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Kinetics and Energetics of Adsorption and Desorption

of Mineral Nutrients from Soil Minerals

A report on work completed
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Submitted by

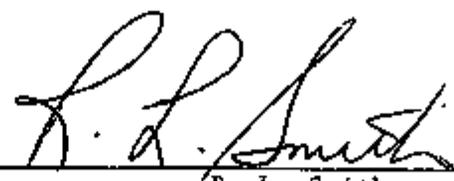Utah State University
and
Utah Agricultural Experiment Station

to the

United States Atomic Energy Commission

Approved:

March 9, 1970

Principal Investigator:

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INTRODUCTION

In principle, obtaining kinetic data of ion adsorption by mineral surfaces is simple. The procedure is to determine how the ion concentration in solution varies with time in the presence of a given amount of solid, holding the temperature of the system constant. However, usually the solid phase must be separated from the aqueous phase before the ion concentration is determined. This is usually done by removing the sample from the thermostat (water bath) centrifuging it in a temperature-controlled high speed centrifuge ($\pm 1^\circ C$) and analyzing the supernatant liquid. Because of the time involved and the lack of precision temperature control using the high speed centrifuge, accurate kinetic data, involving short reaction times, are precluded.

The past year was dedicated to a study of experimental techniques which would allow elimination of the centrifuge in adsorption kinetic studies. The feasibility of using a dialysis membrane bag to separate the solid from the aqueous solution was investigated. The membrane allows the free diffusion of ions in solution but restrains the solid phase with the bag. The aqueous solution can then be readily pipetted from a reaction flask and analyzed without removing the reaction flask from the water bath.

THEORY

The presence of the solid in a dialysis bag divides the total ion (adsorbate) concentration into 3 distinct regions: 2) the solution outside the dialysis bag, b) the solution within the dialysis bag, c) the

surface (adsorbed) phase of the solid. At equilibrium, the concentration in region A and B are equal however, prior to equilibrium the ion concentration can vary between regions A and B. The mechanism of adsorption of an ion from solution on a solid restrained in a dialysis bag is

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C$$
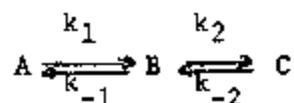
where A, B, and C represent the regions described above, k_1 and k_{-1} are the rate constants for diffusion in and out of the dialysis bag, and k_2 and k_{-2} is the rate constant of adsorption and desorption, respectively. If the concentration of the ion in question is a, b, and c in regions A, B, and C respectively, the kinetic equations are

$$1. - \frac{da}{dt} = k_1 a - k_{-1} b$$

$$2. \quad \frac{db}{dt} = k_1 a - k_{-1} b - k_2 c + k_{-2} c$$

$$3. \quad \frac{dc}{dt} = k_2 b - k_{-2} b$$

The solutions of equations (1), (2), and (3) are simplified if certain conditions exist. If the solid within the dialysis bag has a high capacity to adsorb the ion (infinite sink) then k_{-2} is not significant (desorption is limited). Further, the rate of adsorption can be regarded as a pseudo first order constant. An additional assumption is that $k_2 \gg k_1$, that is, the rate of adsorption is greater than the rate of diffusion, k_{-1} becomes negligible. The reaction now becomes

$$A \overset{k_1}{\longrightarrow} B \overset{k_2}{\longrightarrow} C$$
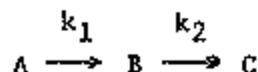
equations 1, 2, and 3 can be rewritten:

$$4. \quad -\frac{da}{dt} = k_1 a$$

$$5. \quad \frac{db}{dt} = k_1 a - k_2 b$$

$$6. \quad \frac{dc}{dt} = k_2 b$$

Although adsorption is usually regarded as a 2nd order reaction, if the adsorption site concentration is much greater than the ion concentration k_2 (equation 6) is pseudo first order.

The solution of equations (4), (5), and (6) is:

$$7. \quad a = a_0 \exp - k_1 t$$

$$8. \quad b = \frac{k_1 a_0}{k_2 - k_1}[(\exp - k_1 t) - (\exp - k_2 t)]$$

$$9. \quad c = \frac{a_0}{k_2 - k_1}[k_2 \, (1 - \exp - k_1 t) - k_1 \, (1 - \exp - k_2 t)]$$

where a_0 = concentration of the ion in region A at $t = 0$. If $k_2 \gg k_1$, i.e., the rate of adsorption is much greater than the rate of diffusion across the membrane, then concentration b is much smaller than concentration a except at equilibrium when $a = b$. Also, the concentration b is much smaller than concentration c if the solid is an infinite sink for the ion. It is assumed that relative to a and c, concentration b is in a steady state over much of the reaction period, thus:

$$\frac{db}{dt} = 0 = k_1 a - k_2 b$$

$$10. \quad \text{or, } k_1 a = k_2 b$$

$$11. \quad k_2 = \frac{1}{b}(k_1 a) = \frac{1}{b}(-\frac{da}{dt}) \quad \text{from equation 4}$$

Substituting   equation 10 in equations (4) and (6) gives

$$12. \quad a = a_o \exp - k_1 t$$

$$13. \quad c = a_o - a_o \exp - k_1 t$$

During a kinetic study only concentration "a" is measured. In this study concentration "a" refers to the concentration of phosphate in solution outside of the dialysis bag (region A). Phosphate will be referred to by the symbol P.

