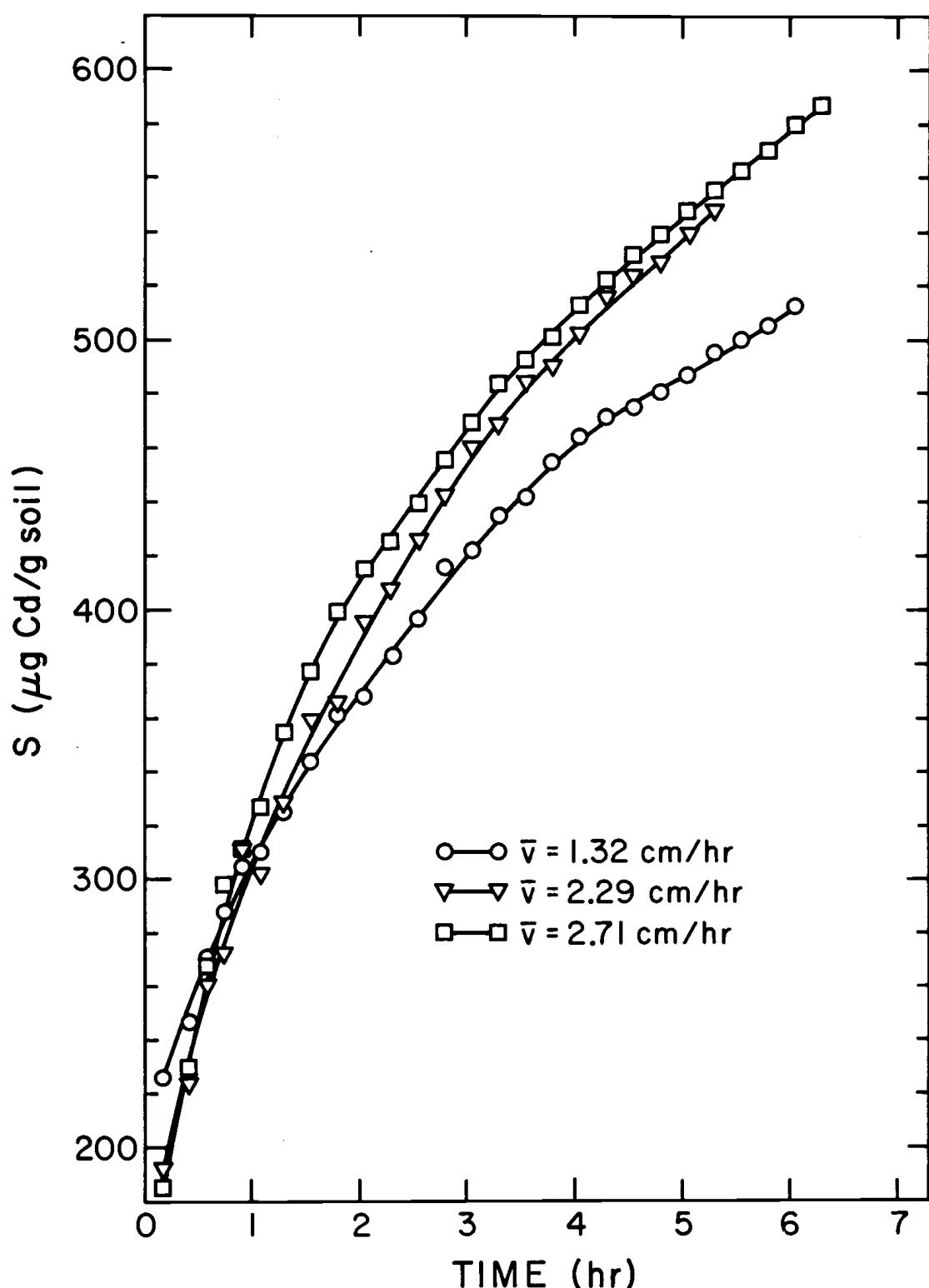


Figure 2-9. Amount of cadmium adsorbed per gram of soil, S_i , as a function of time at $\bar{v} = 1.32$, 2.29 and 2.71 cm/hr .

Table 2-3. Values of β_i and T_i for the 2-spline curve fitting functions for $C_i(t)$ and $S_i(t)$.

	$\bar{v} = 0.0 \text{ cm/hr}$		$\bar{v} = 1.32 \text{ cm/hr}$		$\bar{v} = 2.29 \text{ cm/hr}$		$\bar{v} = 2.71 \text{ cm/hr}$	
	$C_i(t)$	$S_i(t)$	$C_i(t)$	$S_i(t)$	$C_i(t)$	$S_i(t)$	$C_i(t)$	$S_i(t)$
β_0	$.587925 \times 10^2$	$.470257 \times 10^3$	$.478766 \times 10^3$	$.204021 \times 10^3$	$.497167 \times 10^3$	$.161437 \times 10^3$	$.480063 \times 10^3$	$.150307 \times 10^3$
β_1	$.220986 \times 10^3$	$-.905615 \times 10^2$	$.813378 \times 10^2$	$.123449 \times 10^3$	$.129666 \times 10^3$	$.181273 \times 10^3$	$.150519 \times 10^3$	$.218431 \times 10^3$
β_2	$-.717736 \times 10^2$	$.294354 \times 10^2$	$.186606 \times 10^2$	$-.211508 \times 10^2$	$.178627 \times 10^2$	$-.383372 \times 10^2$	$.115067 \times 10^2$	$-.468540 \times 10^2$
β_3	$.732197 \times 10^2$	$-.300387 \times 10^2$	$-.523422 \times 10^2$	$.183530 \times 10^2$	$-.746896 \times 10^2$	$.329367 \times 10^2$	$-.676638 \times 10^2$	$.372519 \times 10^2$
β_4	$-.112959 \times 10$	$.476610$	$.392080 \times 10^2$	$-.581798 \times 10$	$.653731 \times 10^2$	$-.623286 \times 10$	$.640922 \times 10^2$	$.520962 \times 10$
β_5	--	--	$-.244285 \times 10^2$	$.118820 \times 10^2$	$-.262474 \times 10^2$	$.950665 \times 10$	$-.196851 \times 10^2$	$.279449 \times 10$
T_1		1.7		1.6		1.3		1.5
T_2		7.7		3.2		2.6		3.1
T_3		---		4.8		3.8		4.6

The curve fitting functions of C_i and S_i were later used for the evaluation of the parameters which appear in the proposed adsorption kinetic equation (Equation 2-27). Figures 2-10 and 2-11 show the rate of adsorption, plotted as a function of both the amount of ions in the solution, $(\theta/\rho_b)C_i$ and the amount of ions adsorbed, S_i . The values of $\partial S/\partial t$ were obtained by differentiation of Equation (2-32) with respect to time. Figure 2-12 shows the relationship between the functions $(\theta/\rho_b)C_i$ and S_i for the three flow rates in comparison with the relationship obtained for equilibrium (isotherm) conditions which was evaluated earlier in the first part of this study using the static system.

