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MECHANISMS OF TRANSPORT OF COPPER, CADMIUM
AND CHROMIUM IN SOILS

PRINCIPAL INVESTIGATORS

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II. RESEARCH

A. COPPER SPECIES IN AQUEOUS SEWAGE SLUDGE EXTRACT

ABSTRACT

The copper in the saturation extract of dried Davis sewage sludge was mainly in a complexed form. A Cu^{2+} specific ion electrode was used to determine the extent of complexation. Adsorption experiments showed that the Kd value for complexed Cu on Yolo soil was 4.0 while Cu added as CuSO_4 had a Kd value of 90 cc g^{-1} . Paper electrophoresis was used to define the complexes according to their mobility in an electric field. Six fractions of positive, negative and neutral charge were isolated. The fraction of Cu in the sludge which was water soluble was found to increase significantly upon drying. The low Kd values on soil and the large percentage of complexed Cu suggested that sewage sludge may be a potential source of contamination of water and plant systems.

It is often assumed that soil is a good filter for copper and other trace metals (e.g. Page, 1974) so that as a rule a small likelihood exists for contamination of plants or ground water with Cu from sludge or sewage application to soils. This conclusion is based on adsorption of inorganic Cu on soils and soil constituents. Cationic copper adsorption in soils is reported to be very strong with applied Cu retained in the surface layer of soils (Sidle and Kardos, 1977; Wentink and Etzel, 1972; Beavington, 1973).

Concentrations of more than 0.1 ppm Cu in solutions can be toxic to plants (Baker, 1974) yet much higher levels in the water extract of sludges are sometimes observed (Bradford et al., 1974). The speciation of Cu in sludge extracts may change with time (Lagerwerff et al., 1976), and the equilibrium solution concentration should vary with it.

The purpose of this paper is to demonstrate that the amount of soluble Cu in sludge may vary greatly with time and that the soluble Cu may exist as a mixture of complexes which are not strongly adsorbed to soil. The relatively free movement of soluble heavy metals derived from secondary effluent has been recently reported. Such mobile forms may contaminate both water and crops. Hodgson et al. (1965) demonstrated that copper in soil solution is mostly in complexed forms and, therefore, the nature and interactions of complexed copper species in soil may be of great interest.

Lagerwerff and coworkers (1976) classified the soluble complexes of heavy metals present in sewage sludge according to their charge by using a series of exchange resins. In the present work, an electrophoresis technique was used to classify complexes by their mobility in an electric field. Thus, a more detailed separation is possible as compared

to the use of exchange resins. A Cu^{2+} selective ion electrode was used to indicate the presence of Cu^{2+} and thus, of complexed Cu by difference. Adsorption on a Yolo Si 1 of Cu added as CuSO_4 and of Cu in a sludge extract was studied to infer the effect of Cu complexation on mobility in soil.

MATERIALS AND METHODS

Materials: Standards of Cu(II) and Cd(II) were prepared from CuSO_4 and CdNO_3 solution in deionized water respectively. Sewage sludges were taken from the Davis, California Municipal Water Treatment Plant. Raw sludge, digested sludge, as well as samples of sludge dried for two and for 12 months in a pond were examined. The sewage did not undergo any treatment during its processing other than sludge activation, biological incubation and the precipitation and drying of the sludge. Specifically, no chemical treatment took place. Samples of 10 liters of the raw and activated sludge and 10 lb of the dried sludges were taken. Four subsamples of each of the dried sludge samples were analyzed separately. The fresh sludges (raw and activated) were analyzed within a few hours of sampling, and the dry sludges were stored at room temperature until they were analyzed. The soil used for adsorption was Yolo silt loam crushed to pass through a 2-mm sieve. The CEC of the soil is 18.9 meq/100 g and the pH of the soil paste was 6.8.

Saturation extracts of the dried sludge in deionized water were obtained. The pastes were allowed to stand for 24 hours, then filtered through No. 2 Whatman filter paper and a 45μ millipore filter. The raw and digested wet sludges were filtered without drying.

Adsorption Data: Adsorption was determined by a batch procedure. Air-dried Yolo soil was shaken for 20 hours with the extract of the sludge dried for 12 months at 1:4 soil-extract ratios. Concentrations of 1 and 2 ppm of Cu as CuSO_4 in deionized water were also shaken with separate samples of Yolo soil. These concentrations were chosen to correspond to the range of copper concentration in the extract of the sludge dried for 12 months. It was ascertained that 20 hours is sufficient to reach equilibrium.

Electrophoresis Measurements: Portions of 0.06 ml of the saturation extract of the sludge dried for 12 months and standard CuSO_4 solutions in deionized water were applied to strips of Whatman 3-mm paper and electrophoresed at 50 mA and 350 V for various intervals up to seven hours. The electrolyte solution was .05 M NaNO_3 .

After electrophoresis, the paper strips were air dried, cut into 1/4-inch strips, and dissolved in a $\text{HNO}_3:\text{H}_2\text{SO}_4:\text{HClO}_4$ 3:1:1 acid mixture at 65°C. The Cu content in the 1/4 inch-strips was then determined by flameless atomic adsorption. The conditions under which Cu determinations were made are: 10 μl sample was injected, dried for 110 seconds at 120°C, ashed for 90 seconds at 650°C and atomized for five seconds at 2700°C in the maximum power mode (high ramp rate) in an N_2 stream.

Electrophoresis runs were made on both the 12-month old sludge saturation extract and on the same extract concentrated ten times by freeze-drying.

Apparatus: Soluble copper and Cd determinations were made on the Perkin-Elmer 403 Atomic Adsorption Spectrophotometer with an HG 2200 graphite furnace and Cu^{2+} was determined with an Orion research cupric ion electrode model 94-29. Electrophoresis was run on the Beckman Model R paper electrophoresis system.

RESULTS AND DISCUSSION

Table 1 gives the soluble Cu found in the sludge in its various stages of processing. For comparison, soluble cadmium is presented in Table 1 as well. The outstanding feature here is the appreciable change in the amount of soluble copper with time of drying. This implies that applying sludge to soil at a given stage may not release Cu immediately, but much more copper may be eventually released. A drought prevailed during the 12 months the sludge was dried in the pond. Subsequently, the pond in which the sludge was dried was exposed to three weeks of heavy rains following which the Cu in the saturation extract was only 70-80 ppb (Table 1). This could possibly indicate leaching of soluble Cu into the soil below the pond, although factors such as microbial immobilization may also play a role. The data in Table 1 suggests that the amount of soluble Cu in sludge varies continuously with time in agreement with Lagerwerff *et al.* (1976) so that long-term release of Cu from applied sludge may be far greater than previously assumed (Page, 1974, p. 81). The data presented in Table 1 suggests that the amount of soluble cadmium released does also change with time but to a lesser extent than copper. Marked changes in the speciation (as distinguished from the concentration) of Cu in the sludge extract after incubation for 13 months at 5°C was reported by Lagerwerff and coworkers (1976).

The extract of the sludge dried for 12 months had an electric conductivity of 7.1 mmhos and a pH of 8. On the basis of solubility equilibrium, precipitation of Cu(OH) would maintain extremely low Cu²⁺ levels in solution (around 3×10^{-8} M) if Cu(OH)₂ controlled the Cu²⁺ activity. Free Cu²⁺ concentration could be even lower if some other

species controlled it. Yet soluble Cu levels greatly exceeded Cu^{2+} concentrations in equilibrium with the existing pH. The Cu concentration in the above extract (Table 1) is higher than the tolerance level for many crops which is around 0.1 ppm (Baker, 1974). Accordingly, by means of the Cu^{2+} ion selective electrode it was found that more than 99% of the Cu was in a form other than free Cu^{2+} , as the electrode measurements indicated less than 10 ppb free Cu^{2+} in the extract. It is not possible that the Cu in the extract is in the free cuprous ion form. This is due to the fact that the redox potential of the $\text{Cu}^+ \rightarrow \text{Cu}$ reaction is higher than that of the $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reaction. Yet, Cu(I) complexes may be present. The Cu in the extract is thus predominantly in a complexed form. This emphasizes the fact that predictions of trace metal concentrations in aqueous systems based on the solubilities of the inorganic salts of the trace cations, such as were made in the past for various heavy metals, may sometimes be erroneous (Hem, 1972). This is certainly true when complexed cations are introduced to the system, but complexation reactions may also affect the copper behavior in soils and aqueous systems to which inorganic forms were originally introduced.

The adsorption results indicate that the complexed Cu is retained far less by the soil as compared with Cu added as CuSO_4 . The extent of adsorption was defined by the distribution coefficient between the solid and aqueous phases (K_d) which was calculated from the difference in solution concentration of copper before and after equilibration with the soil. The distribution coefficients were 4 and 90 cc/g for the Cu in the extract of the sludge dried 12 months and Cu added as CuSO_4 , respectively. Complexation may, therefore, increase the water soluble fraction of copper in sludge as well as the mobility of this fraction in soil and be a potential hazard to both crops and ground water.

The velocity of the motion of charged species in an electric field which was measured in the electrophoretic runs is a function of the ratio of the ion's charge to its apparent radius. The actual velocity (or mobility which is velocity per unit electric field) will depend on factors such as the ion's shape, interaction of the ion with the paper (adsorption), and the ionic strength of the solution. Thus ionic charges cannot be easily determined, but the direction of the movement under the electric field will give the sign of the ionic charge. The procedure will also allow separation and isolation of the various copper species and even their identification if a standard were available.

In the electrophoresis of the saturation extract of the 12 month dry sludge, six peaks were observed. One large peak of mobility zero, two peaks of positive charge and three peaks of negative charge were detected. Table 2 lists the velocities and the amounts of Cu found in the different peaks observed in the electrophoresis runs of an extract of the sludge dried for 12 months.

Since complicated solubility and complexation equilibria control the copper speciation in solution, concentration and dilution will affect that speciation. Soil wetting and drying are rather common, and therefore simulating the effect of the drying process on Cu speciation by concentrating the extract was attempted. Thus, the saturation extract of the sludge dried for 12 months was concentrated tenfold by freeze-drying. As a result, about half of the soluble Cu precipitated, and upon electrophoresis, four significant peaks were observed; one at zero mobility, and three with positive charge (Table 2). This is very different from the situation in the unconcentrated saturation extract and it points out the complexity of the speciation of Cu and most

likely other heavy metals in the natural aqueous environment. Figure 1 presents an actual electrophoretic run of the concentrated extract of the sludge dried for 12 months.

The experimental error in quantifying the Cu in the electrophoresis peaks was \pm 15%. Since the distance traveled along the paper strip was determined only within sections 1/4-inch wide, the resolution in velocity is only 1/4 inch divided by the duration of the electrophoretic run. Thus, peaks 2 and 3 of the saturation extract concentrated 10 times (Table 2 and Fig. 1) may actually represent one peak. The recovery of the Cu in the peaks was over 80% of the total copper in the extract. Much of the rest of the copper appeared as background between the major peaks and may consist of peak tails or very small peaks (Fig. 1).

Cu²⁺ exhibited a wide peak in electrophoresis typical to species strongly adsorbed to the paper (Block et al., 1958). It also exhibited a low velocity (peak maximum below 1 cm/hr) again indicating adsorption. Clearly, as expected, both the concentrated and the original saturation extracts did not contain detectable quantities of Cu²⁺.

When sludge is applied to the soil, copper in soil solution may exceed the concentrations toxic to plants or allowed for drinking water (EPA, 1973). Sludges often contain large quantities of heavy metals and even though only small fractions of these heavy metals are maintained in solution, the amounts may exceed the tolerance levels of plants to these metals (Bradford et al., 1975). The low adsorption of complexed Cu (as demonstrated in this work) and of a number of heavy metals found in secondary effluent³ suggests that under some conditions heavy metals may be released from sludge to soil solution and pose an ecological and health hazard even if the released fraction of the total heavy metal

content in the sludge is small. Typical values of total Cu in sludge are in the hundreds of $\mu\text{g/g}$ dry matter and the water extractable fractions are generally up to 2% (e.g. Page, 1974 and Lagerwerff et al., 1976). The often made assumption that the soil is a good filter for heavy metals, which is based on studies on inorganic species of such metals, may not hold in many cases due to the complexation of the heavy metals. This should be taken into consideration in the use of sludge and effluent in agriculture. The continuing change in speciation due, for example, to microbial activity, wetting and drying cycles, and temperature fluctuations makes it difficult to make predictions based on isolated or short-term studies, such as this. In view of the findings of this and previous studies, a model for the equilibrium adsorption of multi-speciated metals such as the soluble copper in the sludge extracts investigated in this study was developed (in preparation). This work is a step towards predicting availability and mobility of soluble heavy metals derived from sludge added to soils.

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LIST OF FIGURES

Figure 1: Copper content found in one quarter-inch segments of the paper strip when the saturation extract of dry Davis sewage sludge was freeze-dried to 10% of its original volume and paper electrophoresed. Each vertical line represents the copper content after electrophoresis for two hours and only segments which included 0.5% or more of the total Cu are presented.

Table 1: Soluble Cd and Cu in Davis sludge at different stages of processing

Processing stage	Concentration ($\mu\text{g}/\ell$)	
	Cd	Cu
Raw sludge	~ 1	~ 10
Digested sludge	not determined	100-200
Saturation extract of sludge dried for 2 months	~ 1	~ 10
Saturation extract of sludge dried for 12 months	~ 5	1000-2000
Saturation extract of sludge dried for 12 months and leached by heavy rains	not determined	70-80

B. A GENERAL MODEL FOR THE ADSORPTION OF TRACE METALS

ABSTRACT

The speciation of heavy metals in solution in the environment may be very complex. An equation for adsorption of a multispeciated metal which takes into consideration both exchange and physical and chemical adsorption is proposed. A comparison of the model with experimental data is also presented.

It has long been recognized that heavy metals often exist in aqueous solutions in the environment as complexes (e.g., Stiff, 1971; Wolfberg, 1978; Hodgson et al., 1965). It was demonstrated that metals often exist as a mixture of a number of species (Mingelgrin et al., 1978; Lagerwerff et al., 1976). In order to enable predictions regarding the behavior of the metals in soil and aquatic environments, an adsorption equation is needed. A number of attempts were made to describe the adsorption of heavy metals by assuming a Langmuir (Langmuir, 1918) or Freundlich adsorption (Freundlich, 1922) or by assuming pure exchange, sometimes on a number of different sites, using the Rothmund Kornfeld equation (Rothmund and Kornfeld, 1918; Harmsen 1977) or a Gapon equation (Lagerwerff and Bower, 1972). When an inorganic heavy metal salt was added to a soil suspension (e.g., Lagerwerff and Bower, 1972; Blom, 1974) exchange interactions may dominate. In the case of natural systems the situation is more complicated due to the possible presence of negative and neutral complexes. Attempts to describe trace metal adsorption by a single Langmuir equation often failed (e.g., Shuman, 1975) and the neglect of exchange adsorption was taken as the reason for this (Harter and Baker, 1977). The form of the adsorption equation for a heavy metal in a natural system is not immediately obvious because of the possible presence of different metal species, each exhibiting different exchange and/or nonexchange adsorption behavior. The present paper proposes such an equation, outlines its derivation and discusses its applicability.