EXPERIMENTAL PROCEDURE

The ion used in the kinetic study was $H_2PO_4^-$ and standard cellophane dialysis membrane was used to make the dialysis bags. Phosphate did not react with the membrane material. In all experiments the initial concentration of phosphate was 75 ppm as KH_2PO_4 at pH 7. The temperature was maintained at $25 \pm 0.1°C$. Phosphate in solution was analysed by the method of Murphy and Riley (1).

Resin Study: 0.5g of Cl-saturated Dowex anion exchange resin was placed in a dialysis bag and 10 ml of distilled water was added. The bag was secured and put into 40 ml of K_2HPO_4 solution which was held in a 125 ml Erlenmeyer flask and the flask shaken. The change in phosphate concentration was measured as a function of time. The resin has an anion exchange capacity of 1.3 meq/g.

Soil study: In this study, Aiken clay loam was used as the sink for phosphate. This is a soil with a high phosphate fixing capacity. Three different amounts of soil was used: 0.5 g, 2.5 g, and 5.0 g. The procedure was the same as that used in the resin system.

RESULTS AND DISCUSSION

Figures 1, 2, and 3 show the experimental data where the decrease in $H_2PO_4^-$ concentration in solution (concentration a) is plotted vs time in minutes. Figures 4, 5, and 6 are the data from figures 1, 2, and 3 plotted kinetically to determine the rate constants in question.

Figures 1 and 4 show how the presence of an infinite sink for phosphate (the resin) within the dialysis bag affects the diffusion of phosphate across the membrane. Figure 4 shows that diffusion across the membrane is the rate determining step in the adsorption of phosphate by the resin. In the presence of a phosphate sink k_{-1} is not significant. The measured k_1 of diffusion across the membrane is 3.2×10^{-5} sec^{-1}. In the absence of a sink in the dialysis bag, k_{-1} becomes important after 60 minutes and the rate of diffusion is greatly reduced.

Figures 2 and 5 show the adsorption of phosphate by the anion resin placed in the dialysis bag and the adsorption by the resin when the dialysis bag is removed. In the absence of the membrane, k_2 was determined as 1.2×10^{-3} sec^{-1} which is a factor of about 40 times the rate of diffusion of phosphate through the dialysis bag ($k_1 = 3.2 \times 10^{-5}$). Of interest is the fact that when the phosphate concentration is lowered to about 20 ppm in solution the rate of adsorption by the resin is independent of whether or not the anion resin is in the dialysis bag (see figure 5). These data suggest that after the accessable sites are filled in the anion resin, simple diffusion into the resin particle is the rate determining step. Since the rate constants are identical, it also corroborates the view that simple diffusion is operating when phosphate moves through the dialysis membrane. The high value of k_2

also indicates that solution b, within the dialysis bag, should be almost void of solution phosphate during the initial phases of the reaction. Figure 5 further supports the contention that the adsorption process acts as a pseudo first order reaction when the adsorptive capacity of a solid for an ion is much greater than the ion concentration in the system.

Figures 3 and 6 show the decrease in phosphate concentration in solution when various amounts of soil are added to the dialysis bag. The reference line drawn in figure 6 is the rate constant plot when the anion resin forms the sink for phosphate in the dialysis bag. The conclusion drawn from these data is again diffusion of phosphate through the membrane is the rate determining step in the adsorption of phosphate by the soil. Further, the more soil in the system the more closely it approximates an infinite sink for phosphate, using the anion resin as the reference sink.

Figure 7 shows a composite of data for the adsorption of P by both 0.5 g anion resin and 5.0 g of soil (data from figures 1 and 3) expressed as ppm P adsorbed vs time for both the resin and soil when placed in the dialysis bag. Figure 7 suggests that P adsorption vs time can be approximated by a straight line of slope 1.85×10^{-3} ppm P/sec. By using this value in equation 11, and assuming k_2 is in the order of 1.2×10^{-3} sec^{-1}, the steady state value (b) of P in the dialysis bag is about 1.5 ppm P.

Figure 8 shows how k_1 varies with temperature in a simple diffusion experiment, where 40 ppm P is placed inside the dialysis bag and the rate at which it diffuses out of the bag measured at 15°, 25°, and 35° C. The calculated activation energy of solution, using the Arrenhius equation is 3.1 k cal/mole. The magnitude of this activation energy indicates only diffusion is important in the movement of phosphate through the

membrane. The activation energy Ea was determined by the equation

$$\log \frac{(k_1)_{T_1}}{(k_1)_{T_2}} = \frac{E_a}{2.3} \cdot \frac{T_2 - T_1}{T_2 T_1}$$

where $(k_1)_{T_1}$ and $(k_1)_{T_2}$ are the rate constants at T_2 and T_1, respectively.