At the beginning of the adsorption process when S was still small, the differences in the amount adsorbed, S , at the same value of $(\theta/\rho_b)C$ between the dynamic functions and the equilibrium function were quite large indicating that the adsorption was still far from equilibrium. As the adsorption process progressed, the dynamic flow curves approached the equilibrium condition at the same time as the rate of adsorption, $\partial S/\partial t$, (Figure 2-11) approached zero.

Obtaining $\partial S/\partial t$, $(\theta/\rho_b)C_i$ and S_i as smooth functions of time, we employed the function minimization by the Nelder-Mead Simplex method as programmed by Lindstrom (1978). The algorithm is based on a non-linear least square procedure. The program was set to evaluate three unknown parameters, namely, the diffusive

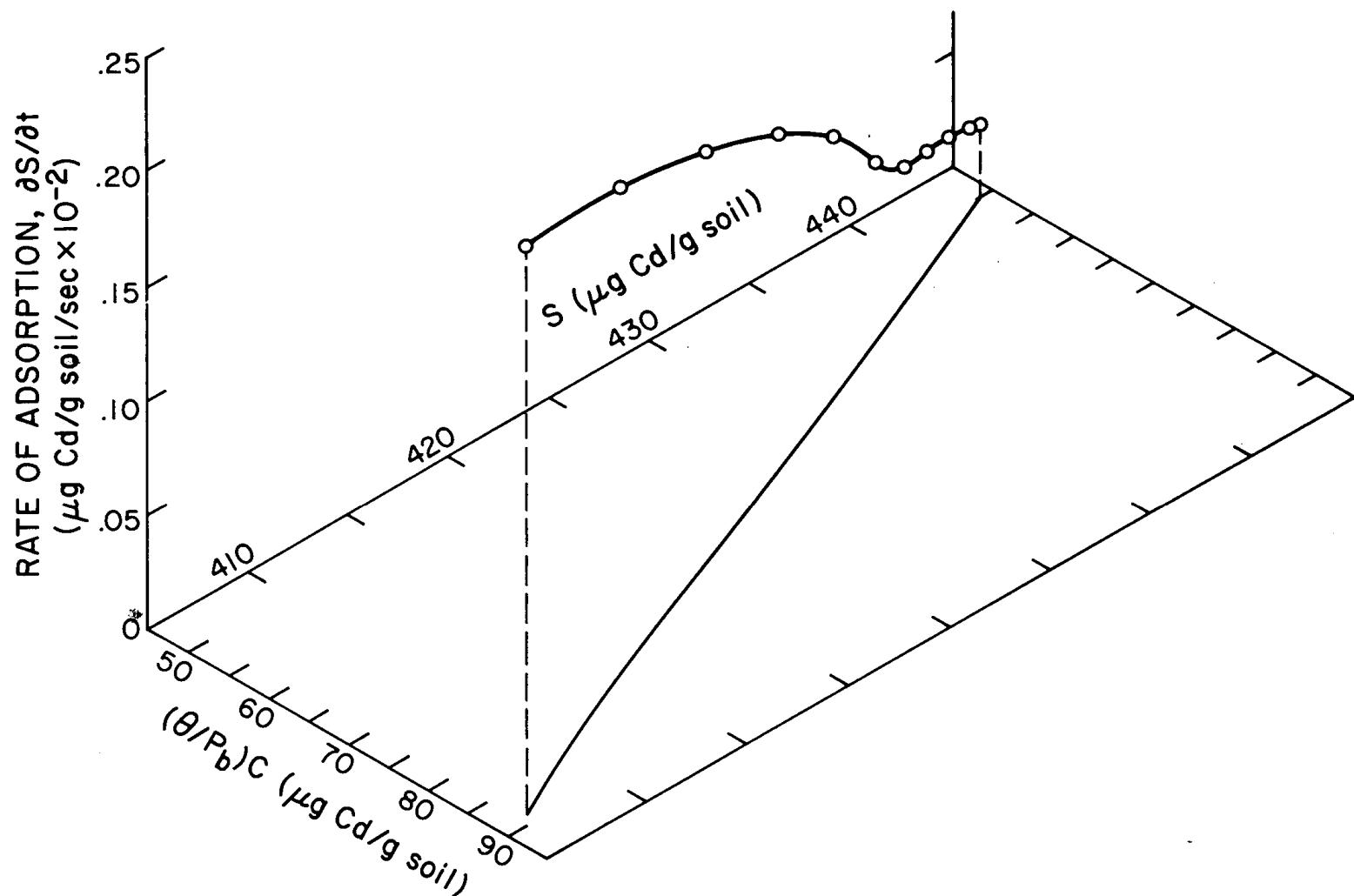


Figure 2-10. The rate of adsorption of cadmium as functions of the amounts in the liquid phase, $(\theta/\rho_b)C_i$ and in the adsorbed phase, S_i , at $\bar{v} = 0.0 \text{ cm/hr}$.