MATERIALS AND METHODS

A solution of 1.5 ppm EDTA together with 1.5 ppm NTA in dionized water was prepared. To it, various concentrations of CdCl_2 were added. The range of Cd concentrations was between 3-1000 ppb. The solutions

were shaken with Yolo silt loam that had been passed through a 2 mm sieve. It was ascertained that adsorption equilibrium was attained after 24 hours when the soil to water ratio was 1:4. A Cd selective electrode (Orion 94-48) was used to establish the extent of complexation of the Cd. Flameless atomic adsorption (Varian Techtron 1150/1250) was used to determine the total Cd concentration in the solution.

The adsorption data thus obtained as well as data from the literature was used to test the adsorption model.

THE ADSORPTION MODEL

Every species of the metal in solutions can undergo either an exchange or a nonexchange adsorption, or both, where the term exchange in this paper refers to cation exchange. The exchange reaction of every individual species may be described by the Gapon equation:

$$\bar{A}_2 = K_2 \left| \frac{(A)}{(B)} \right|^{1/k} \bar{B} \text{ where } K > 0 \quad (1)$$

\bar{A}_2 is the quantity of species A adsorbed by cation exchange. \bar{B} is the quantity of a major exchangeable cation adsorbed. B is assumed to be of the same valence as A. K_2 is the Gapon selectivity coefficient and k is the valence of A. The quantities in parentheses are the concentrations of species A and B in solution. If A and B are not of the same valence, $\left| \frac{(A)}{(B)} \right|^{1/k}$ is replaced by $\frac{(A)^{1/ka}}{(B)^{1/kb}}$ where ka and kb are the valences of species A and B, respectively.

The nonexchange adsorption of any species is assumed to be of the Langmuir form. That is

$$\bar{A}_1 = \frac{k_1(A)}{K_1 + (A)} \quad (2)$$

where \bar{A}_1 is the amount of species A_1 adsorbed without exchange and k_1 and K_1 are constants. The assumption of a Langmuir adsorption term for the nonexchange adsorption of one species is especially good at the low concentrations of the trace metals which exist in soils and natural waters.

If different exchange sites are simultaneously important, equation (1) still holds if $\bar{B}_j \gg \bar{A}_j$, where the subscript j represents the j 's adsorption site. In this case

$$\bar{A}_2 = \sum_j K_j \left| \frac{(A)}{(B)} \right|^{1/k} \bar{B}_j = \left| \frac{(A)}{(B)} \right|^{1/k} \sum_j K_j \bar{B}_j \quad (3)$$

Since $\bar{B}_j \gg \bar{A}_j$ at all (A) of interest, $\sum_j K_j \bar{B}_j$ is a constant and

$$\bar{A}_2 = K_2 \left| \frac{(A)}{(B)} \right|^{1/k} \bar{B} \quad (4)$$

where \bar{B} , the total amount of B adsorbed, is also a constant. Since in general $\bar{B}_j \gg \bar{A}_j$ for trace metals, where B is often Na, Ca or Mg, equation (4) holds with $K_2 = \sum_j K_j \bar{B}_j / \bar{B}$. Note that in general due to the low trace metal concentrations in natural systems, (B) and all \bar{B}_j are larger than (A) and all \bar{A}_j , respectively, and both (B) and \bar{B} may be taken as constants.

If a single species of a metal is present in solutions, as in some experiments using inorganic salts of the metals, \bar{A}_1 or \bar{A}_2 will often dominate and then k_1 or K_2 will vanish. For $PbCl_2$ in soil for example, a good fit was obtained with $k_1 = 0$, $k = 2$ and K_2 soil dependent (Lagerwerff and Bower, 1973).

The Rothmund Kornfeld equation,

$$\frac{\bar{A}}{\bar{B}} = K \left(\frac{(A)}{(B)} \right)^h \quad (5)$$

where h and K are adjustable parameters, is useful when there is more than one adsorption site (Harmsen, 1977) and (A) is not much smaller than (B) . This is true for a number of experimental conditions reported, but not, in general, for natural systems if A is a species of a trace metal.

If part of species A undergoes fixation, a constant term F may be added to the adsorption. If fixation dominates the nonexchange adsorption, K_1 will vanish in the \bar{A}_1 term of equation (2) and no other modification such as adding a constant is necessary. If the fixation is time dependent, namely it is slow enough to be followed experimentally, the total adsorption becomes

$$\bar{A}_T = \frac{K_1(A)}{K_1 + (A)} + K_2 \left| \frac{(A)}{(B)} \right|^{1/k} \bar{B} + F(t) \quad (6)$$

where F is in this case time dependent. $F(t)$ is an additional parameter equal to the intercept of the adsorption isotherm. When no fixation exists, the intercept, and hence F , vanish.

Aside from fixation, transformation of complexed species of trace metals must be considered. Transformation may result in the formation of another complex or a free metal ion. Transformation is a slow process as compared to adsorption especially in natural systems which undergo some period of stabilization such as occurs in ground water or secondary effluent. The role of transformation of various trace metal-organic complexes needs more study, but can be neglected in many adsorption investigations.

In general, in natural systems, trace metals may appear in various complexed forms (Lagerwerff et al., 1976; Wolfberg, 1978; Mingelgrin et al., 1978). In addition, many metals will exhibit adsorption induced hydrolysis from M^{+n} to $M(OH)_\ell^{n-\ell}$ (Harmsen, 1977). The nonexchange

adsorption consists then of a sum of Langmuir terms. That is

$$\bar{A}_1 = \sum_j \bar{A}_{1j} = \sum_j \frac{k_j (A_j)}{K_j + (A_j)} \quad (7)$$

For the complexed species A_j the following holds:

$$\frac{(A_j)}{(M)(L_j)^m} = K_{sj} \quad (8)$$

where L_j is the ligand in A_j , K_{sj} is the appropriate stability constant and M is the uncomplexed metal ion. For most natural systems the ligand- L_j is either in large excess of the free trace metals or is kept constant by the buffering capacity of the system (such as OH in soil systems). In that case, $(L_j)^m K_{sj}$ is a constant for the system, and

$$\Sigma(A_j) = M \Sigma_j (L_j)^m K_{sj} \quad (9)$$

It is then possible to substitute in every individual term in equation (7) the total metal concentration in solution $\Sigma(A_j)$ for (A_j) with K_j replaced by the constant

$$\frac{K_j \Sigma_j (L_j)^m K_{sj}}{(L_j)^m K_{sj}}$$

The result is a sum of Langmuir terms with a common variable -- the total metal concentration in solution.

At the low concentrations at which trace metals are usually found in natural systems (excepting some industrial effluents for example) the Langmuir terms often approach linearity and hence, the above sum of Langmuir terms can be approximated well by one Langmuir term with the appropriate

constants. The same holds true for sufficiently large metal concentrations. Thus, the asymptotic behavior may be described by one Langmuir term with the total metal in solution as the variable. This will allow a good fit with one Langmuir term throughout the whole concentration range by a parametric fit.

From equations (4), (8), and (9), the exchange term for a multispecies system is

$$\bar{A}_2 = \sum_k \bar{A}_{2k} = \sum_{k=n}^1 K_k \frac{\sum_j (A_j)^{1/k}}{(B)^{1/kb}} \bar{B} \quad (10)$$

In this case n is the valence of the free metal cation. Equation 10 is derived by replacing (A) in every exchange term of equation (4) by $\sum_j A_j$, defining K_k accordingly from equations (8) and (9) and collecting all the terms with the same k . For a divalent metal the sum in equation (10) becomes

$$\bar{A}_2 = a(\sum A_j) + b(\sum A_j)^{1/2} \quad (11)$$

where a and b are constants.

For small enough $\sum A_j$ as is usually the case with trace metals in natural systems

$$\bar{A}_2 = A \left[e^{B(\sum A_j)^{1/2}} - 1 \right] \quad (12)$$

where A and B are again constants defined from parameters a and b in equation (11) by the Taylor expansion of equation (12). For higher valence cations, equations (11) and (12) must be replaced by a suitable equation derived from

equation (10). For a divalent cation the total adsorption isotherm in a multispeciated system can be written as

$$\bar{A}_T = \frac{k\Sigma A_j}{K+\Sigma A_j} + \frac{\bar{B}}{(B)^{1/kb}} \left(a' \Sigma A_j + b' (\Sigma A_j)^{1/2} \right) \quad (13)$$

where \bar{A}_T is the total adsorption of all species of the metal. The term $\frac{B}{(B)^{1/kb}}$ may be embedded in the constants a' and b' to give the constants a and b in equation (11) for most systems. This is so, since in general $(B) \gg \Sigma(A_j)$ and $\bar{B} \gg \Sigma\bar{A}_j$ and hence \bar{B} and B are practically constants. The constants in equation (13) may be extracted from the asymptotic behavior at $\Sigma A_j \rightarrow 0$ and $\Sigma A_j \gg K$ or from a nonlinear least squares fit.

RESULTS AND DISCUSSION

In comparing the model to experimental data, it would be useful to consider the two limits of the model. A) All the metal present is negatively or neutrally complexed -- in this case the parameters $a = 0$, $b = 0$ and the adsorption should be a Langmuir adsorption. B) The metal is uncomplexed -- in this case the Gapon equation should hold and $k = 0$ and $a = 0$ for a divalent cation. If the model holds for these two limiting cases, it would hold for a system of a more complicated speciation as the adsorption is then a sum of the exchange and Langmuir expressions. Comparisons for the limiting cases are preferable to comparisons in cases where both Langmuir adsorption and exchange are important since one obtains for the limiting cases a physical justification for the model rather than a more complex parametric fit. When none of the parameters in equation (13) vanish, it is more difficult to demonstrate that the fit is attained due to the physical meaning of the adsorption model rather than by empirical parametric fit.

While it is easy to produce a system which is totally complexed, it is more complicated to ensure that a single uncomplexed ion is present in any system simulating natural conditions. For example, in soil solutions organic components may bring about complexation, and hydrolysis in solution or at the surface will bring about the presence of hydroxiated species. Other inorganic complexes may also be present such as CdCl^+ if the Cl^- level is sufficiently high. In many experiments reported such as those of Lagerwerff and Bower (1972, 1973) for Cd and Pb adsorption, Cl or OH complexes played a significant role (Harmsen, 1977).

A system in which all the Cd in solution is in a complexed form was prepared as described in the Materials and Methods section. The adsorption isotherm on Yolo soil for initial Cd concentrations in solution up to 185 ppb is given in Fig. 1. Such Cd levels may seem usually high for solutions found in the environment except as derived from sewage effluents or sludge extracts (e.g., Bradford *et al.*, 1975). The best fit to the experimental data was obtained with $a = 0$, $b = 0$, $k = 15.57 \mu\text{eq/kg}$, and $K = 2.94 \mu\text{eq/l}$. The adsorption in this totally complexed system may be described by a Langmuir type of equation.

A number of adsorption studies on soils have been made using Cl salts of various trace metals (e.g., Blom, 1974; Lagerwerff and Bower, 1972, 1973). In all the soils studied with the concentration of the trace metals in the order of magnitude usually found in natural systems, the adsorption is well described by equation (13) with $k = 0$. Thus, exchange dominates with some of the divalent trace metals found as monovalent complexes. The presence of CdCl^+ complexes at significant quantities under the experimental conditions in all of the above studies was pointed out by Harmsen (1977).

In the case of the lead studies (Lagerwerff and Bower, 1973) the best fit was obtained with $a = 0$, $k = 0$, and b assuming different values for different soils. This suggests that Pb^{+2} exchange adsorption dominated in the case of lead. The stability constant of $CdCl^+$ is higher than that of $PbCl^+$ and this may contribute to the increased importance of parameter a in the Cd exchange adsorption. Organic ligands complexation in the soil solution may further affect the adsorption. Thus the data of Blom (1974) indicates that at Cd concentrations between 10^{-5} and 10^{-4} N when Cd was added as $CdCl_2$ to a sample of the mineral clinoptilolite, only the divalent exchange term contributed to adsorption ($k = 0$, $a = 0$). With soils (rather than with a mineral sample) both parameters a and b could contribute. Blom's data (1974) on the adsorption of Cd applied to $CdCl_2$ to a Windsor loamy fine sand (both horizons A and B were studied) fit very well to an adsorption isotherm with $k = 0$, and $b \ll a$. That is, monovalent adsorption dominates. Adsorption of Cd added as $CdCl_2$ to various soils studied by Lagerwerff and Bower (1972) was well described by an adsorption isotherm with $k = 0$, and both parameters a and b contributing, indicating that both monovalent and divalent cations are of importance. If $k = 0$ equation (13) becomes

$$a\Sigma A_j + b(\Sigma A_j)^{1/2} = \bar{A}_T \quad (14)$$

or

$$a(\Sigma A_j)^{1/2} + b = \frac{\bar{A}_T}{\Sigma A_j^{1/2}} \quad (15)$$

Plotting $(\Sigma A_j)^{1/2}$ vs. $\frac{\bar{A}_T}{\Sigma A_j^{1/2}}$ should yield a straight line with a slope of a

and an intercept of b. The parameters a and b derived for the Yolo, Windsum and Cecil soils from the data of Lagerwerff and Bower (1972) are given in Table 1. The fit of equation (15) to the data is shown in Fig. 2. Harmsen (1977) indicated that the data of Lagerwerff and Bowers is described by the Rothmund-Kornfeld equation.

$$\frac{Cd_s}{Ca_s} = K \left(\frac{Cd_0}{Ca_0} \right)^{1/n} \quad (16)$$

Here n and K are constants, subscript s denotes surface concentration and subscript 0 denotes equilibrium concentration in solution. Equation (14) can always be well approximated by a Rothmund-Kornfeld term with $1 \geq \frac{1}{n} \geq 0.5$. Indeed $1/n$ ranged between 0.69-0.77 (Harmsen, 1977) for the three soils studied by Lagerwerff and Bower (1972).

SUMMARY

An adsorption isotherm is proposed for trace metals which includes both exchange and nonexchange adsorption. The isotherm is applicable to a system where one species of the metal dominates or to a system with mixed species of the trace metal when the concentration of the trace metal is smaller than that of its complexing agents or when the ligand concentration is kept constant by buffering. These conditions generally exist in natural systems. The model was tested on both complexed Cd (neutral and negative complexes) and on Cd and Pb added as chlorides in which case the dominant species are monovalent and divalent cations (Harmsen, 1977). The proposed model fit the data reasonably well.