The data from the studies which were described suggest that the use of a dialysis bag in a kinetic study of adsorption is not feasible. Even with the presence of an infinite sink for phosphate within the dialysis bag, the rate of movement of phosphate through the membrane was constant. The rate limiting step in adsorption is the rate of diffusion through the membrane. The dialysis bag can be used for equilibrium adsorption studies.

REFERENCE

1) Murphy, J. and J. P. Riley. 1962. Anal. Chim. Acta. 27:31.
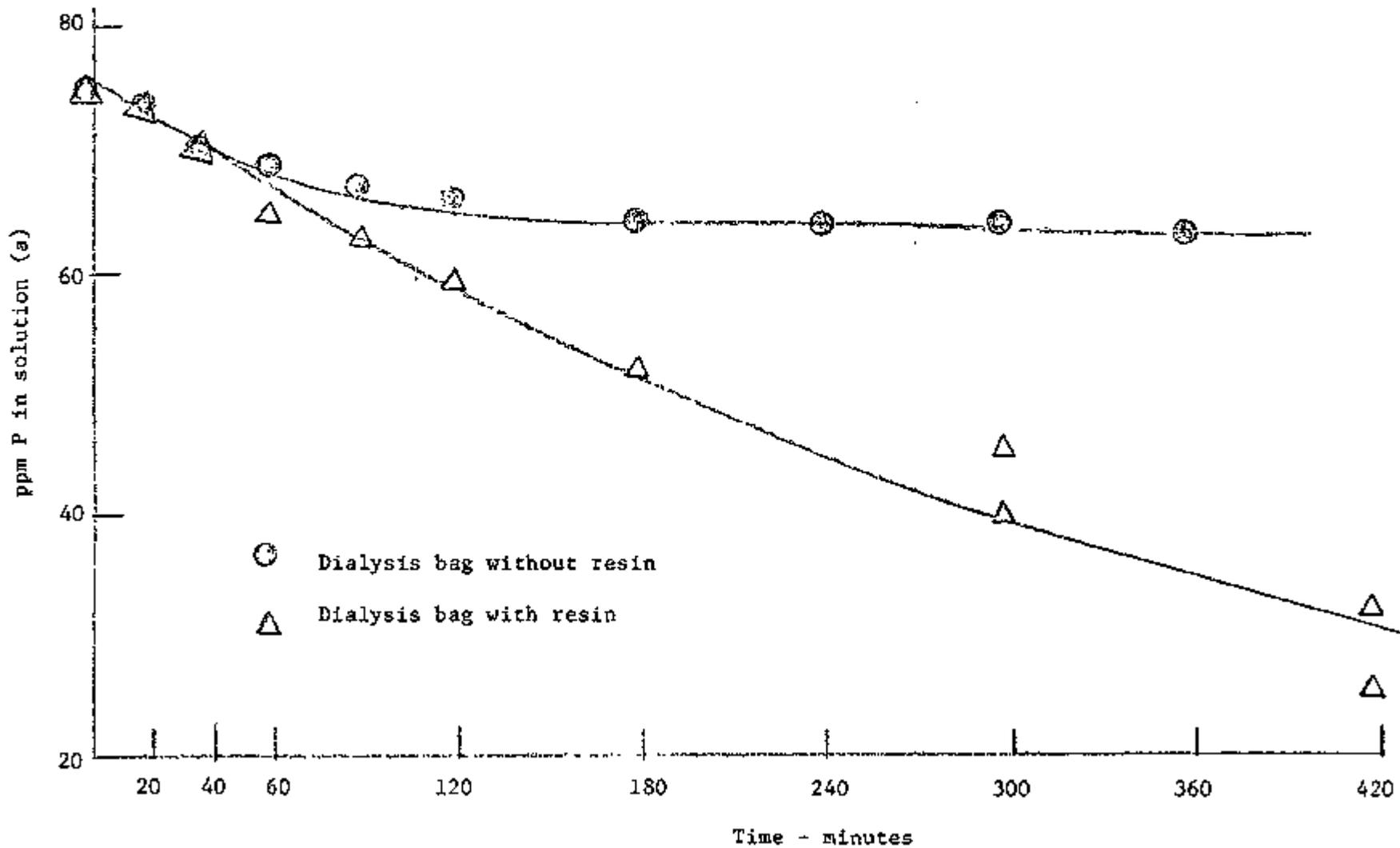
Figure 1. Diffusion of Phosphate into the Dialysis Bag
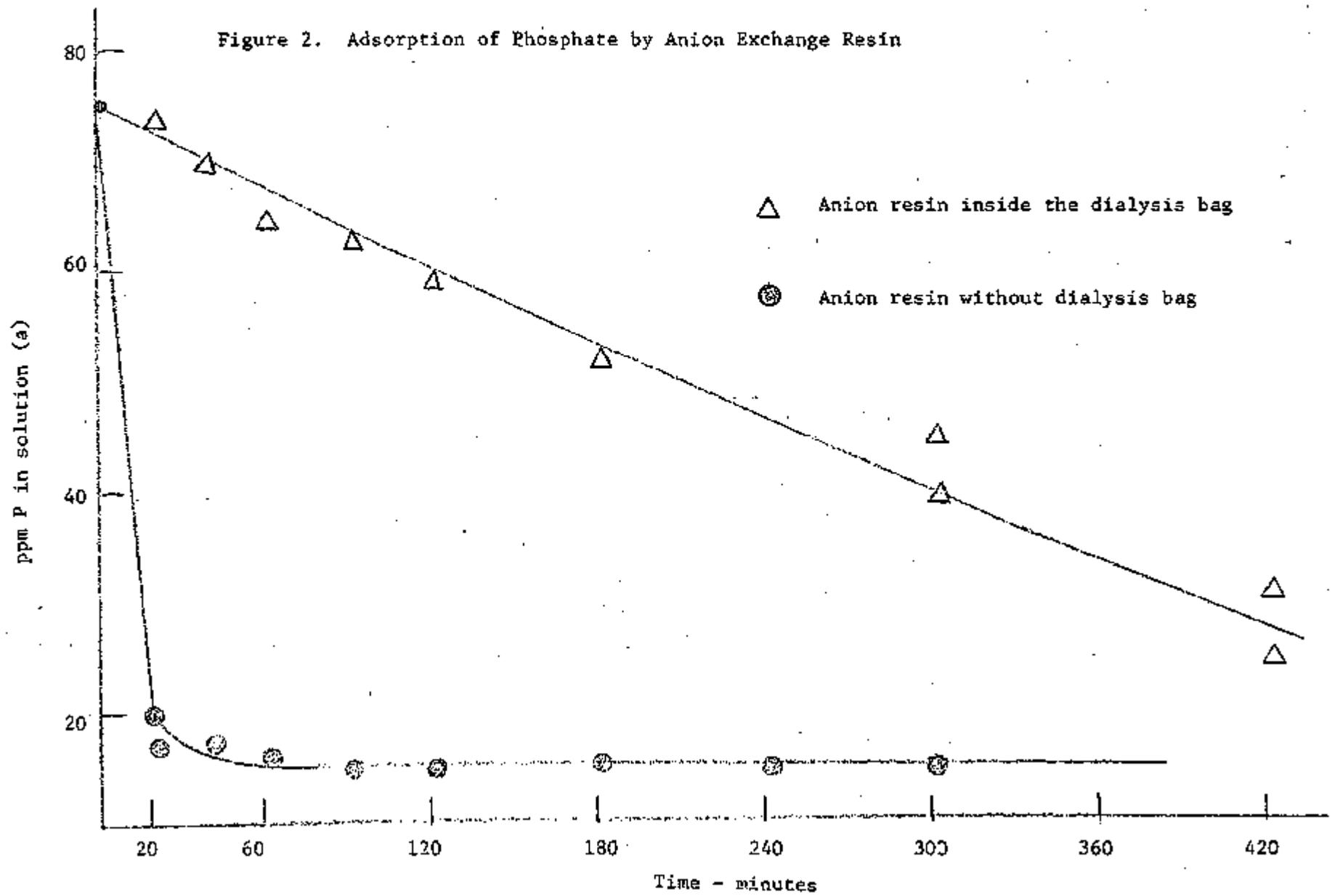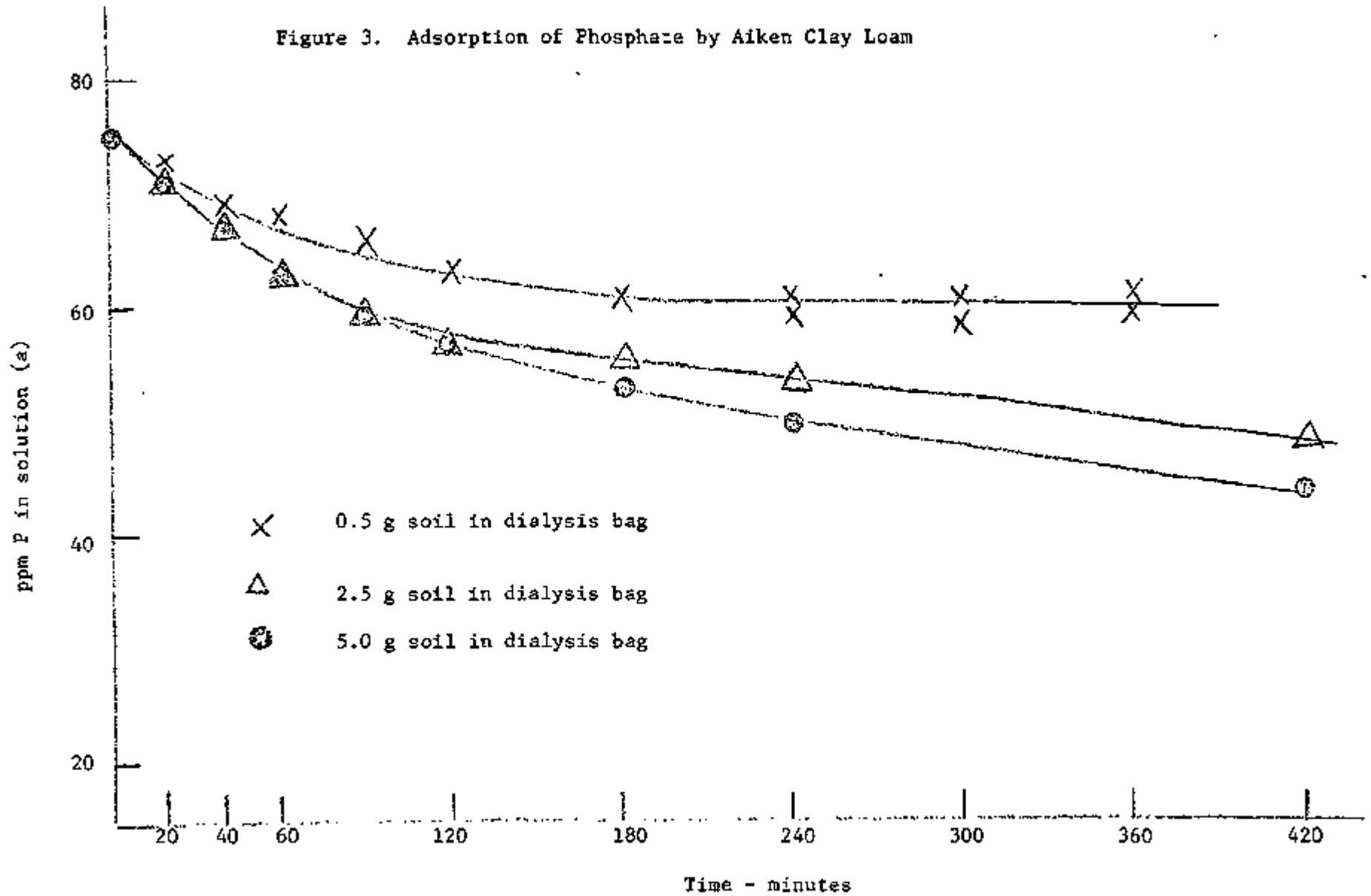
Figure 2. Adsorption of Phosphate by Anion Exchange Resin