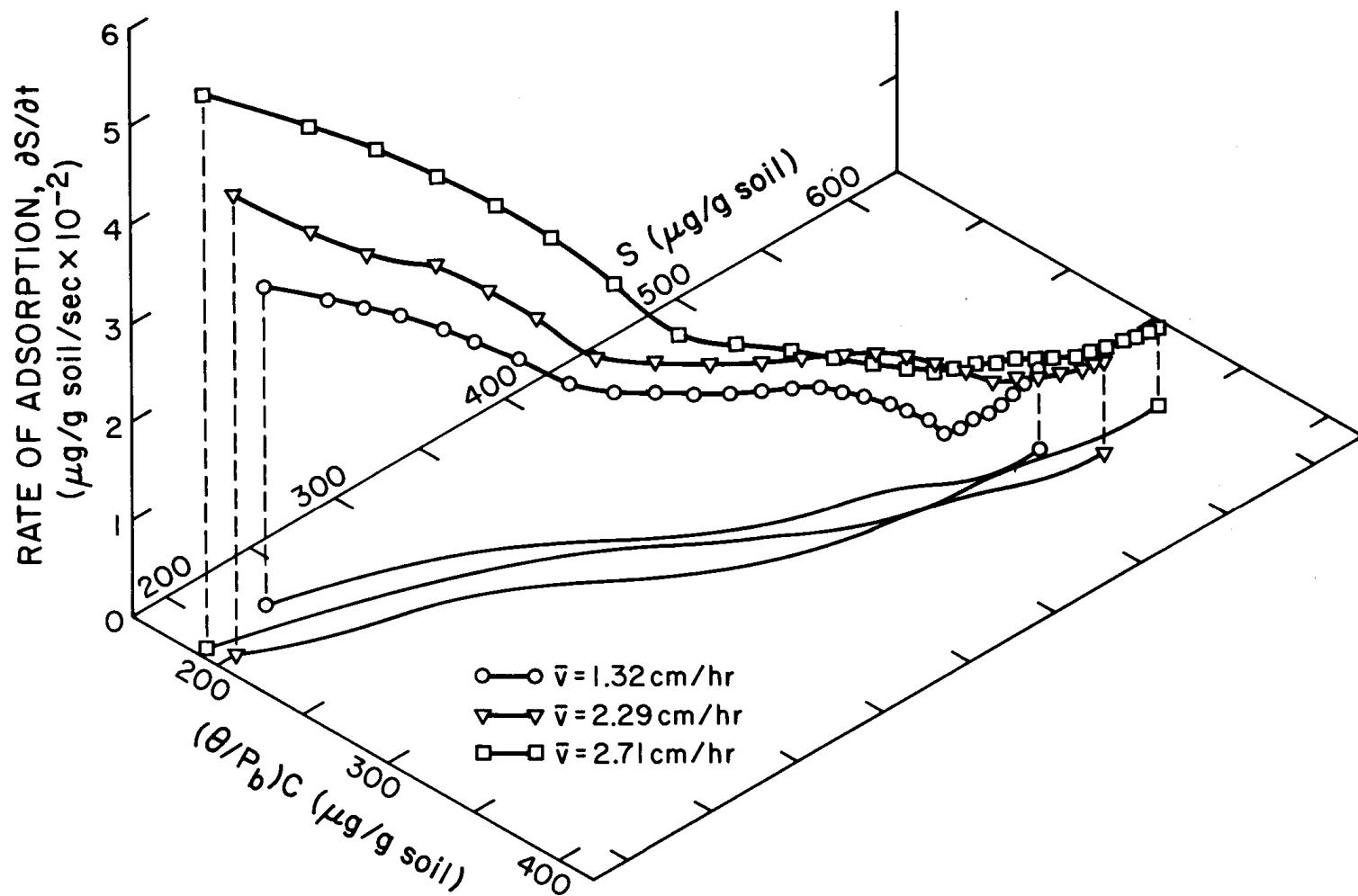


Figure 2-11. The rate of adsorption of cadmium as functions of the amounts in the liquid phase $(\theta / \rho_b)C_i$ and in the adsorbed phase, S_i , at $\bar{v} = 1.32, 2.29$ and 2.71 cm/hr .

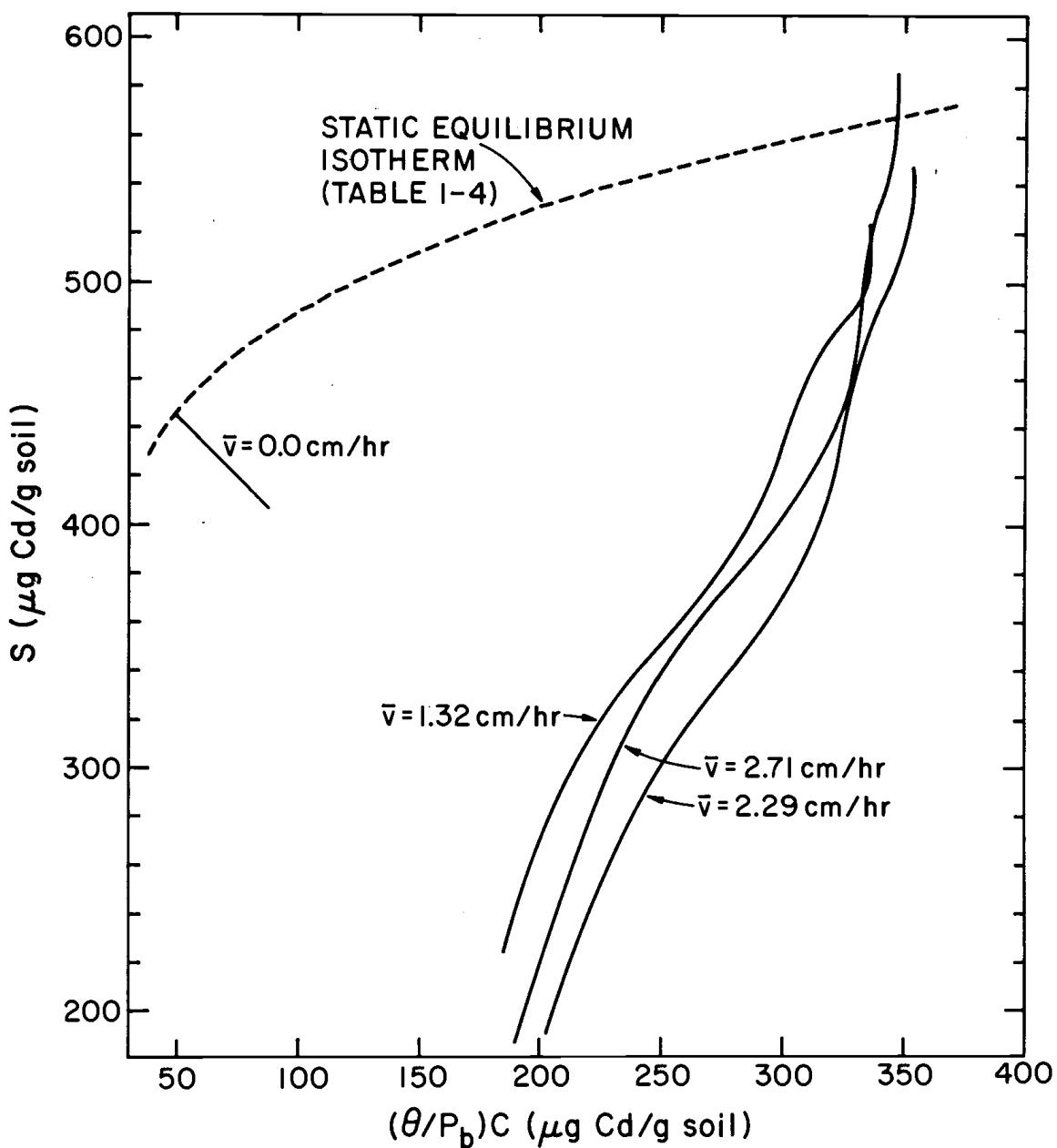


Figure 2-12. Relationships between the amounts of cadmium in the liquid phase, $(\theta/P_b)C_i$, and the adsorbed phase, S_i , for the dynamic and static experiments.