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Table 1: Parameters for the adsorption isotherm of Cd on three soils.

(Data from Lagerwerff and Bower, 1972, ΣA_i in $\mu\text{eq}/\ell$ and \bar{A}_T in % in C.E.C. ΣA_i and \bar{A}_T defined as in equation (14) in text.)

Soil	a ($\ell/\mu\text{eq}$)	b ($\ell/\mu\text{eq}$) ^{1/2}	k ($\ell/\mu\text{eq}$)	C.E.C. ($\mu\text{eq}/\text{g}$)
Yolo	.08	0.145	0.0	184
Cecil	.02	.02	0.0	59
Winsum	.05	.0145	0.0	205

Table 2: The distribution of soluble Cu in Davis sludge dried for 12 months as revealed by the different peaks from paper electrophoresis.

Peak #	Net Charge	Velocity (cm/hr)	Cu content (µg/l)
Saturation extract			
1	+	4.75	134
2	+	2.5	129
3	0	0.0	384
4	-	1.9	200
5	-	3.75	274
6	-	5.0	154
Saturation extract concentrated X10			
1	+	3.5	2930
2	+	1.9	712
3	+	1.65	1356
4	0	0	1250

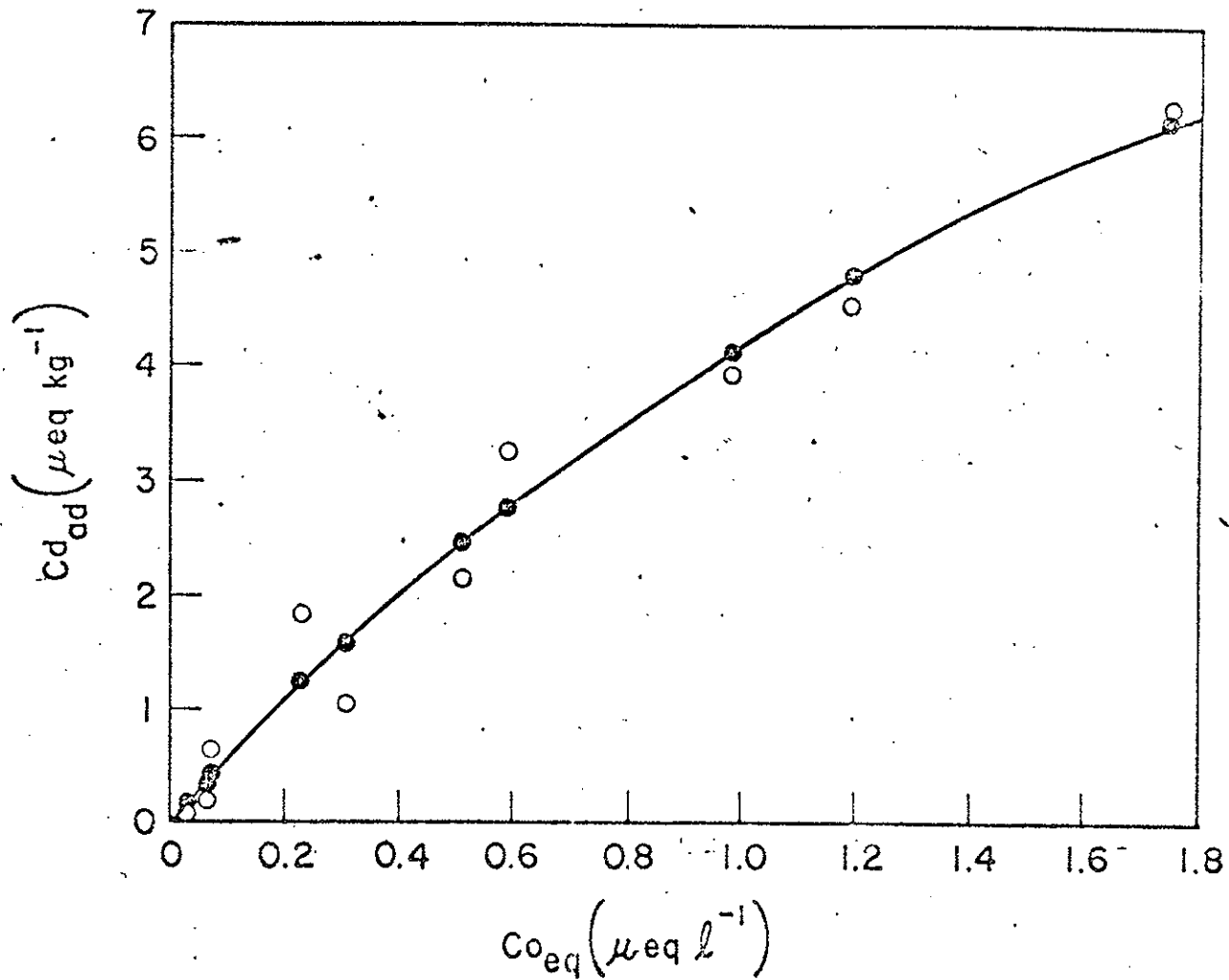


Fig 1. The adsorption isotherm of complexed Cd added as CdCl_2 to Yolo silt loam in the presence of excess EDTA and NTA. The fit to the proposed model is also given.

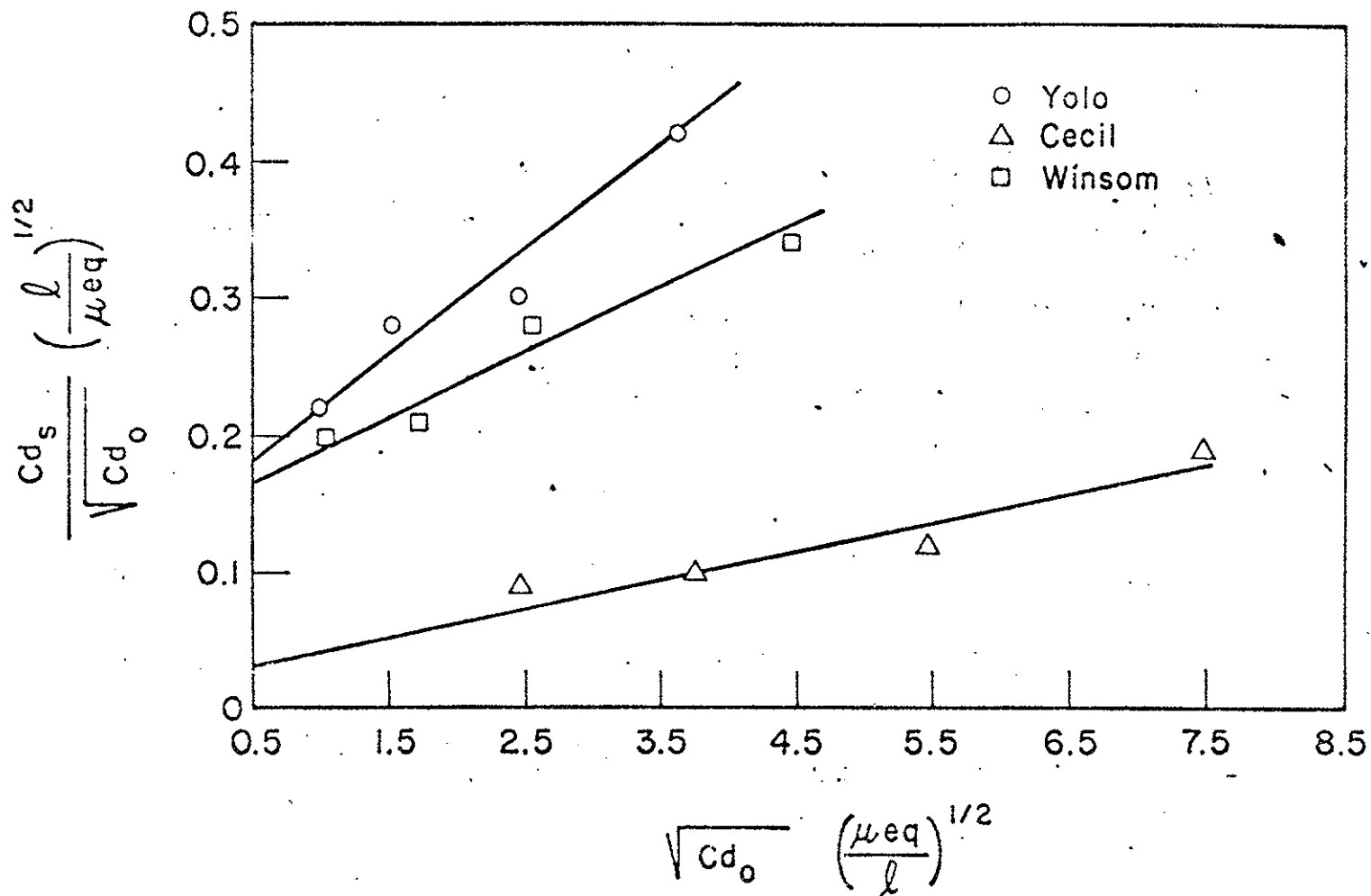


Fig. 2. A plot of the surface concentration divided by the square root of the equilibrium concentration vs. the square root of the equilibrium concentration of Cd in suspensions of Yolo, Cecil and Winsum soils. Data from Lagerwerff and Brown 1972 with Ca^{+2} concentration maintained at 14.3 meq/l, surface concentration of Cd is given as % of C.E.C., Cd added as $CdCl_2$ and Ca as $CaCl_2$.

C. TRANSPORT OF CADMIUM IN SOILS

Abstract

The transport of Cadmium in Hanford sandy loam and Yolo silt loam soil was examined in 35 columns of soil, 7.5 cm D x 1 cm L. Soils were passed through a 2 mm sieve and uniformly packed between two fritted glass plates attached to a lucite tube. Constant flow of solution was maintained in the system by a positive displacement pump and effluent was collected in glass vials in a fraction collector. Solutions of Cd in 0.01 N CaCl_2 were introduced into the saturated soil in both the ionic and chelated form. Cadmium concentrations were 100 and 1000 ppb and EDTA concentrations of 0.0, 1.5, 3.0 and $15 \text{ mg } \ell^{-1}$ were used to chelate the metal. The pH of the solutions was either 3.7 or 6.75 and fluxes of 1.06 and 6.98 cm hr^{-1} were imposed. Effluents were analyzed for Cd ion and total Cd by specific ion electrode and atomic absorption respectively. The pH was also recorded. Both adsorption and desorption curves were examined for a large number of experiments. Significant effects of EDTA and pH on the position and shapes of the breakthrough curves were observed with the effect varying depending upon whether the Cadmium form was ionic or chelated. Flux had much less effect on the BTC than did the chemical environment and this effect was different depending upon the form of the Cd. As might be anticipated desorption curves differed from adsorption curves. A suitable model has yet to be developed to describe the shapes and position of the BTC, although a model to describe batch reaction results has been partially successful.

C. TRANSPORT OF CADMIUM IN SOILS

I. INTRODUCTION

The objective of this project has been to discover what factors affect the transport of cadmium in soil under steady state saturated flow conditions. Particular emphasis has been placed on examining the transport of cadmium chelated with ethylenediaminetetraacetic acid, EDTA.

Laboratory soil column studies were conducted by varying factors such as cadmium concentration, EDTA concentration, pH, flux and type of soil. Both uptake and desorption of cadmium were monitored by testing column effluent for ionic and complexed species. Adsorption isotherm experiments were also obtained using the same cadmium and EDTA concentrations that were used in the column studies. A detailed description of the experimental variables can be found in Table 1. A standard column design was developed and influent solution composition, flux or soil was varied for each column, #4 through #31.

Cadmium concentrations of $1.771 \mu\text{eq } \ell^{-1}$ (100 ppb) and $17.706 \mu\text{eq } \ell^{-1}$ (1000 ppb) were used in conjunction with EDTA concentrations of 0, 0.15, 0.3 $\text{mg } \ell^{-1}$ for 100 ppb Cd^{+2} and 0, 0.15, 3.0, 15.0 $\text{mg } \ell^{-1}$ for 1000 ppb Cd^{+2} . Each of these possible combinations of cadmium and EDTA was varied by having a pH of 3.7 or 6.75 and a flux of 1.065 cm hr^{-1} or 6.98 cm hr^{-1} . Most of the data collected was for a Hanford soil but studies were conducted with a Yolo soil at the 1000 ppb Cd^{+2} concentration and 6.98 cm hr^{-1} flux by varying EDTA concentration and pH.

II. EXPERIMENTAL METHODS AND MATERIALS

Soil Description and Analysis

The soil used for columns #1 through #24 was a Hanford sandy loam taken from the Kearney Field Station of the University of California. The

Table 1. Experimental variables for soil columns. All columns have 1.0 cm length except those marked with "*".

Column #	Initial Cd Concentration (ppb)	EDTA Concentration (mg L^{-1})	pH	Flux (cm hr^{-1})	Soil
1*	490	1.50		0.503	Hanford
2*	81	1.50	6.46	0.503	"
3*	490	1.50	6.24	4.53	"
4	1000	3.00	3.81	6.981	"
5	1000	3.00	3.81	1.065	"
6	1000	3.00	6.75	1.065	"
7	1000	3.00	6.75	6.981	"
8	100	0.30	6.75	1.065	"
9	100	0.30	6.75	6.981	"
10	1000	0.00	3.70	1.065	"
11	1000	1.50	3.70	1.065	"
12	1000	15.00	3.70	1.065	"
13	1000	0.00	6.75	1.065	"
14	1000	1.50	6.75	1.065	"
15	1000	15.00	6.75	1.065	"
16	100	0.30	3.70	1.065	"
17	100	0.15	3.70	1.065	"
18	100	0.30	3.70	6.981	"
19	100	0.15	6.75	1.065	"
20	100	0.00	4.90	1.065	"
21	100	0.00	3.70	1.065	"
22	0	0.00	3.70	1.065	"
23	0	0.00	6.75	1.065	"
24	100	0.00	6.75	1.065	Hanford
25	1000	3.00	3.70	6.981	Yolo
26	1000	3.00	6.75	6.981	"
27	1000	0.00	3.70	6.981	"
28	1000	0.00	3.70	6.981	"
29	1000	0.00	6.75	6.981	"
30	1000	1.50	3.70	6.981	"
31	1000	1.50	6.75	6.981	"

sample was air dried to a moisture content of 0.7% and was passed through a 2 mm sieve. The soil used for columns #25 through #31 was a Yolo silt loam taken from an experiment plot at the University of California, Davis. The sample was air dried to a moisture content 2.8% and passed through a 2 mm sieve.