△ Anion resin inside the dialysis bag

⊚ Anion resin without dialysis bag

Figure 3.   Adsorption of Phosphate by Aiken Clay Loam

Figure 4. Diffusion of Phosphate into the Dialysis Bag

$k_1 = 3.2 \times 10^{-5} \text{sec}^{-1}$
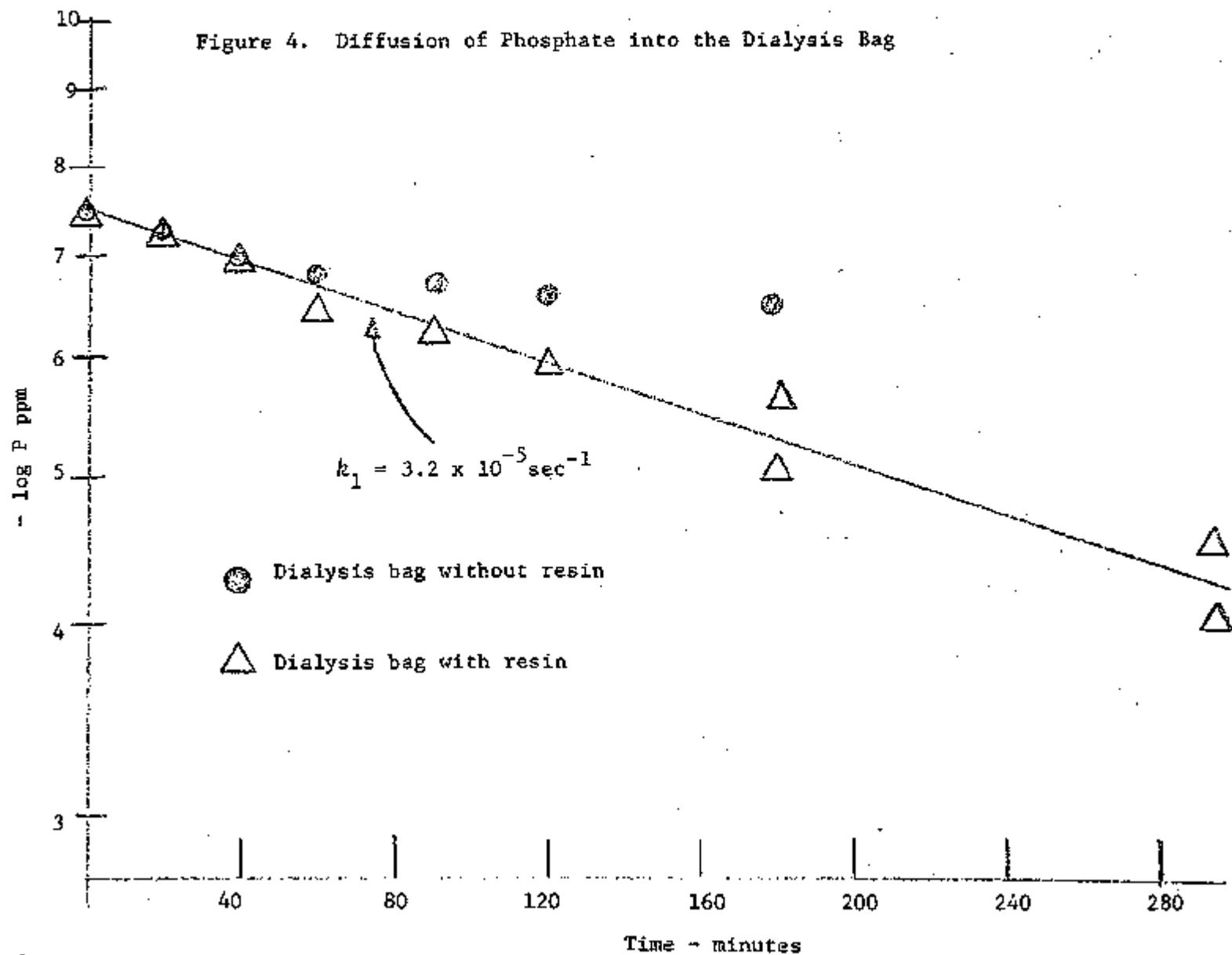
⊙ Dialysis bag without resin

△ Dialysis bag with resin

- log P ppm

Time - minutes