conductance, K_d , and the rate constants, k_1 and k_2 , of Equation (2-27) using $b = b_3/2 = 3.3913$ for cadmium as derived from the earlier studies at equilibrium conditions. The objective function for the minimization was

$$F(\alpha_1, \alpha_2, \alpha_3) = \sum_{i=1}^n \left(S'_i - \frac{\alpha_1 \tilde{C}_i - \alpha_2 S_i^\gamma}{\alpha_2 + \alpha_3 S_i^b} \right)^2, \quad (2-33)$$

where α_1 , α_2 and α_3 represent the three unknowns K_d , k_1 and k_2 respectively. $S' = \partial S / \partial t$, $\tilde{C} = (\theta / \rho_b) C$, $\gamma = 2b+1$ and n is the number of data points. The method is to search over the subset \mathbb{R}^{3+} for that point $(\tilde{\alpha}_1, \tilde{\alpha}_2, \tilde{\alpha}_3)$ where $\min_{\mathbb{R}^3} F$ is achieved. The resulting values of K_d , k_1 and k_2 were listed in Table 2-4.

Table 2-4. Calculated values of diffusive conductance, K_d , the forward rate, k_1 , and the backward rate constant, k_2 , as a function of pore water velocity.

\bar{v}	K_d	k_1	k_2	k_1/k_2
<u>cm/hr</u>	- - - - -	<u>1/sec</u>	- - - - -	
0	$.0697 \times 10^{-3}$	$.6003 \times 10^5$	$.5987 \times 10^{-14}$	10.03×10^{18}
1.32	$.3318 \times 10^{-3}$	$.3819 \times 10^5$	$.1510 \times 10^{-14}$	25.29×10^{18}
2.29	$.2912 \times 10^{-3}$	$.5491 \times 10^5$	$.1821 \times 10^{-14}$	30.15×10^{18}
2.71	$.4209 \times 10^{-3}$	$.6086 \times 10^5$	$.1147 \times 10^{-14}$	53.06×10^{18}
Equilibrium isotherm				8.88×10^{18}

Discussion

In the study of adsorption kinetics there is a basic difference between using a static or a dynamic procedure. In the static procedure, the system is a closed one, therefore the amount of ions in the liquid phase decreases with time as more and more ions are being adsorbed onto the soil surface (Figure 2-6). The dynamic flow procedure, on the other hand, provides a continuous flow of fresh solution into the system to replenish the ions that move out of the liquid phase by becoming adsorbed. Figure 2-7 showed the concentration to increase with time as more ions are adsorbed.

The implication of this fact is significant. The equilibrium isotherm obtained from a dynamic study will have a higher amount adsorbed than from a static study when the concentration of the soil solution is at the same level. Supplied with a solution of the same concentration, soil samples with solution flowing past them will be exposed to a greater mass of ions (concentration \times flow rate \times time) than the static sample (concentration \times solution volume) by the time equilibrium is established. More importantly, with solution flowing through the soil system, the solution does not only bring in more ions but also removes the desorbed ions of other species that were present originally.

Figure 2-12 shows that the amount of cadmium adsorbed under dynamic conditions ($\bar{v} = 2.7 \text{ cm/hr}$) exceeds the amount adsorbed at equilibrium under static conditions. The greater amount adsorbed in the dynamic flow experiments seems to indicate that the introduced ions can be adsorbed to a greater extent to replace the original ions which are desorbed. The desorbed ions moved also in accordance with the rules of adsorption kinetics towards the bulk solution where there is low or zero concentration of these ions.

In the process of evaluating the parameters K_d , k_1 and k_2 , we assumed the value of b which is associated with the activation energies of adsorption and desorption, to be the same for all experiments including the static as well as the dynamic ones. Since the value of b was obtained from the static equilibrium isotherm, it should only be applied to the static adsorption kinetic study, because the influence of the initially adsorbed ions on the energies of adsorption is not the same in the static and dynamic flow systems. However, to obtain equilibrium isotherms using dynamic flow systems would be very time consuming. Without having performed the dynamic isotherm studies we cannot be sure whether our assumption that the b value is the same for the static and dynamic systems is indeed valid.

Pore water velocity has an interesting effect on rate of adsorption. Figure 2-11 clearly showed that the higher the flow rate, the faster the rate of adsorption. It might be postulated that the higher

flow rate would leave shorter residence time for the ions in the soil and cause lower rates of adsorption. Apparently, the high flow rate brings in more mass of ions over the same span of time and thus produces a higher concentration in the bulk solution (Figure 2-7) which drives more ions towards the surfaces of the soil particles.

It is also possible that the higher flow rate induces an increase in the extent of dynamic flow regions of the soil solution. Flow of the solution in the soil pore channels is normally described as a laminar flow. A velocity boundary layer is developed near the soil particles where the solution is immobile or has a flow velocity much smaller than that of the bulk velocity. Ions have to move across this region to the surfaces of the soil particles mainly by molecular diffusion. The thickness of this velocity boundary layer is a function of the bulk solution velocity. Therefore, the higher the flow rate, the greater the part of solution in the pores becomes mobile (dynamic) and the shorter the thickness of the stagnant layer that ions have to diffuse across.

The computed parameter, K_d , for the diffusion process is of the most interest. As might be expected, the K_d value was the lowest when the solution was static ($0.0697 \times 10^{-3} \text{ sec}^{-1}$) and was the highest at $0.4209 \times 10^{-3} \text{ sec}^{-1}$ at the fastest flow rate of $\bar{v} = 2.7 \text{ cm/hr.}$ There was a trend indicating that the conductance of lateral diffusion of ions increases with increasing rate of bulk flow through the soil (Figure 2-13). The decrease in resistance, i.e.,

increase in conductance, may be regarded as evidence supporting the hypothesis stating that the thickness of the boundary layer decreases with increasing velocity.