Exchangeable cation concentrations were determined by standard methods using 1.0 N ammonium acetate, pH 7.0. Solutions were analyzed by flame emission spectrophotometry for Ca^{+2} , Mg^{+2} , Na^+ and K^+ .

Soluble cations were determined by preparing a saturation extract with distilled water and analyzing the extract by flame emission spectrophotometry. The results of the soil analysis for Hanford and Yolo soils are indicated in Tables 2 and 3.

Influent Solution Composition

All solutions were prepared from distilled-deionized water. Columns were wet and equilibrated by pumping 0.010 N CaSO_4 solution through them at the experimental flux for at least 24 hrs prior to the introduction of the Cd solutions. All influent solutions had a 0.010 N CaCl_2 concentration.

A 1000 ppm Cd stock solution was used to prepare influent solutions and standards for analysis. The stock was prepared from CdCl_2 and was acidified with 1.00% HNO_3 for stability. Solutions containing 1000 ppb Cd have 1.00×10^{-3} HNO_3 or 1.59×10^{-4} N NO_3^- . The addition of HNO_3 gives an experimentally determined pH of 3.7. For some solutions, the pH was adjusted to 6.75 by adding 0.1 NaOH which yields 1.59×10^{-4} Na^+ . Solutions having a 100 ppb Cd concentration were adjusted to pH 3.7 by the addition of HNO_3 which gives a 1.59×10^{-4} N NO_3^- concentration. Solutions of pH 6.75 were prepared by adding NaOH, yielding a Na^+ concentration of 1.59×10^{-4} N.

Table 2. Analysis of Hanford soil: exchangeable cation concentrations and soluble cation concentrations.

	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	Total
Total cation					
Concentration (meq/100 g soil)	6.50	1.00	1.50	0.00	9.0
Soluble cation					
Concentration (meq/100 g soil)	0.041	0.002	0.007	0.000	0.05
Exchangeable cation					
Concentration (meq/100 g soil)	6.46	1.00	1.49	0.0	8.95

Table 3. Analysis of Yolo soil: exchangeable cation concentrations and soluble cation concentrations.

	Ca ⁺²	Mg ⁺²	Na ⁺	K ⁺	Total
Total cation					
Concentration (meq/100 g soil)	12.0	12.0	1.0	1.0	26.0
Soluble cation					
Concentration (meq/100 g soil)	0.09	0.15	0.09	0.02	0.35
Exchangeable cation					
Concentration (meq/100 g soil)	11.91	11.85	0.91	0.98	25.65

Columns #1, #2, and #3 are exceptions to the above. Cd was introduced by adding CdCl_2 without the addition of HNO_3 or NaOH .

EDTA was added as the disodium salt which introduces additional Na^+ to the solutions. This is reflected in Table 4 which shows the influent solution composition for each column. For each $\text{mg } \ell^{-1}$ of EDTA there is 5.4×10^{-3} meq ℓ^{-1} of Na^+ .

Soil Columns

A standard column design was developed which was used for columns #4 through #31. It consisted of an acrylic cylinder having an inside diameter of 7.5 cm with a 1.0 cm length and two fritted glass plates which were attached to each end of the cylinder and sealed with silicone rubber sealant. This configuration is illustrated in Figure 1. There is a volume of solution between the top of the soil column and the end of the tube leading to the fraction collector. This volume was calculated by the weight difference between a wet and dry column and found to be 20.05 ml.

Each column was packed in a consistent manner in order to eliminate packing differences as much as possible. Columns were packed with 66.0 g of air dried Hanford soil having a moisture content of 0.7% or 61.0 g of air dried Yolo soil having a moisture content of 2.8%. This gives a bulk density of 1.452 g cm^{-3} for Hanford columns and 1.371 g cm^{-3} for the Yolo columns.

Columns #1 through #3 are exceptions to the standard design. Column #1 was similar to the standard column but the column length was 4.0 cm and was packed with 273 g of Hanford soil. Column #2 had a 1.8 cm length and was packed with 111 g of Hanford soil. Column #3 was a small glass column with a 2.5 cm diameter and 2.0 cm length, packed with 12.7 g of Hanford soil.

Table 4. Influent solution composition.

Column #	Total Cd		EDTA (mg l ⁻¹)	Ca ⁺⁺ (meq l ⁻¹)	Na ⁺ (meq l ⁻¹)	Cl ⁻ (meq l ⁻¹)	NO ₃ ⁻ (meq l ⁻¹)
	(ppm)	(μeq l ⁻¹)					
1	490	8.676	1.50	10.00	0.008	10.01	0.000
2	81	1.436	1.50		0.008	10.00	0.000
3	490	8.676	1.50		0.008	10.01	0.000
4	1000	17.706	3.00		0.175	10.02	0.159
5	1000	17.706	3.00		0.175	10.02	
6	1000	17.706	3.00		0.175	10.02	
7	1000	17.706	3.00		0.175	10.02	
8	100	1.771	0.30		0.161	10.00	
9	100	1.771	0.30		0.161	10.00	
10	1000	17.706	0.00		0.159	10.02	
11	1000	17.706	1.50		0.167	10.02	
12	1000	17.706	15.00		0.240	10.02	
13	1000	17.706	0.00		0.159	10.02	
14	1000	17.706	1.50		0.167	10.02	
15	1000	17.706	15.00		0.240	10.02	
16	100	1.771	0.30		0.161	10.00	
17	100	1.771	0.15		0.160	10.00	
18	100	1.771	0.30		0.161	10.00	
19	100	1.771	0.15		0.160	10.00	
20	100	1.771	0.00		0.159	10.00	
21	100	1.771	0.00		0.159	10.00	
22	0	0.000	0.00		0.159	10.00	
23	0	0.000	0.00		0.159	10.00	
24	100	1.771	0.00		0.159	10.00	
25	1000	17.706	3.00		0.175	10.02	
26	1000	17.706	3.00		0.175	10.02	
27	1000	17.706	0.00		0.159	10.02	
28	1000	17.706	0.00		0.159	10.02	
29	1000	17.706	0.00		0.159	10.02	
30	1000	17.706	1.50		0.167	10.02	
31	1000	17.706	1.50	10.00	0.167	10.02	0.159

Packing the soil was very difficult for column #3 and shifting and separation of the soil occurred during the experiment so this column design was abandoned.

Column Experiments

Influent solutions were pumped with a Harvard Apparatus Model 950 infusion-withdrawal pump which was connected to the columns with a combination of Teflon tubing and Omnifit Teflon connectors and valves. Fractions were collected with either an Eldex universal fraction collector or ISCO Model 568 fraction collector. All experiments were performed in constant temperature chambers at $25.0 \pm 0.3^\circ\text{C}$.

Columns were saturated with a 0.01 N CaSO_4 solution using 50 cc syringes. This gives a flow rate of $0.784 \text{ ml min}^{-1} \pm 0.007$ when experimentally determined for a given column. This flow corresponds to a flux of 1.065 cm hr^{-1} and was maintained for at least 24 hrs prior to the introduction of the cadmium solution to a given column. If a column was to be run at 6.98 cm hr^{-1} , the 0.01 N CaSO_4 was pumped at 1.065 cm hr^{-1} for 24 hrs and then switched to 6.98 cm hr^{-1} for at least 6 hrs before the CaCl_2 solution was applied.

After equilibration with the 0.01 N CaSO_4 , a valve between the column and fraction collector was closed while a valve between the column and pump was opened. The CaSO_4 solution was flushed out of the system and the influent solution containing 0.01 N CaCl_2 , cadmium and EDTA was introduced. The valves were then adjusted to permit the flow of influent solution through the column to the fraction collector.

Fractions were collected for a suitable time to achieve breakthrough of cadmium. After column #10 desorption data was collected. This was achieved by introducing a 0.01 N CaCl_2 solution containing no cadmium or EDTA. The

pH of this solution was adjusted with HNO_3 or NaOH to match the pH of the solution which contained the cadmium. The CaCl_2 solution was pumped at the same flux and fractions were collected until most of the cadmium had leached out of the column.

The pore volume, V_0 , for each column was determined by drying the soil column at 110°C until constant weight was achieved.

Adsorption Isotherm Experiments

All adsorption isotherm experiments were performed using a procedure incorporating a soil to solution ratio of 1:4. Twenty grams of soil was added to 80 ml of solution in an Erlenmeyer flask which was covered with parafilm and shook at 25°C for 24 hrs. Samples were removed, centrifuged for 25 min at 10,000 rpm, and then filtered through a $0.45\ \mu\text{m}$ Millipore filter. The filtrate was then analyzed for pH, cadmium by atomic absorption spectroscopy and cadmium ion using a specific ion electrode.

Experiments were carried out using applied concentrations of 0, 100, 250, 500, 750 and 1000 ppb or 0, 1.771, 4.427, 8.853, 13.280 and $17.706\ \mu\text{eq}\ \ell^{-1}$. For each concentration of cadmium, four EDTA concentrations were used which were proportional to the cadmium concentration. For example, 0.0, 0.15, 0.30 and $1.5\ \text{mg}\ \ell^{-1}$ were used in conjunction with the 100 ppb cadmium concentration, while 0.0, 1.5, 3.0 and $15.0\ \text{mg}\ \ell^{-1}$ were used for the 1000 ppb cadmium concentration. The four concentrations of EDTA represent various levels of complexation with the cadmium.

Two pH's were used for each of the possible combinations of EDTA and cadmium. Solutions were adjusted to pH 6.75 or pH 3.7 with NaOH or HNO_3 . A detailed account of the applied solution composition is illustrated in Table 6 in the Results section of this report.

Atomic Absorption Analysis

All cadmium samples were analyzed with a Perkin-Elmer Model 403 atomic absorption spectrophotometer equipped with a deuterium lamp background corrector. Flame analysis was performed using an air-acetylene mixture. Standards ranged from 10 ppb to 2 ppm Cd^{+2} and were prepared weekly from a 1000 ppm standard.

Samples with cadmium concentrations of less than 25 ppb were analyzed using a Perkin-Elmer HGA-2200 heated graphite furnace accessory. Standard solutions ranged from 1 ppb to 30 ppb Cd^{+2} and the acceptable detection limit was 0.1 ppb Cd^{+2} . Samples were delivered by a 10 μl pipette equipped with disposable plastic tips. Each sample was assayed at least three times because of the variability of low level measurement.

Specific Ion and pH Measurements

An Orion Model 94-48A Cd^{+2} specific ion electrode and Orion Model 90-01 single junction reference electrode were used with an Orion Model 801 digital pH/mV meter to measure Cd^{+2} activity. Samples from columns #21 through #31 were analyzed using an Orion Model 901 microprocessor ion analyzer. A low level calibration curve was generated by measuring electrode potentials of Cd^{+2} standards according to the instructions provided with the 801 meter. No calibration curve was needed with the Model 901 meter because it reads out Cd^{+2} concentration directly when calibration with two standards and a blank. Standard concentrations used for the Model 901 meter were 100 ppb and 1000 ppb Cd^{+2} . For all cadmium ion analysis of samples and standards, the ionic strength was adjusted to 0.1 M with sodium nitrate.

pH measurements were made using an Orion Model 91-03 internal reference pH electrode with an Orion Model 801 or Model 901 meter.

Treatment of Glassware and Samples

All glassware was washed with soap and water and rinsed with a solution containing 1% EDTA and 2 N NaOH in order to remove any contaminating metals. This was followed by at least two rinses with distilled water and a 24 hr soak in 1% HNO₃. The glassware was then rinsed several times with distilled water and then distilled-deionized water.

All samples were stored in air-tight polyethylene or glass containers and refrigerated to minimize precipitation and any microbial activity.

III. RESULTS

Column Calculations and Data Tables

The results of each column experiment are presented in column data tables. " V/V_0 " represents the number of pore volumes of effluent passed through a given column. This number has not been corrected for the volume of solution between the column and fraction collector. This correction factor is approximately 1 pore volume and is not a significant source of error in the breakthrough curves, which typically have a range of at least 400 pore volumes. But the correction factor is important for modeling purposes and is indicated for each column in Table 5. The number of pore volumes, V/V_0 , can be corrected by subtracting the V/V_0 correction listed in the table.

"ppb Cd" refers to the cadmium concentration for a fraction of column effluent which has been determined by atomic absorption spectroscopy, A.A. " Cd/Cd_0 " is the ratio of effluent cadmium concentration, determined by A.A. to influent cadmium concentration determined by A.A. Table 5 lists the Cd_0 value for each column which has been used in the calculations. Cd_0 was not determined by A.A. for columns #24 through #31, so the prepared concentration was used rather than the A.A. concentration.

Table 5. Pore volume and influent cadmium concentration used for calculating breakthrough curves. V/V_0 correction is the number of pore volumes of solution between the column and fraction collector.

Column #	Pore Volume V_0 (ml)	V/V_0 Correction	Influent Cadmium Concentration, Cd_0 (ppb)
1	78.60	0.255	502
2	37.77	0.531	99
3	4.70	----	545
4	22.93	0.874	1034
5	21.62	0.927	1036
6	22.75	0.881	1000
7	21.55	0.930	990
8	20.46	0.985	110
9	19.41	1.033	107
10	19.14	1.048	1021
11	18.78	1.068	1005
12	22.06	0.909	1000
13	19.43	1.032	1004
14	20.53	0.981	1010
15	19.41	1.033	1025
16	20.90	0.959	131
17	18.51	1.083	145
18	21.42	0.936	123
19	21.00	0.955	120
20	20.21	0.992	115
21	20.13	0.996	116
22	18.63	1.076	0
23	20.64	0.971	0
24	22.88	0.876	100
25	21.92	0.915	1000
26	23.21	0.864	1000
27	22.47	0.892	1000
28	21.62	0.927	1000
29	22.53	0.890	1000
30	25.45	0.788	1000
31	21.92	0.919	1000

"ppd Cd^{+2} " refers to the cadmium ion concentration for a given fraction which was determined by a specific ion electrode. " $\text{Cd}^{+2}/\text{CD}_0$ " is the ratio of effluent cadmium ion to influent cadmium concentration as determined by A.A. and listed in Table 5.

The data tables also list the pH for fractions of column effluents.

Breakthrough Curves

The results for each column experiment may be found in the data tables which were generated according to the method described in the column calculations and data tables section. The results are also presented in breakthrough curves which are a plot of C/C_0 on the y-axis and V/V_0 on the x-axis, where C/C_0 is the ratio of effluent cadmium concentration by A.A. to influent cadmium or the ratio of effluent cadmium ion concentration by specific ion electrode to influent cadmium concentration. V/V_0 is the number of pore volumes of effluent passed through the column.