Figure 5. Adsorption of Phosphate by Anion Exchange Resin

$k_1 = 3.2 \times 10^{-5} \text{sec}^{-1}$

$k_2 = 1.2 \times 10^{-3} \text{sec}^{-1}$

- log P ppm

Time - minutes

⊕ Anion resin without dialysis bag

△ Anion resin inside of dialysis bag
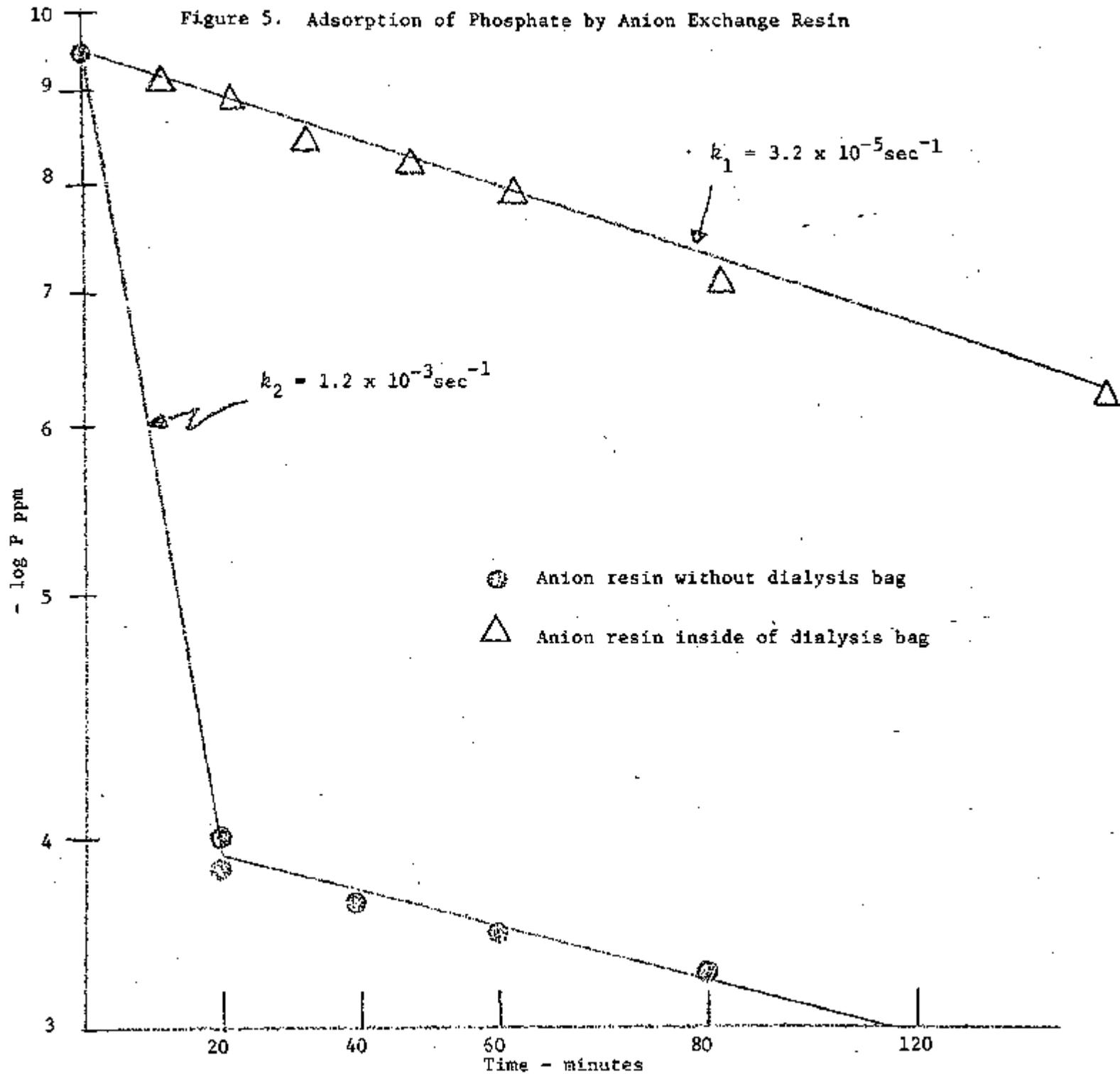
Figure 6. Adsorption of Phosphate by Aiken Clay Loam