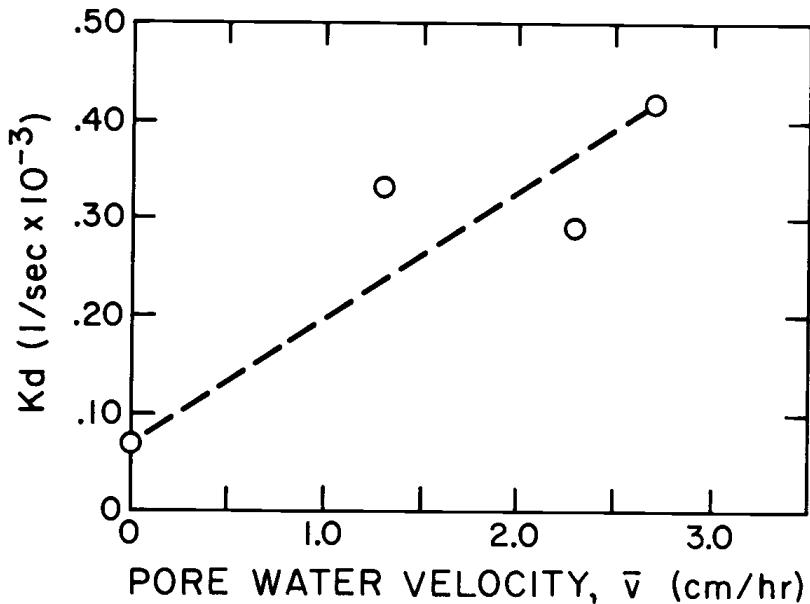


Figure 2-13. Diffusive conductance, K_d , as a function of pore-water velocity, \bar{v} .

However, with respect to our objective of combining the diffusion process and surface reaction to form a new kinetic adsorption equation, it is not quite as important to us to show that K_d is a function of \bar{v} as it is to show that K_d exists with a magnitude sufficiently small to induce a diffusion limiting process, especially as adsorption is far from equilibrium. Consider Equation (2-25),

$$\frac{\partial S}{\partial t} = \frac{k_1 \zeta^{-b} (\theta/\rho_b) C - k_2 \zeta^b S}{(k_1 \zeta^{-b}/K_d) + 1}, \quad (2-25)$$

we can see that the kinetics of adsorption will be governed solely by the surface reactions (numerator term), only if the denominator term is unity, namely,

$$\frac{\partial S}{\partial t} \rightarrow \text{a surface reaction if } \frac{k_1 \zeta^{-b}}{K_d} \ll 1.$$

The values of the ratio $k_1 \zeta^{-b}/K_d$ at different amounts of ions adsorbed, $S = \zeta$, for the four experiments are shown in Table 2-5. We can immediately see that the diffusion process is important in limiting the rate of adsorption as $k_1 \zeta^{-b}/K_d$ is not negligible especially at the beginning of the adsorption process when the amount of ions adsorbed is still low. Figure 2-11 also showed that the rates of adsorption differed the most as a function of \bar{v} at the lowest values of S . As S increases, the activation energies of adsorption, ζ^{-b} , and desorption ζ^b , play a more dominant role. The rates of adsorption for all \bar{v} subsequently approached each other asymptotically as the lateral diffusion process was mostly complete and the adsorption process moved towards equilibrium where its rate is determined by the surface reaction process. We conclude that the

lateral diffusion process cannot be ignored in the consideration of adsorption kinetics.

Table 2-5. Values of the ratio $(k_1 \zeta^{-b} / K_d)$ at different amounts of ions adsorbed, $S = \zeta$, as a function of pore water velocity.

\bar{v} (cm/hr)	Ratio of $k_1 \zeta^{-b} / K_d$				
	$\zeta = 200$	$\zeta = 300$	$\zeta = 400$	$\zeta = 500$	$\zeta = 600$
0.0	13.54	3.423	1.291	.6055	.3263
1.32	1.810	.4575	.1725	.08092	.04360
2.29	2.965	.7495	.2825	.1326	.07143
2.71	2.273	.5748	.2167	.1017	.0548

Unexpectedly, not only is K_d a function of \bar{v} , but the ratio k_1/k_2 also increases with the flow rate (Table 2-4). From the earlier studies on cadmium equilibrium isotherms, we obtained $k_1/k_2 = k_a S_{\max}^{b_3} / k_d = 8.88 \times 10^{18}$ which agreed excellently with the value of 10.03×10^{18} obtained from the kinetic study using the similar static procedure. But when adsorption kinetics were evaluated using a soil system under dynamic flow conditions, the ratio k_1/k_2 increased to two to five times this value. We may consider this result as evidence supporting our earlier argument that the magnitude of the amount adsorbed is higher for an equilibrium isotherm obtained from a dynamic study than from a static study. To be specific, for the Freundlich isotherm, $S = a(C_{eq})^c$, the characteristic constant a which is associated with the ratio k_1/k_2 will have a larger value for

the dynamic flow studies than for the static studies of adsorption isotherms.

The term of the maximum amount adsorbed has been incorporated in the parameters k_1 and k_2 , such that

$$k_1 = k_a \zeta_{\max}^b$$

and

$$k_2 = k_d \zeta_{\max}^{-b}$$

it is therefore possible that ζ_{\max} is not a constant value. Nor-

mally ζ_{\max} is assumed to be the amount adsorbed at $t \rightarrow \infty$.

Obviously, the number of the introduced ions which can be adsorbed also depends on how easily they can be exchanged with other ions of different kinds already adsorbed by the soil surfaces. With a closed system, the exchange cannot be complete without building up the concentration of the replaced ions in the bulk solution. This would, in turn, drive these ions back into the adsorbed phase. But in an open, flowing system the exchange can be complete as the replaced ions are continuously carried out of the system while more of the introduced ions can take their places.

Consider $\zeta_{\max} = 1.00$ for the static system, the relative ζ_{\max} values for other dynamic systems are shown in Table 2-6.

Table 2-6. The relative values of ζ_{\max}
evaluated for the dynamic and
static experiments.

v (cm/hr)	Relative ζ_{\max}
0.0	1.000
1.32	1.146
2.29	1.176
2.71	1.278

Consequently, the adsorption process in the soil is not as simple as attraction of ions onto the clean charged surfaces, a system on which the kinetic surface reaction involving simple activation energies is based. The adsorbed ions must also compete and exchange with ions present in the adsorbed layer originally. In order to describe the kinetic adsorption for the purpose of simulation of solute flow in soil, it is likely that we not only have to consider the diffusive conductance as a function of \bar{v} but must also evaluate the parameters for surface reaction, i.e., k_1 , k_2 and b as a function of \bar{v} so that the ion exchange process can be accounted for appropriately.

SUMMARY AND CONCLUSION

In recent years, simulation of flow of water and solute through soil under a wide range of initial and boundary conditions has been made possible by the advancement of computing capabilities. To describe solute flow, we must be able to characterize the adsorption processes in soils under conditions where the soil is not saturated and the water content is changing. Until now these aspects of solute flow have received little attention in terms of theory or experimental procedures. The currently used experimental procedure for determination of adsorption isotherms is the shaking batch method. This method considers the adsorption process to be a surface reaction only. Other limitations are that the shaking procedure destroys the structure of the soil and allows only measurements for saturated conditions without flow through a soil system. The objectives of this study were to evaluate limitations of current procedures by considering the theoretical background and proposing a new experimental procedure for the study of adsorption kinetics.