The breakthrough curves are presented in three groups. The first group consists of the preliminary columns which do not have the standard design dimensions. The first group consists of columns having an influent cadmium concentration of 1000 ppb, the second group consists of columns having an influent cadmium concentration of 100 ppb and the third are those columns which used Yolo soil rather than Hanford soil.

In each group the breakthrough curves are plots of two or more columns which will show the effect of varying one experimental parameter such as EDTA concentration, pH, flux or soil type while keeping the others constant. The curves are generally presented in pairs, indicating either total cadmium by A.A. or ionic cadmium by specific ion electrode. The desorption data, when available, is presented after the absorption data.

Figures 2 and 3 show the effect of EDTA on the efflux of Cd and Cd ion respectively. The BT of the complexed ion is rapid in comparison with the ionic form. Figures 4 and 5 illustrate the leaching of Cd for two treatments shown in Figures 2 and 3. Although the adsorption and desorption curves are similar in shape they are not concurrent.

Figures 6 and 7 present breakthrough curves (BTC) for conditions similar to Figures 2 and 3 except the pH is now 3.7 instead of 6.75. As expected, the effect of pH is quite significant. Although repeated analysis of columns 10 and 11 were conducted, the C/C_0 values exceeded 1.0 in every case.

Figures 9 and 10 illustrate the effect of flux on the BTC for one treatment of EDTA. While measureable differences are observed, the effect of flux is much less significant at a pH of 6.75 than is observed at a pH of 3.8 as shown in Figures 11 and 12. In addition, the effect of flux on Cd as compared with Cd ion is significantly different.

Figures 13, 14, 15, and 16 are BTC for Cd at two pH values during adsorption and desorption, again illustrating the effect of pH but without the addition of EDTA.

Figures 17, 18, 19, and 20 present BTC of Cd and Cd ion at two pH values and EDTA concentration of $1.5 \text{ mg } \ell^{-1}$. Similar experimental conditions were present for results shown in Figures 21 through 24 except the concentration of EDTA was increased to 3.0 and $15 \text{ mg } \ell^{-1}$. Obviously both pH and EDTA have a profound effect on the displacement of Cd and Cd ion. In most cases, the concentration of Cd exceeded $C/C_0 = 1.0$ at a pH = 3.7.

Figures 25 and 26 compare BTC for two different pH values at a flux of 6.75 for an EDTA concentration of $3 \text{ mg } \ell^{-1}$. As before at the lower flux, the influence of pH is significant both for Cd and Cd ion.

Breakthrough curves in group two for Hanford soil, illustrated in Figures 27 through 40, were all obtained with an input concentration of Cd of 100 ppb. While the flux was either 1.065 or 6.98 cm hr⁻¹, and pH either 6.75 or 3.7, the EDTA concentrations were 0.0, 0.15 and 0.30 or somewhat less than for group one. In these cases the patterns of Cd and Cd ion behavior are entirely different from those at the higher input Cd concentration. Not only are the shapes of the curves different but the positions of the curves relative to one another are different. The affect of flux is much more pronounced for some treatments at this level of Cd concentration input. The unexpected results observed for Cd behavior at pH 3.7 at the higher Cd concentration of group one experiments were also observed in this group. The adsorption and exchange of the Cd ion and complex forms interacting with changes in pH EDTA concentration and flux make predictions hazardous if one is to base predictions of behavior at 100 ppb on results at 1000 ppb. Most if not all previous experiments, of which there are few, have examined Cd displacement at higher concentrations. Yet it can be argued that environmentally significant concentrations occur mainly in the 100 ppb range. Greater difficulties are encountered, however, when working in the lower concentration range.

Breakthrough curves for group 3 illustrate results for Yolo loam and comparisons of Yolo loam and Hanford sandy loam soil.

Figures 41 and 42 demonstrate similar BTC for Cd for the two soils at an EDTA concentration of 3.0 mg l⁻¹ although the BTC for Cd ion are different. When the pH is 3.7 instead of 6.9, however, the BTCs are distinctly different as shown in Figures 43 and 44.

The Yolo soil did not demonstrate the unexpected pH effects at the lower pH that were evident for the Hanford soil. The exception to this

observation is shown in Figures 51 and 53 where the initial desorption of Cd exceeded $C/C_0 = 1.0$ by a measureable amount and the reason is not evident.

The various interactions that occur at pH 3.7 and EDTA at 3 concentrations involving Cd ion and complexed forms is shown in Figures 47 and 48. The curve for total Cd at EDTA equal to $3.0 \text{ mg } \ell^{-1}$ lies between those at 0 and $1.5 \text{ mg } \ell^{-1}$. A different position of the curves exists for breakthrough of the Cd ion. It is quite evident the interplay between exchange and adsorption of the ionic form and complexed form as affected by pH is quite complex even though the system might be considered as a relatively simple one. Further analysis of these systems utilizing models will be conducted in an attempt to account for the changes in species and their interaction with the soil during displacement.

Table 6. Adsorption Isotherm Experiment: pH 6.75

Initial Solution Concentration			Equilibrium Solution Concentration				pH	Adsorbed Cd ($\mu\text{eq Kg}^{-1}$)
cadmium (ppb)	EDTA ($\mu\text{eq l}^{-1}$)	EDTA (mg l^{-1})	cadmium (ppb)	cadmium ($\mu\text{eq l}^{-1}$)	specific ion Cd^{+2} (ppb)	specific ion Cd^{+2} ($\mu\text{eq l}^{-1}$)		
0	0	0	9.4	0.166	3	0.053	6.03	-0.664
100	1.771	0	13.4	0.237	3	0.053	7.05	6.136
100	1.771	0.15	27.8	0.492	18	0.319	6.91	5.116
100	1.771	0.30	66	1.169	32	0.567	6.76	2.408
100	1.771	1.5	95	1.682	0	0	5.94	0.356
250	4.428	0	6.0	0.106	0	0	7.35	17.288
250	4.428	0.375	81	1.434	3.6	0	7.37	11.976
250	4.428	0.750	155	2.744	0	0	7.39	6.736
500	8.855	0	12.1	0.214	0	0	7.49	34.564
500	8.855	0.75	140	2.479	0	0	7.34	25.504
500	8.855	1.5	269	4.763	0	0	7.39	16.368
750	13.283	0	17.5	0.310	1.0	0.018	7.37	51.892
750	13.283	1.125	237	4.195	3.1	0.055	7.49	36.352
750	13.283	2.25	392	6.941	0	0	7.39	25.368
1000	17.706	0	58	1.027	42	0.744	6.24	66.716
1000	17.706	1.5	687	12.167	14	0.248	5.83	22.156
1000	17.706	3.0	791	14.009	78	1.381	6.06	14.788
1000	17.706	15	1049	18.574	0	0	6.71	-3.472

Table 7. Adsorption Isotherm Experiment: pH 3.7

Initial Solution Concentration			Equilibrium Solution Concentration				pH	Adsorbed Cd ($\mu\text{eq Kg}^{-1}$)
cadmium (ppb)	EDTA ($\mu\text{eq l}^{-1}$)	cadmium (ppb)	cadmium ($\mu\text{eq l}^{-1}$)	specific ion Cd ²⁺ (ppb)	specific ion Cd ²⁺ ($\mu\text{eq l}^{-1}$)			
0	0	0	13.1	0.232	5	0.089	6.20	-0.928
100	1.771	0	16.6	0.294	10	0.1771	6.78	5.908
100	1.771	0.15	26.6	0.471	14	0.248	6.80	5.200
100	1.771	0.30	44	0.779	23	0.407	6.67	3.968
100	1.771	1.5	92	1.629	0	0	6.60	0.568
250	4.428	0	6.5	0.115	0	0	7.08	17.252
250	4.428	0.375	80	1.416	0	0	7.14	12.048
250	4.428	0.75	135	2.390	0	0	7.15	8.152
500	8.855	0	8.0	0.142	0	0	7.31	34.852
500	8.855	0.75	168	2.975	0	0	7.32	23.520
500	8.855	1.5	352	6.232	0	0	7.19	10.492
750	13.283	0	9.3	0.165	1.7	0.030	7.19	52.472
750	13.283	1.125	266	4.710	6.8	0.120	7.25	34.292
750	13.283	2.25	465	8.233	8.6	0.152	7.22	20.200
1000	17.706	0	124	2.196	83	1.470	6.60	62.040
1000	17.706	1.5	425	7.527	85	1.505	6.76	40.716
1000	17.706	3.0	721	12.769	38	0.673	6.76	19.748
1000	17.706	15.0	1054	18.662	0	0	6.83	2.824

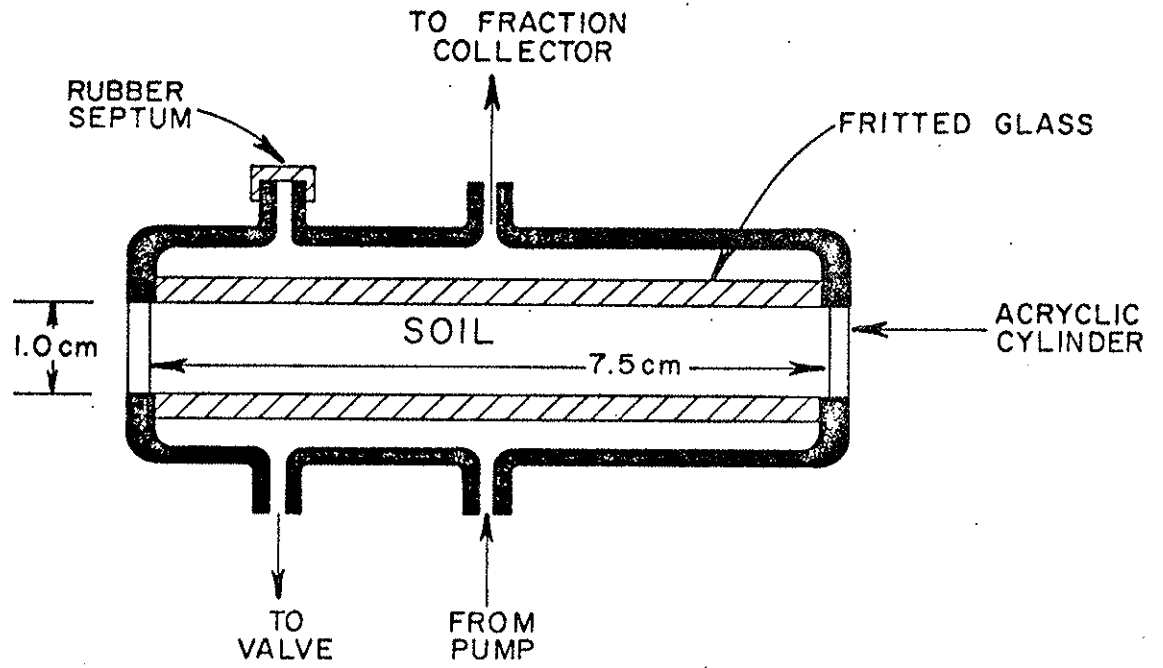


Figure 1. Soil column design.

Breakthrough Curves, Group One: These columns are those which have Hanford soil and an influent cadmium concentration of 1000 ppb.

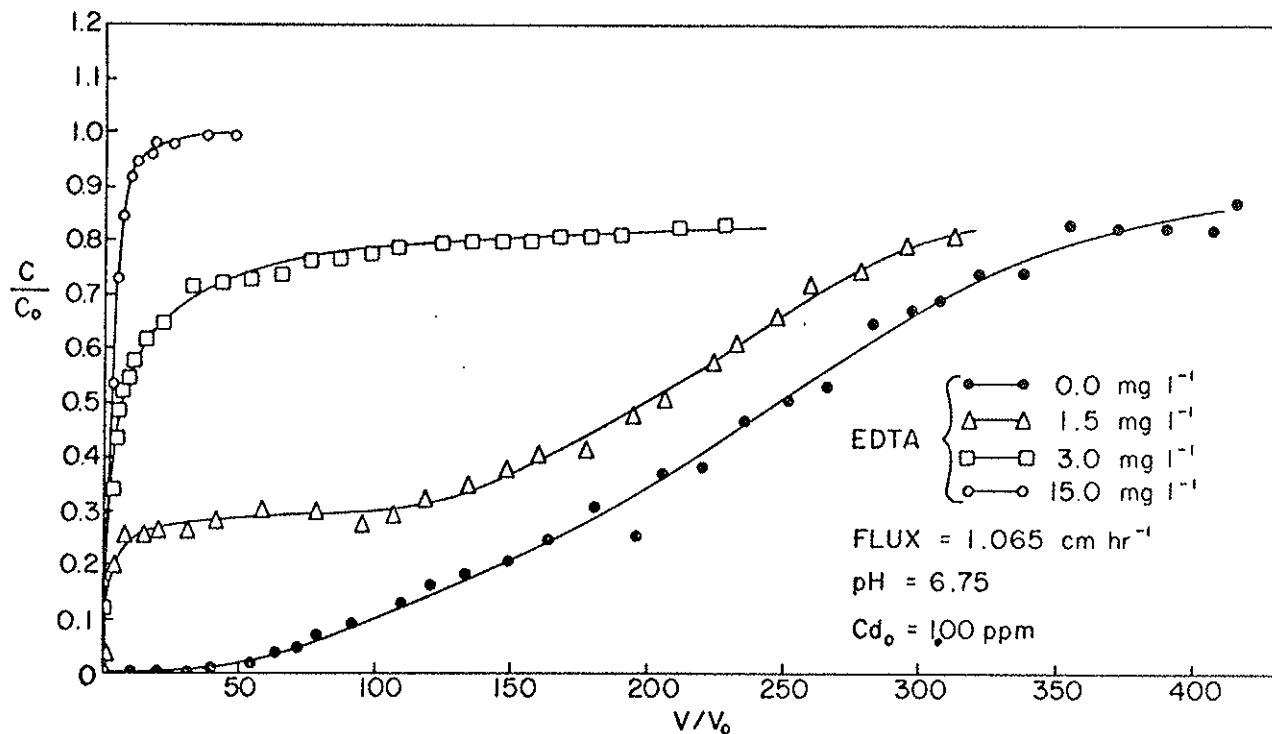


Figure 2. Effect of EDTA concentration on breakthrough of Cadmium at a flux of 1.065 cm hr⁻¹, pH of 6.75 and initial Cadmium ion concentration of 1 ppm. EDTA concentrations of 0.0, 1.5, 3.0 and 15 mg l⁻¹ correspond to columns 13, 14, 6 and 15 respectively.