$k_1 = 3.2 \times 10^{-5} sec^{-1}$

✕   0.5 g soil in dialysis bag

△   2.5 g soil in dialysis bag

⊙   5.0 g soil in dialysis bag
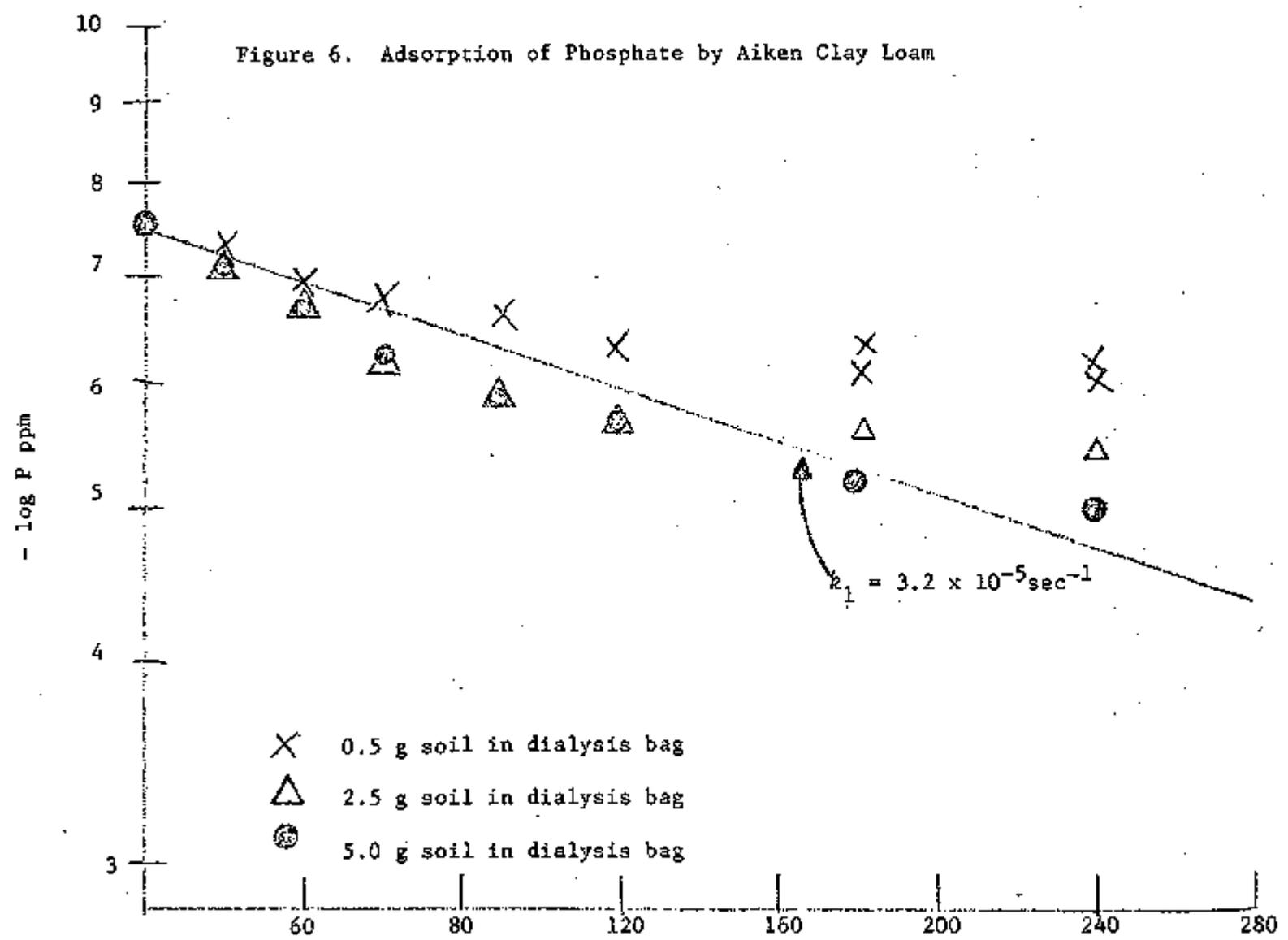
Figure 7. Adsorption of Phosphate by Soil and Resin