Adsorption was treated as a process described by a mechanism involving three steps. First, there is a lateral diffusion of the ion from the bulk solution to the "subsurface" layer of the soil particles which is considered to be a rate limiting process for which a diffusion resistance must be incorporated into the adsorption kinetic equation

when the lateral diffusion has not been accounted for in a one-dimensional analysis of solute flow. Then the diffusion of the ion across the subsurface layer was assumed to be steady so that the subsurface layer is perceived as a concentration boundary layer. Lastly, ions from the subsurface layer are then adsorbed onto the surfaces of the soil particles. This process was described by a rate limiting surface kinetic reaction. To be able to describe the surface reaction properly, an equilibrium isotherm must first be measured experimentally to obtain the function for the heat of adsorption. The activation energies for adsorption and desorption are then calculated based on the acquired functions of the heat of adsorption.

Kinetic adsorption experiments were conducted in order to evaluate the parameters for the diffusion and surface reaction processes which take place concurrently. The kinetic adsorption was measured under several pore water velocities to describe the diffusion parameter as a function of flow rate of water through the pores.

A new experimental procedure for the determination of adsorption isotherms was proposed which involves the use of a short soil column. For the studies of equilibrium isotherms, the short soil column method is similar to and equally simple to use as the shaking batch. Solution is added to soil packed in a short column. At equilibrium, the soil solution is extracted using the pressure membrane apparatus. However, the short soil column has the advantage that it

is adaptable to the measurement at unsaturated conditions and that it can be used for studies of adsorption kinetics with or without solution flowing through the soil system. For dynamic flow studies, the soil column is kept in a pressure chamber so that adsorption kinetics can be studied under unsaturated condition with a constant rate of flow through the soil sample. The rate of flow can be predetermined. It can be maintained at a constant level or may be varied.

Equilibrium isotherms were measured for a cation and an anion represented by cadmium and iodide. The experimental objectives were to evaluate the heat of adsorption as a function of the amount of ions adsorbed as well as to compare the adsorption isotherms obtained by the short soil column with those obtained by the conventional shaking batch method. The resulting isotherms for both cadmium and iodide could be expressed by the Freundlich isotherm of the form $S = a\gamma^c$, where S and γ are the amount of ions per gram of soil in the adsorbed and liquid phases, respectively and a and c are the characteristic constants. As a consequence, the heat of adsorption is described by a logarithmic function of the surface coverage, namely, $q = b_2 \ln(S/S_{max})$.

For iodide, the characteristic constants c obtained by the shaking batch were similar to those obtained by the short soil column. But the magnitudes of the characteristic constants a were three to six times higher when a short soil column procedure was used over

the entire range of concentrations used. For the cation cadmium, the constants c were quite different between the two procedures with the magnitude of adsorption distinctly greater in the short soil column. It was speculated that in the soil column where the structure of soil particles is maintained, ions in the pore solution are subjected to stronger potential field exerted by the soil particles, not only because of the presence of the surface charges but also by the presence of the soil mass as a whole. The translational freedom of the ions is lower in the environment of the soil column than in the shaking batch environment where there is excess solution in the soil system. We must conclude that results obtained by the shaking batch procedure are not representative of the adsorption process in a soil in its natural state and strongly recommend that the short soil column procedure be used for such studies.

The equilibrium studies also suggest that the theoretical expressions of isotherms might not be adequate to describe the adsorption process in the soil. In a soil system, the surfaces of soil particles are not 'clean' to start with but always contain various kinds of adsorbed ions. In order to be adsorbed, the introduced ions must exchange with these native ions. The competition between existing and newly introduced ions affects the energies of adsorption. Furthermore, ions are adsorbed in two regions, namely the diffuse layer and the Stern layer, each of which has a different level of energy.

Therefore, the isotherms can not be described by one smooth function over the entire range of adsorption. Discontinuities in the slopes of the isotherms over the range of S used in our studies can be explained by changes in adsorption energies.

Based on the assumption that for the adsorbing surfaces which obey the Freundlich isotherm, the activation energies of adsorption and desorption relate to the heat of adsorption in a linear fashion, we have determined the surface reaction process to be described by:

$$\frac{\partial S}{\partial t} = k_1 \zeta^b \left(\frac{\theta' C'}{\rho_b} \right) - k_2 \zeta^{-b} S. \quad (2-19)$$

It is recommended that before applying kinetic adsorption equations to studies of solute transport in soil, an equilibrium isotherm first be evaluated so that functions of energies of adsorption can be determined. Then a kinetic equation should be chosen which complies with the particular soil system being studied.

After the kinetic surface reaction equation (2-19) was established a lateral diffusion process was incorporated into the equation. The final expression for adsorption kinetics proposed in our study is

$$\rho_b \frac{\partial S}{\partial t} = \left[\frac{1}{1/K_d + 1/(k_1 \zeta^{-b})} \right] \theta C - \left[\frac{1}{(k_1 \zeta^{-2b}/k_2)(1/K_d) + 1/(k_2 \zeta^b)} \right] S. \quad (2-27)$$

Experiments were carried out to measure the kinetic adsorption of the cation cadmium for a static system and for a dynamic system employing three pore water velocities, namely, $\bar{v} = 1.3, 2.3$ and 2.7 cm/hr with water potential of about -0.126 bars or about 87% of saturation. The calculated values of the diffusive conductance K_d , showed an increase with increasing \bar{v} implying that at higher flow rates, the movement of ions towards the soil surface is enhanced due to a decrease in the thickness of the "subsurface" layer.

The magnitudes of K_d were calculated to be about 0.07 to $0.4 \times 10^{-3} \text{ sec}^{-1}$. These values are sufficiently low to indicate that diffusion across the subsurface layer is the rate limiting step. This is very important, especially when the adsorption is far from equilibrium. These results undeniably support our argument that lateral diffusion must be taken into account in the studies of the adsorption kinetics.

The ratio k_1/k_2 for the surface reaction also increased as a function of \bar{v} . Ion exchange is considered to proceed at a faster rate with solution flow through the soil sample. The continuous supply of solution serves as a continuous source for the introduced ions as well as an indefinite sink for the desorbed ions of other species which were present originally. Consequently, the accelerated rate of adsorption induced by flow regimes in the soil may be attributed to two factors. First, there is an increase in the diffusion process as more regions

of the soil solution become dynamic, i. e., the thickness of the subsurface layer decreases. Secondly, there is an increase in the rate of the kinetic surface reaction as the ion exchange process proceeds in the presence of the continuous sink.