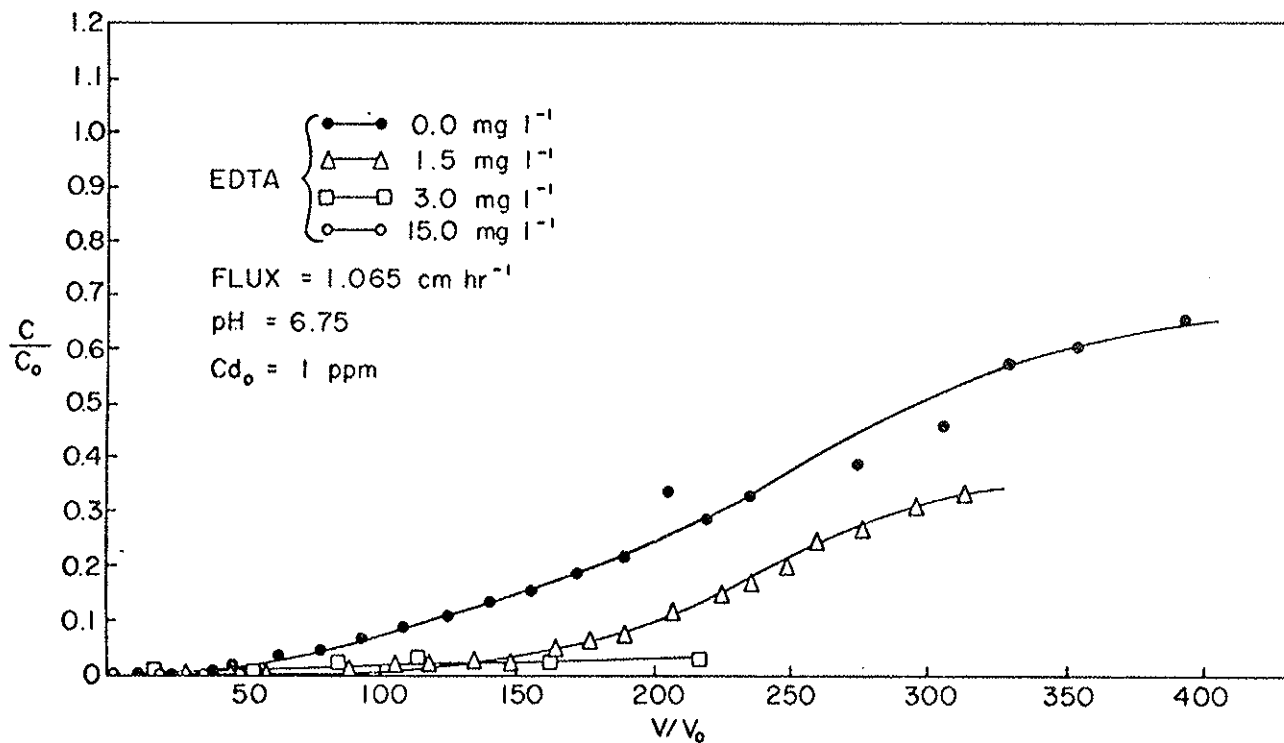


Figure 3. EDTA effect on breakthrough of Cadmium ion.

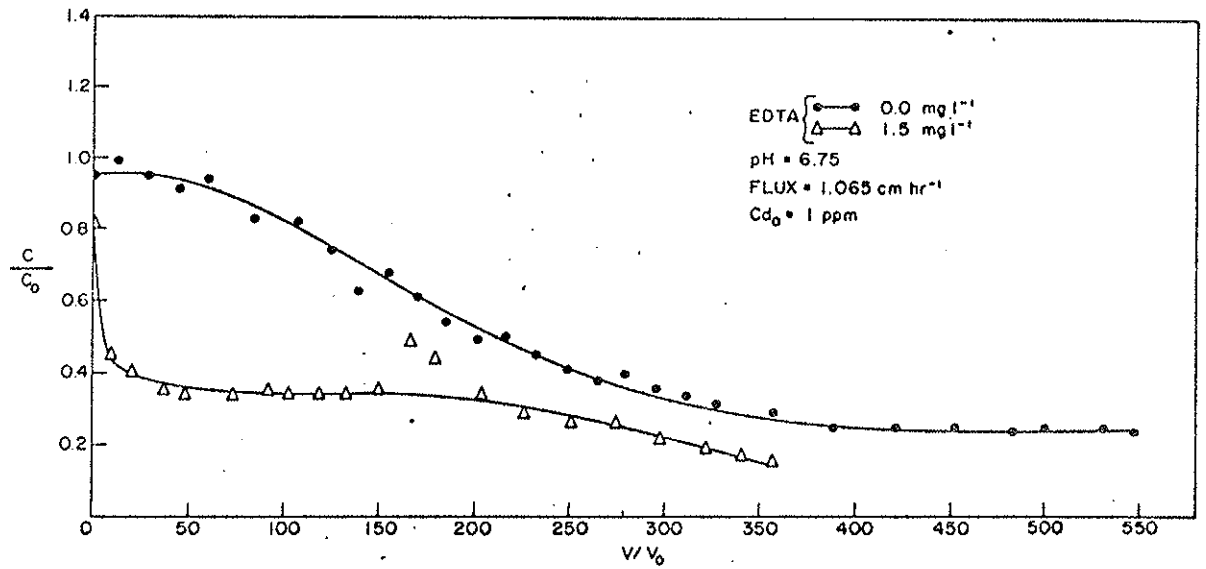


Figure 4. Desorption breakthrough curves for Cadmium by A.A. showing EDTA effect at a flux of 1.065 cm hr⁻¹, pH of 6.75 and initial Cadmium concentration of 1 ppm. Column #13 has 0 mg l⁻¹ EDTA and column #14 has 1.5 mg l⁻¹ EDTA.

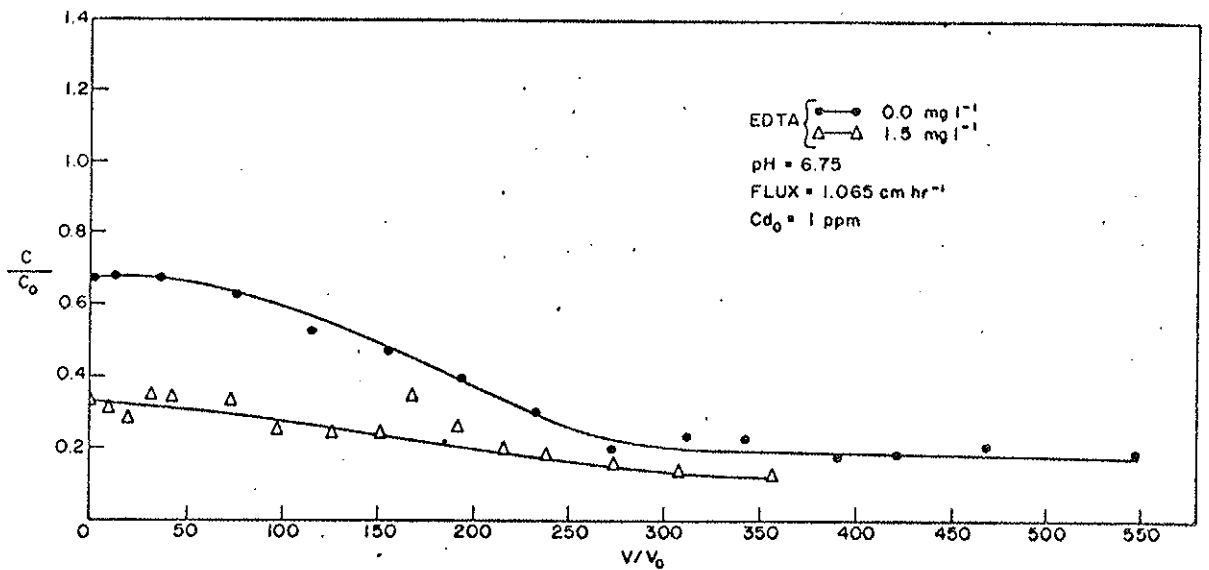


Figure 5. Desorption curves for Cadmium ion showing EDTA effects for above column conditions.

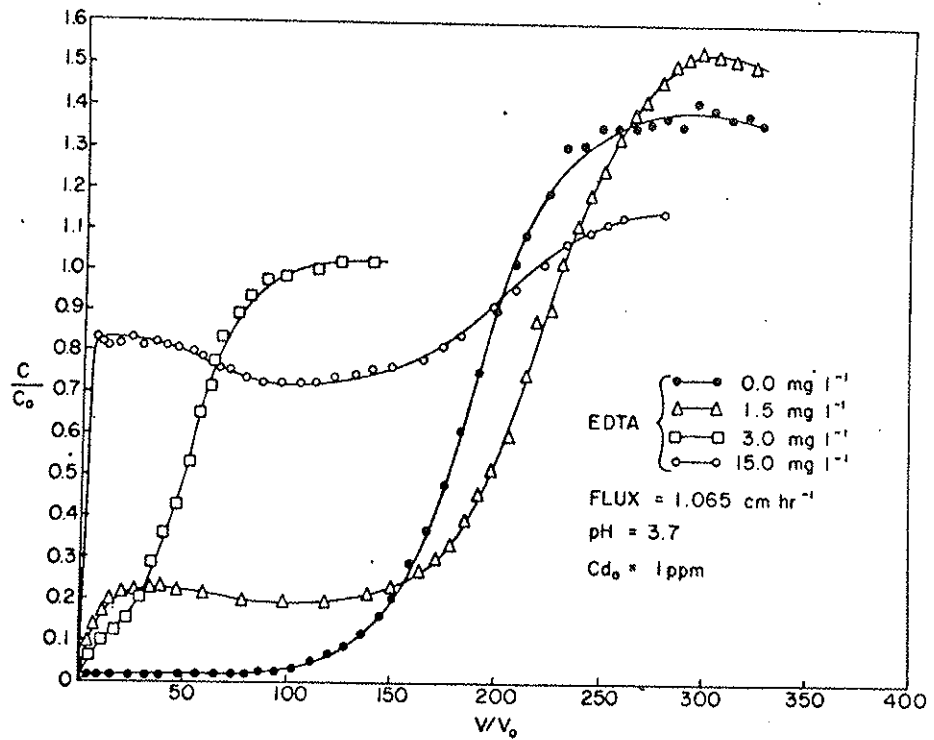


Figure 6. Effect of EDTA concentration on breakthrough curves of Cadmium at a flux of 1.065 cm hr⁻¹, pH 3.7 and initial Cadmium concentration of 1 ppm. EDTA concentration of 0, 1.5, 3.0 and 15.0 mg l⁻¹ correspond to columns 10, 11, 5 and 12 respectively.

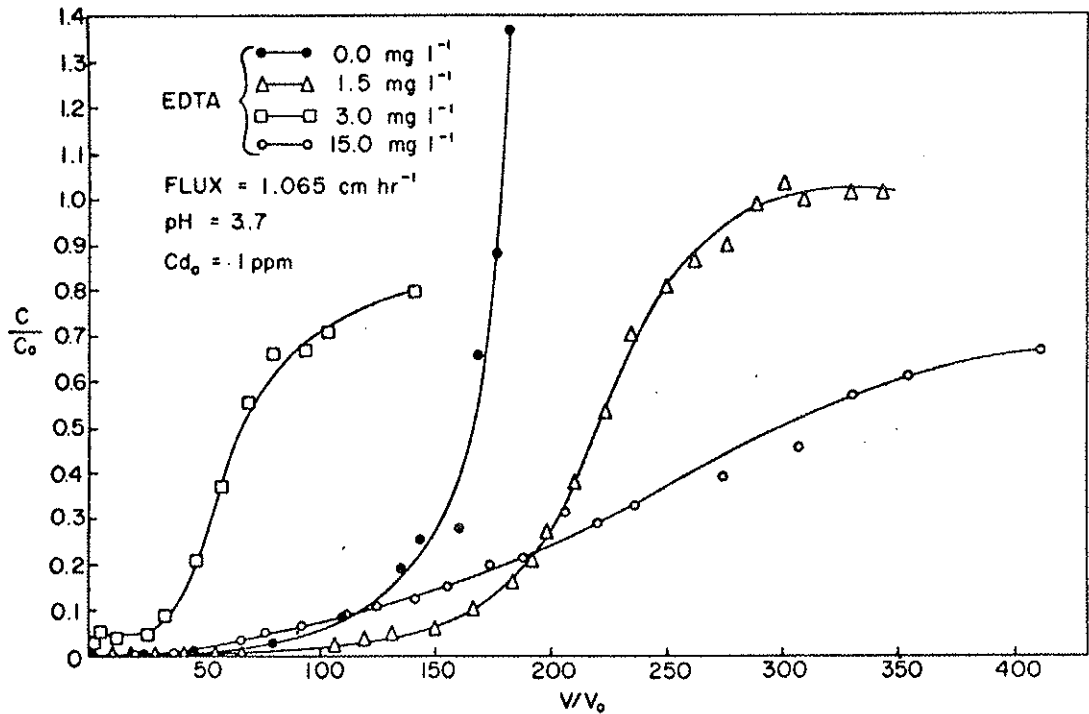


Figure 7. Effect of EDTA concentration on breakthrough of Cadmium ion. Column #10, EDTA = 0 mg l⁻¹, shows very high Cadmium ion concentration having C/C_0 much greater than 1.0

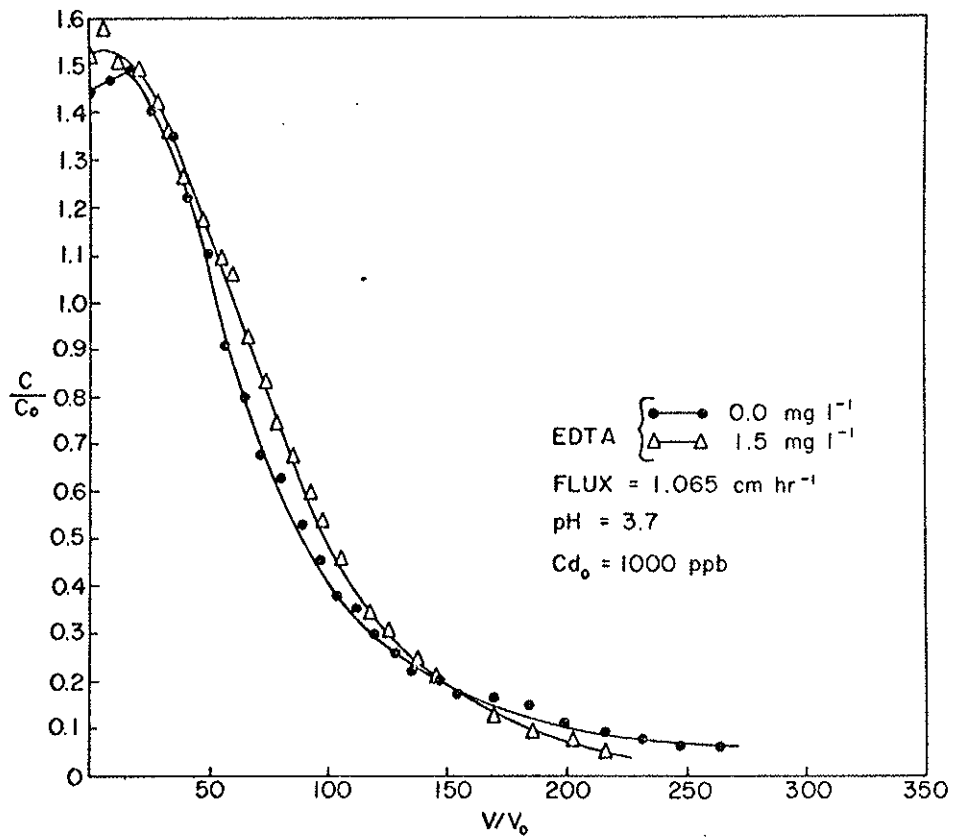


Figure 8. Desorption breakthrough curves for Cadmium showing EDTA effect at a flux of 1.065 cm hr^{-1} , pH of 3.7 and initial Cadmium concentration of 1 ppm. EDTA concentrations of 0.0 and 1.5 mg l^{-1} correspond to columns 10 and 11, respectively.