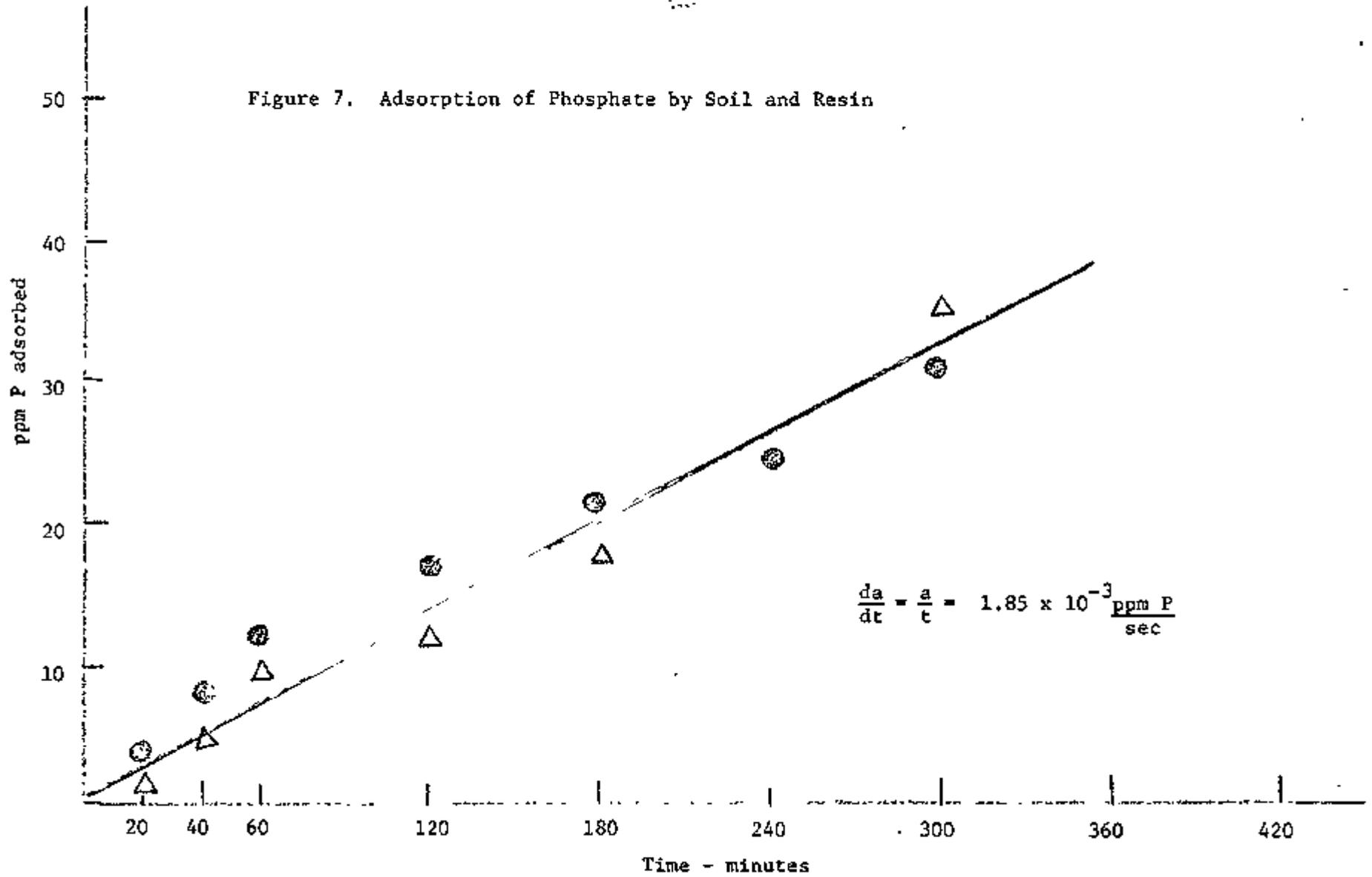
$$\frac{da}{dt} = \frac{a}{t} = 1.85 \times 10^{-3} \frac{ppm\ P}{sec}$$

Time − minutes

Figure 8. Variation of k_1 with Temperature