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APPENDIX

APPENDIX

Properties of the Pope Ridge Soil

The Pope Ridge soil is developed from volcanic deposits and is classified as a Cindery Frigid Typic Vitradept. Samples were taken from the depth of 0-15 cm from soil surface. Location of sampling was near Ardenvoir, Washington, township 29 N, range 18E and section 14.

I. Physical Propertiesa. Particle Size Distribution

	<u>% of Total</u>
Sand	
Very coarse (2-1 mm)	2.75
Coarse (1-.5 mm)	5.03
Medium (.5-.25 mm)	4.26
Fine (.25-.10 mm)	20.24
Very fine (.10-0.05 mm)	<u>19.45</u>
Total sand	51.73
Silt	
Coarse (0.05-0.02 mm)	24.08
Fine (0.02-0.002 mm)	<u>21.94</u>
Total silt	46.02
Total clay	2.25

Texture: Sandy loam

b. Soil Water Characteristic Curve

Drying Curve. For the high water potential region ranging from 0 to 1/3 bars, the curve was generated using a soil column packed in the same manner as described in the studies of adsorption with a bulk density of 1.12 g soil/cm³. The soil sample was saturated for 24 hours, then water was extracted using the pressure chamber described in the adsorption studies. At lower water potentials, smaller samples of which bulk densities were not controlled were used in generating the curve by means of the pressure membrane apparatus.

Wetting Curve. The curve was obtained using a hanging water column technique with soil samples packed to a bulk density of 1.12 g soil/cm³.

The concept of Brooks and Corey (1966) on effective saturation, S_e , has been included in the results. The expression for S_e is

$$S_e = \frac{S - S_r}{1 - S_r},$$

where S is the degree of saturation, $S = \theta / (\theta \text{ at saturation})$ and S_r is the residual saturation which was chosen to be the water content at water potential of -15 bars for this study. Data about the soil water characteristic curves are listed in Table 3-1 and in Figure 3-1. The potential-water content relationship can be expressed in terms of the effective saturation as

Table 3-1. Water potential and the corresponding water content, θ_w , degree of saturation, S, and the effective saturation, S_e , of the Pope Ridge soil.

Water Potential <u>bar</u>	<u>cm water</u>	θ_w	S	S_e
<u>Drying Curve</u>				
0.0	0.0	.4727	1.000	1.000
0.05	51.7	.4342	.9186	.9062
0.10	103.4	.4260	.9012	.8861
0.123	125.1	.4211	.8908	.8742
0.136	138.5	.3897	.8244	.7976
0.153	156.1	.3625	.7669	.7314
0.213	217.1	.3055	.6463	.5924
0.337	344.5	.1950	.4125	.3230
1.0	1033.6	.1158	.2450	.1300
2.0	2067.2	.0894	.1891	.0656
5.0	5168.0	.0724	.1532	.0242
15.0	15504.0	.0625	.1322	.000
<u>Wetting Curve</u>				
0.049	50.0	.4294	.9084	.8944
0.098	100.0	.4054	.8576	.8359
0.107	110.0	.3451	.7301	.6890
0.117	120.0	.3465	.7330	.6923
0.128	130.0	.3166	.6698	.6195
0.147	150.0	.3110	.6579	.6058
0.196	200.0	.2605	.5511	.4827

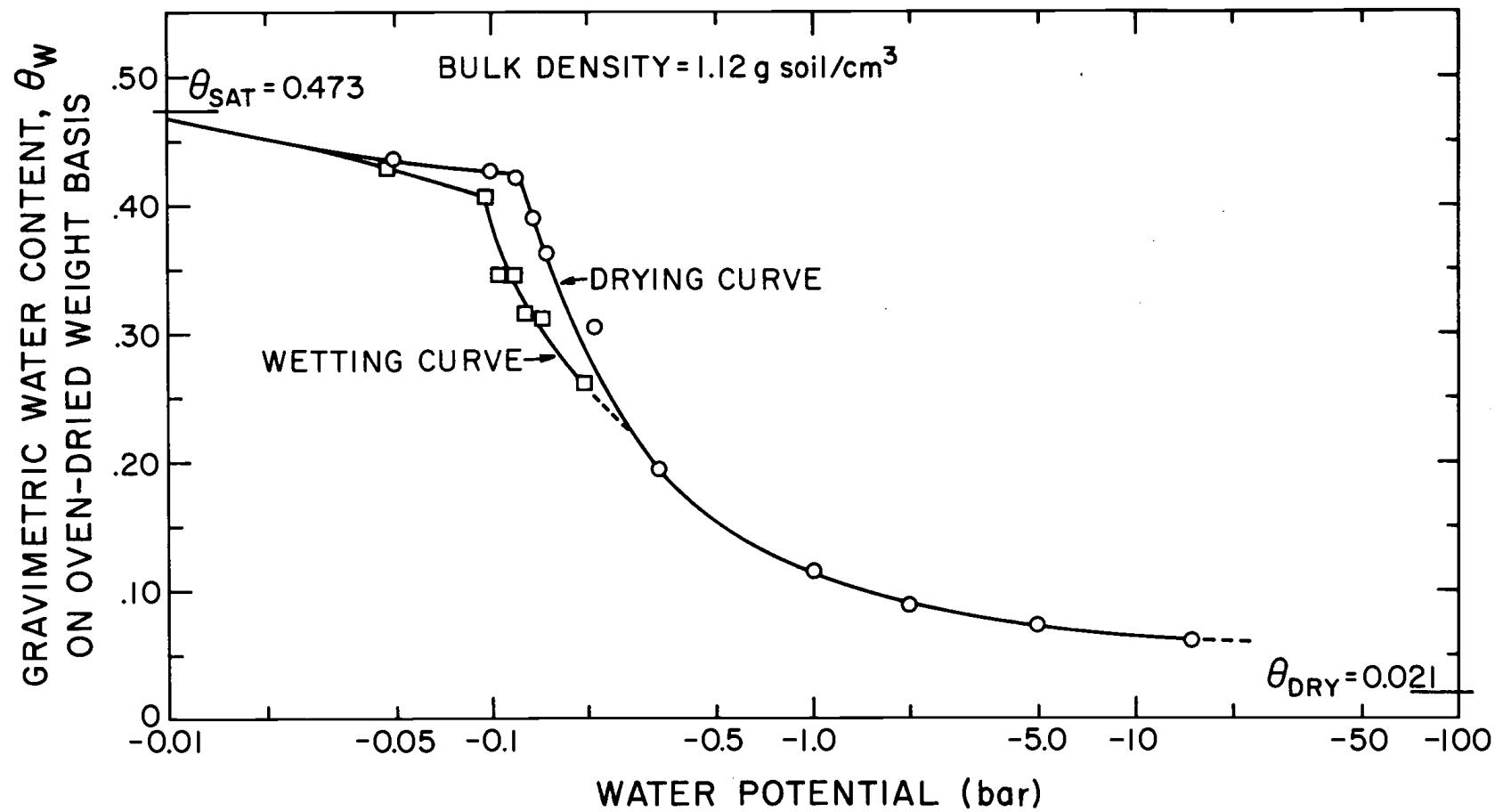


Figure 3-1. Soil water characteristic curve for the Pope Ridge soil.