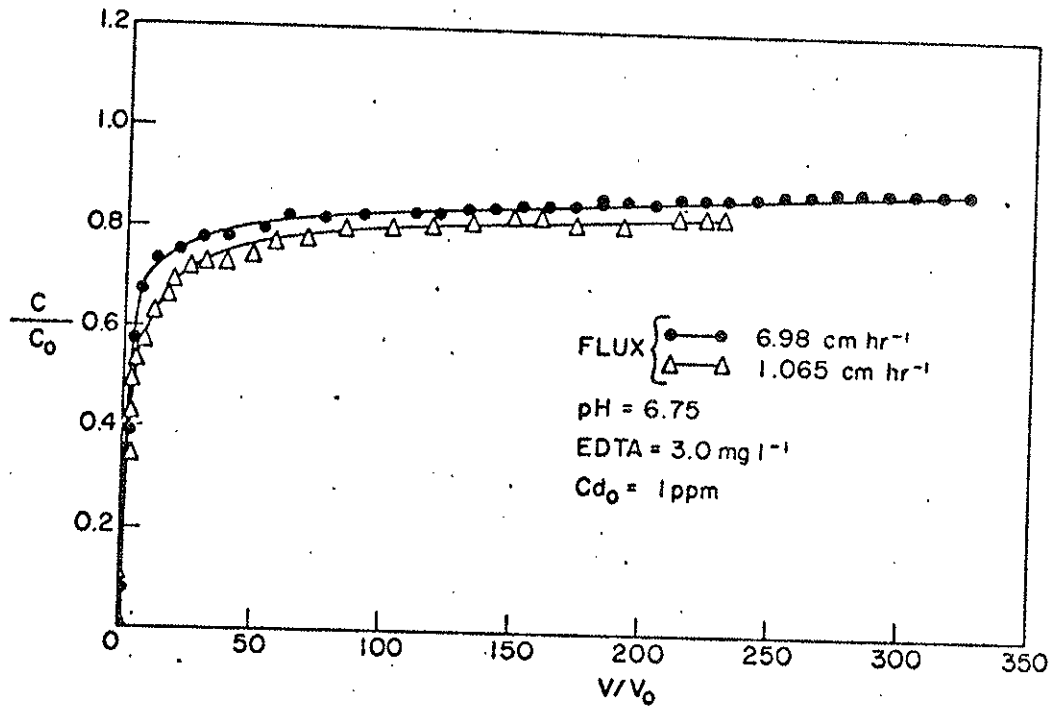


Figure 9. Effect of flux on Cadmium breakthrough curves for columns having a pH of 6.75, 3.0 mg l⁻¹ EDTA and initial Cadmium concentration of 1 ppm. Fluxes of 6.9 and 1.06 cm hr⁻¹ correspond to columns 7 and 6, respectively.

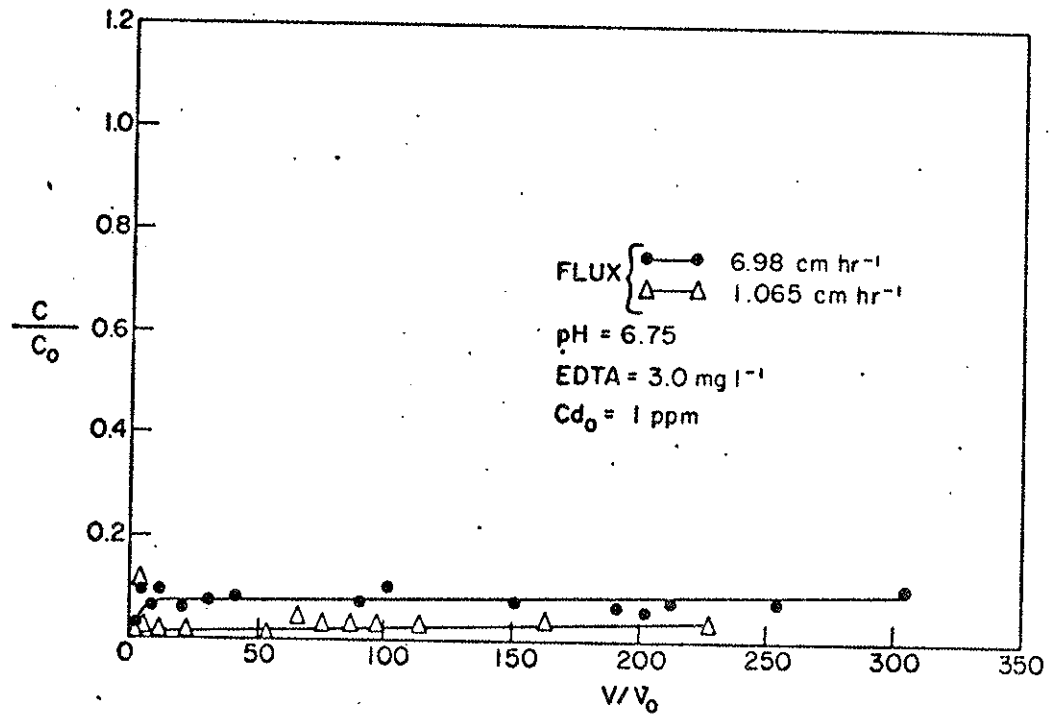


Figure 10. Effect of flux on Cadmium ion breakthrough curve for above condition.

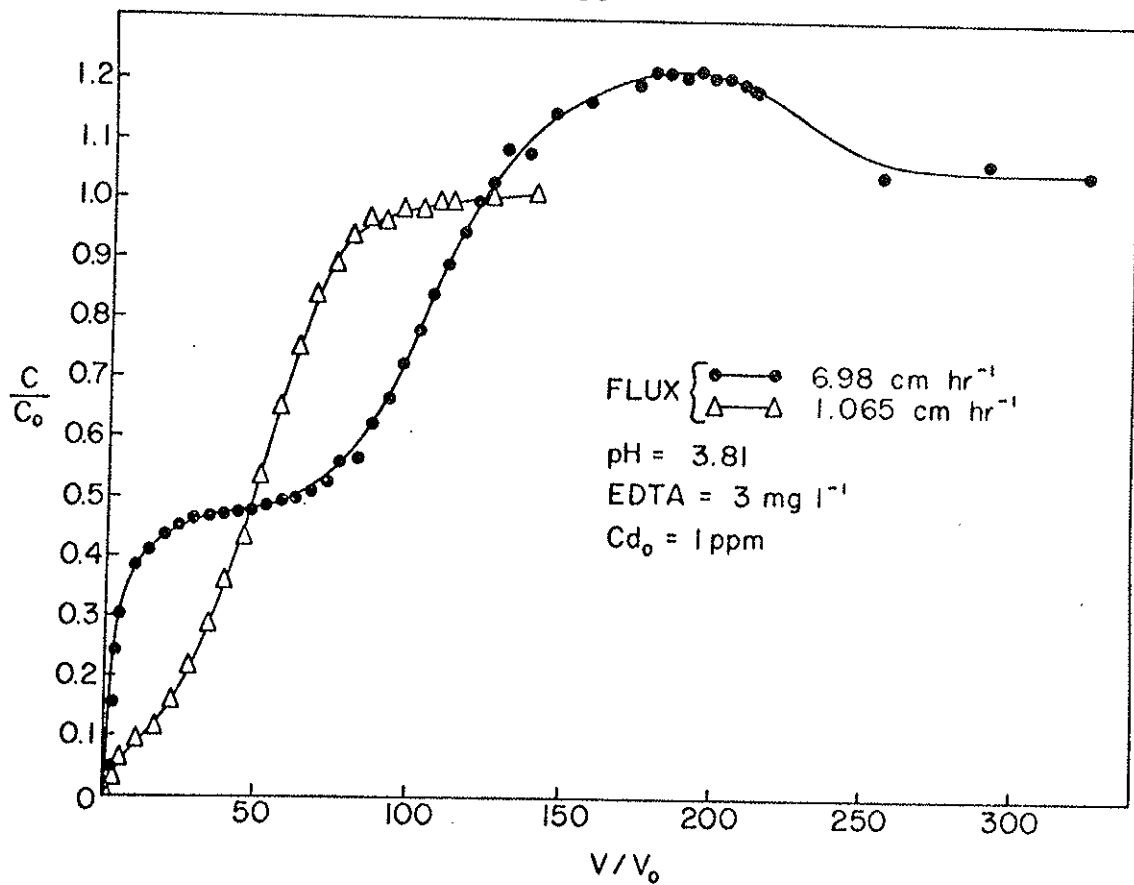


Figure 11. Effect of flux on breakthrough of Cadmium for columns having pH of 3.81, 3 mg l^{-1} EDTA and initial Cadmium concentration of 1 ppm. Fluxes of 6.98 and 1.06 cm hr^{-1} correspond to columns 4 and 5, respectively.

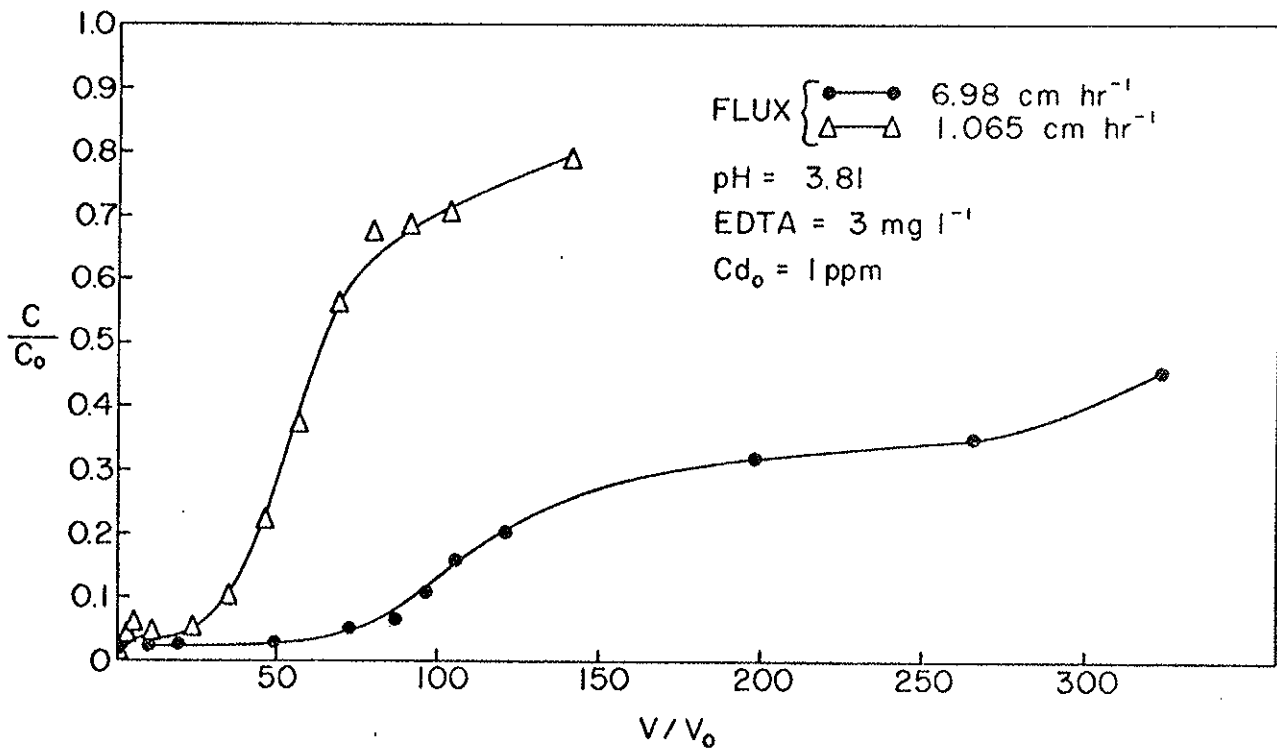


Figure 12. Effect of flux on breakthrough of Cadmium ion for above conditions.