$$S_e = \left(\frac{h_d}{h_c} \right)^\lambda$$

where h_d (cm) is the potential head at air-entry pressure and h_c (cm) is the water potential head. The parameters h_d and λ can be determined by plotting $(\log S_e)$ as a function of $(\log h_c)$ as shown in Figure 3-2, since

$$\log S_e = \lambda \log h_d - \lambda \log h_c$$

The slope of the line gives the value of λ , namely, the pore size distribution index, and the intercept at $S_e = 1.0$, gives the value of h_d . For the Pope Ridge soil, these values were

$$h_d = 107.7 \text{ cm of water}$$

and $\lambda = 0.9$

$$\text{or } S_e = \left(\frac{107.7}{h_c} \right)^{0.9}$$

A high value of λ indicates a poorly graded porous medium while a low value of λ indicates a well-graded sample. For typical porous media, λ is about 2. Soils with well-developed structure have values of λ less than 2 (Corey, 1977, p. 47). The low value of λ for our soil confirms the textural study that the soil is a very well-graded soil.

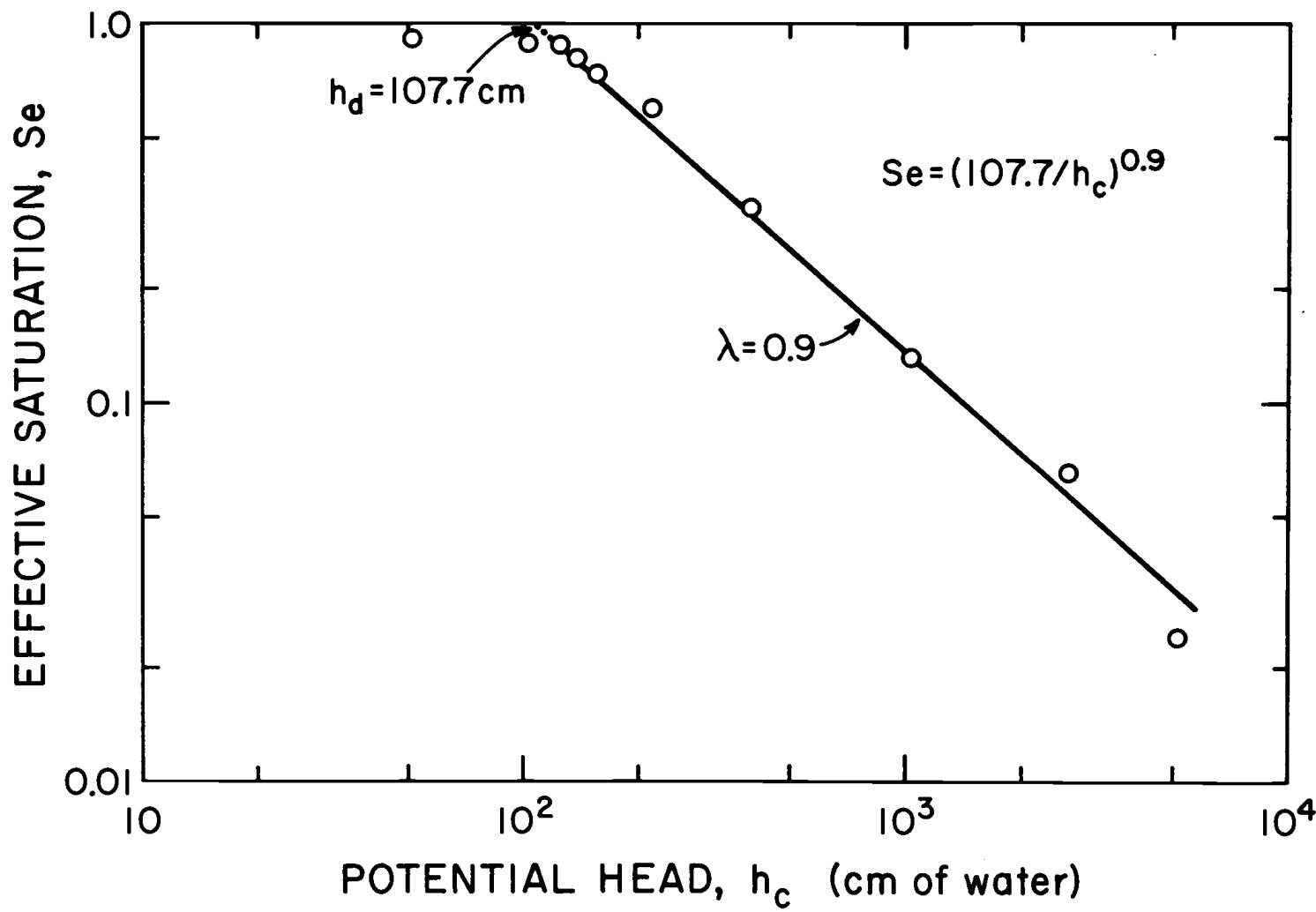


Figure 3-2. Effective saturation as a function of potential head.

c. Hydraulic Conductivity at Saturation

The measurement was obtained using a constant head permeameter. The value of $K(\theta_{sat})$ was 2.09 cm/hr.

II. Chemical Properties

Chemical properties were analyzed using procedures employed by the Soil Testing Laboratory at Oregon State University (Kauffman and Gardner, 1976). The results were listed in Table 3-2.

Table 3-2. Chemical analysis of the Pope Ridge soil.

pH	5.9
C. E. C. (meq/100 g soil)	7.43
Extractable base (meq/100 g soil)	
K	0.10
Ca	1.20
Mg	0.20
Na	0.12
Exchangeable Na (meq/100 g soil)	0.13
Salt conductivity (mmhos/cm)	<.10
Organic matter (%)	2.4
NO_3^- -N (ppm)	2.10
Total N (%)	0.05
$\text{SO}_4^{=}$ -S (ppm)	1.9
P (ppm)	14