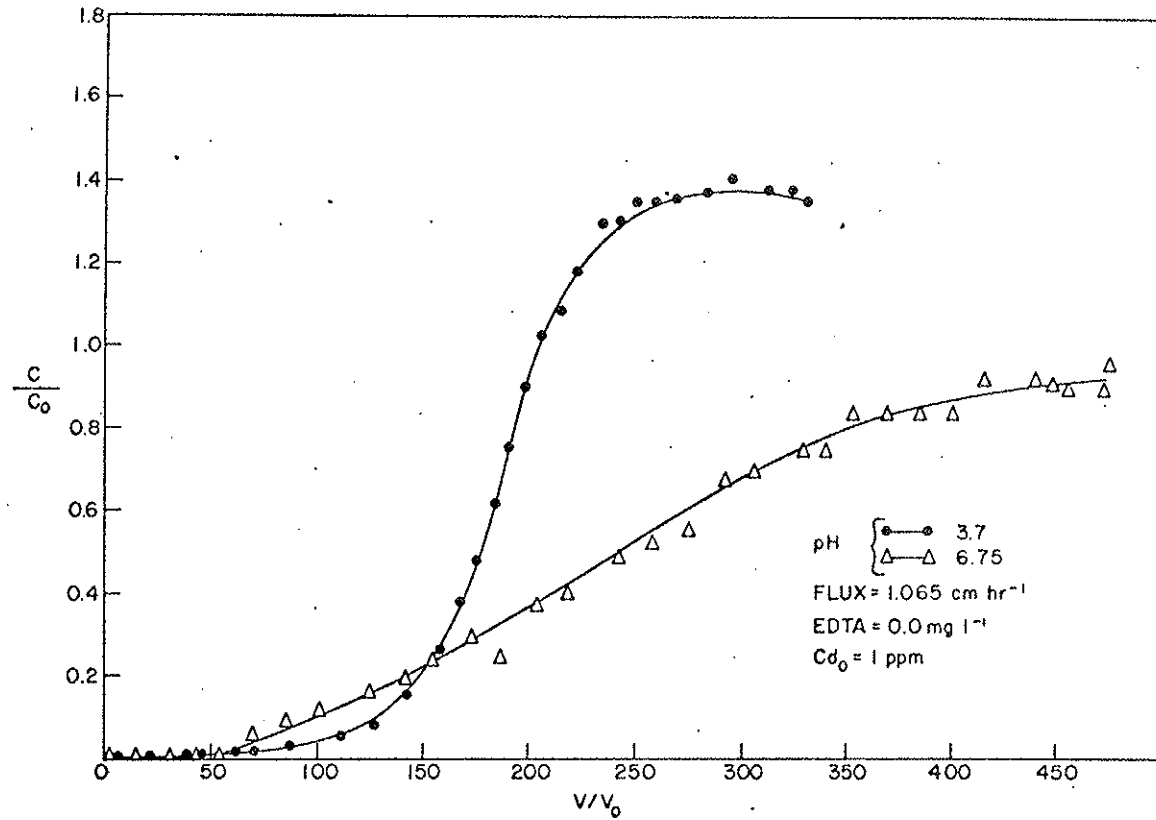


Figure 13. Effect of pH on the Cadmium breakthrough curve for a flux of 1.065 cm hr⁻¹, 0.0 mg l⁻¹ EDTA and initial Cadmium concentration of 1 ppm. Column #10 has a pH of 3.7 and column #13 has a pH of 6.75

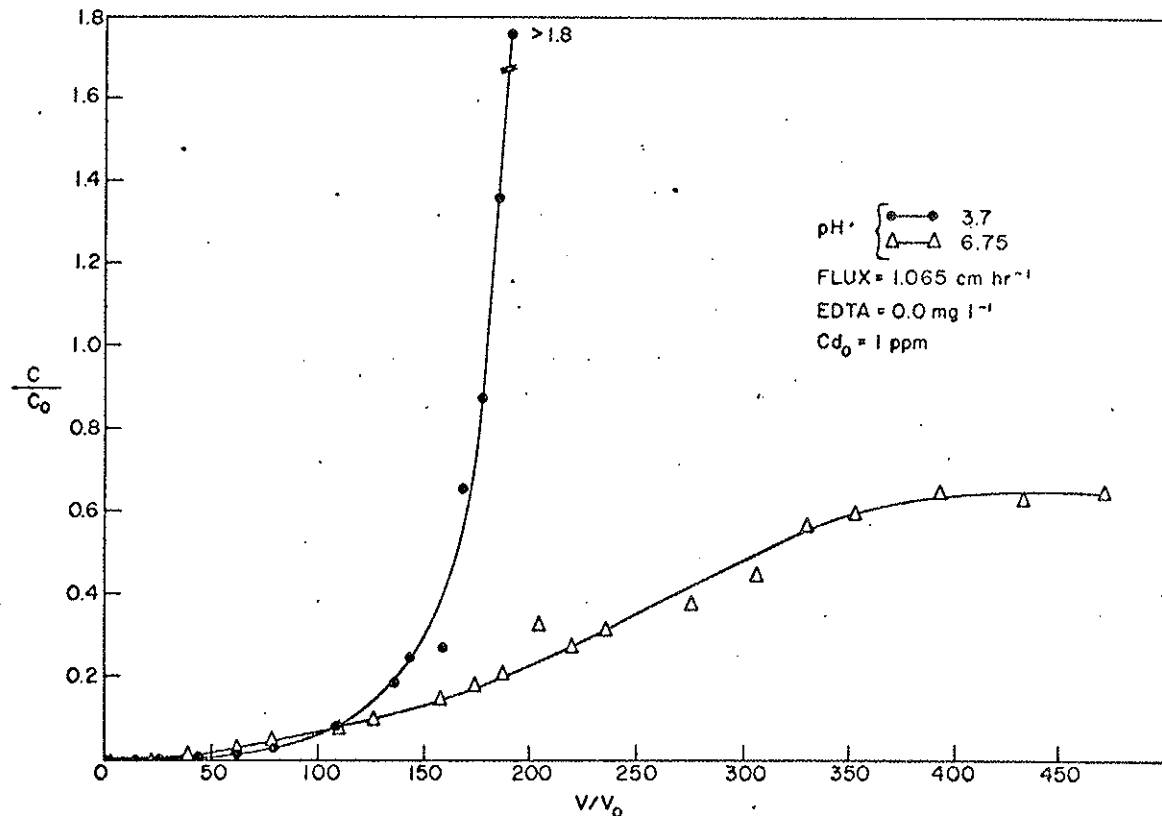


Figure 14. Effect of pH on the cadmium ion breakthrough curve. Column #10, pH 3.7, has Cadmium ion concentrations of C/C_0 greater than 1.8.

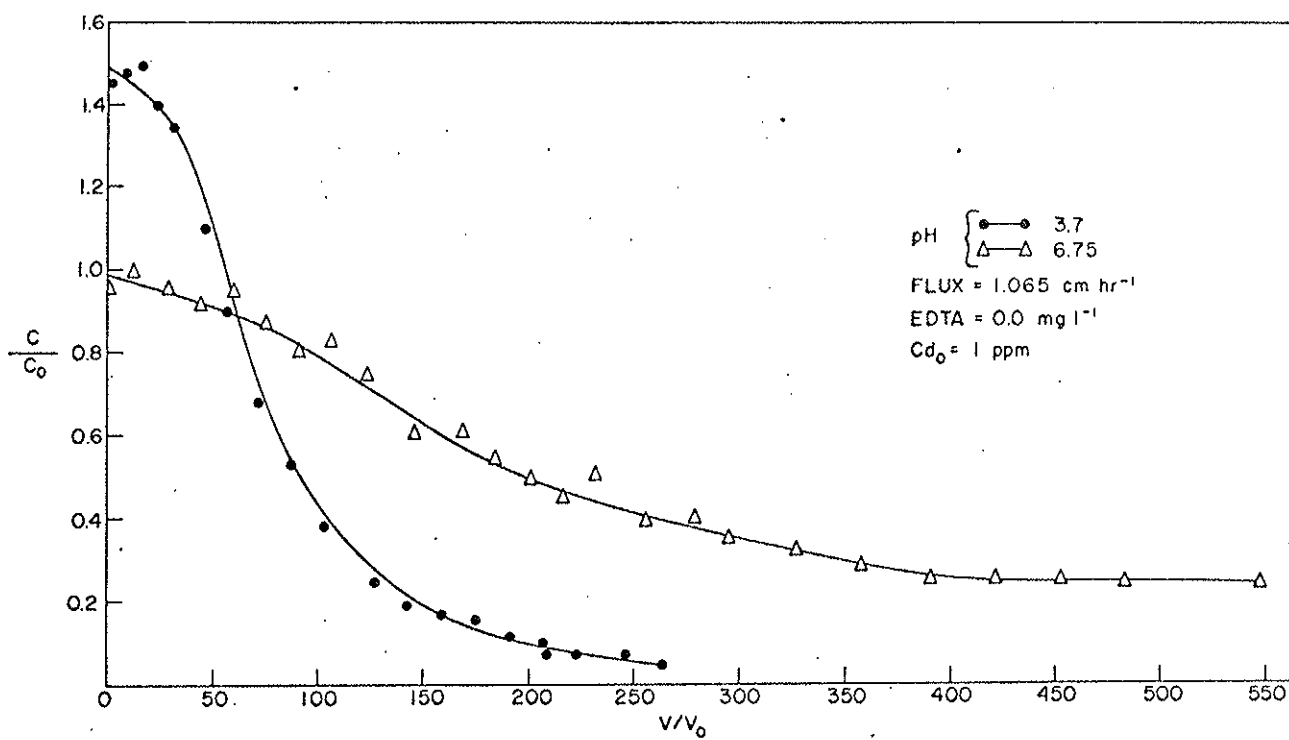


Figure 15. Effect of pH on the Cadmium desorption curve for a flux of 1.065 cm hr⁻¹, 0 mg l⁻¹ EDTA and an initial Cadmium concentration of 1 ppm. Column #10 has a pH of 3.7 and column #13 has a pH of 6.75.

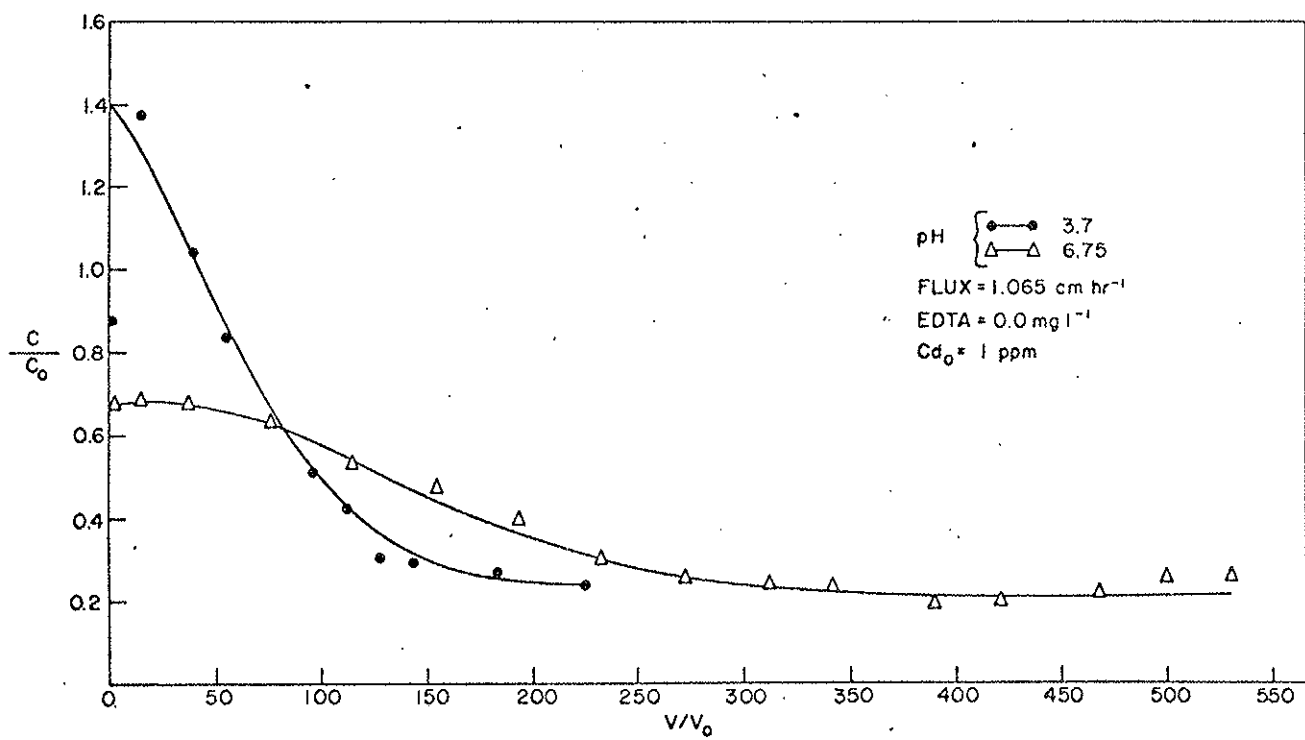


Figure 16. Effect of pH on the Cadmium ion desorption curve.

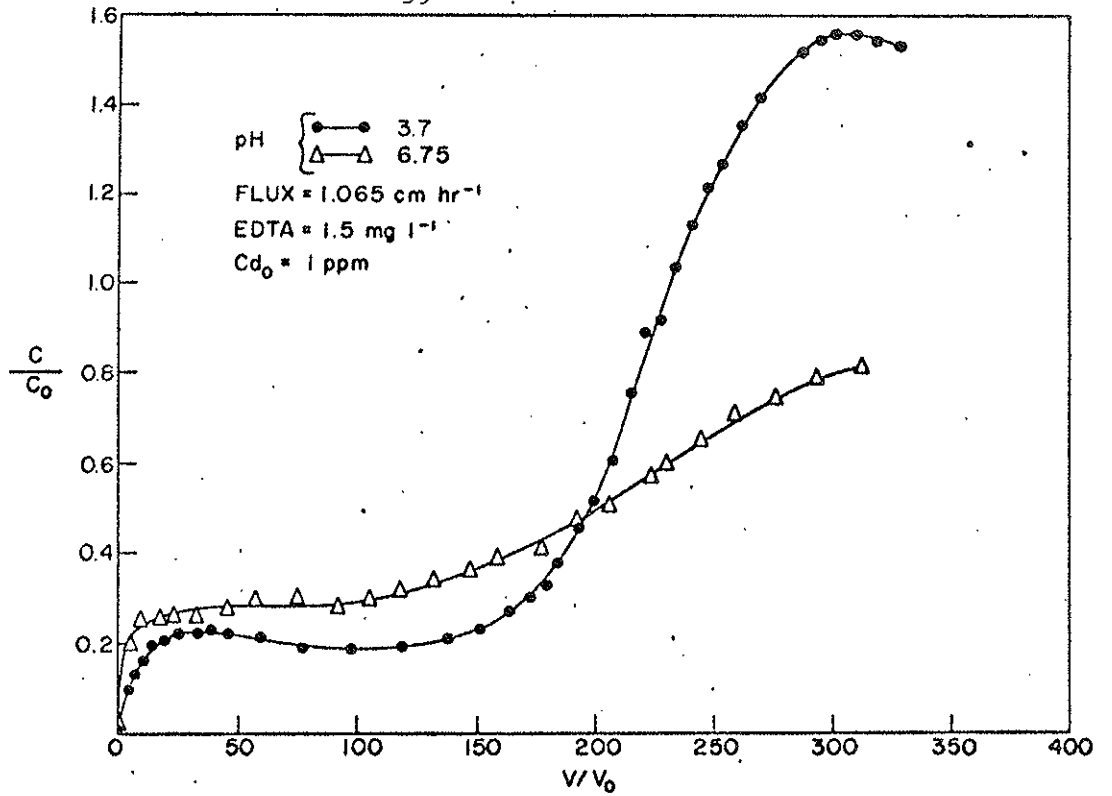


Figure 17. Effect of pH on the Cadmium breakthrough curve for a flux of 1.065 cm hr⁻¹, 1.5 mg l⁻¹ EDTA and 1 ppm initial Cadmium concentration. Column #11 has a pH of 3.7 and column #14 has a pH of 6.75.

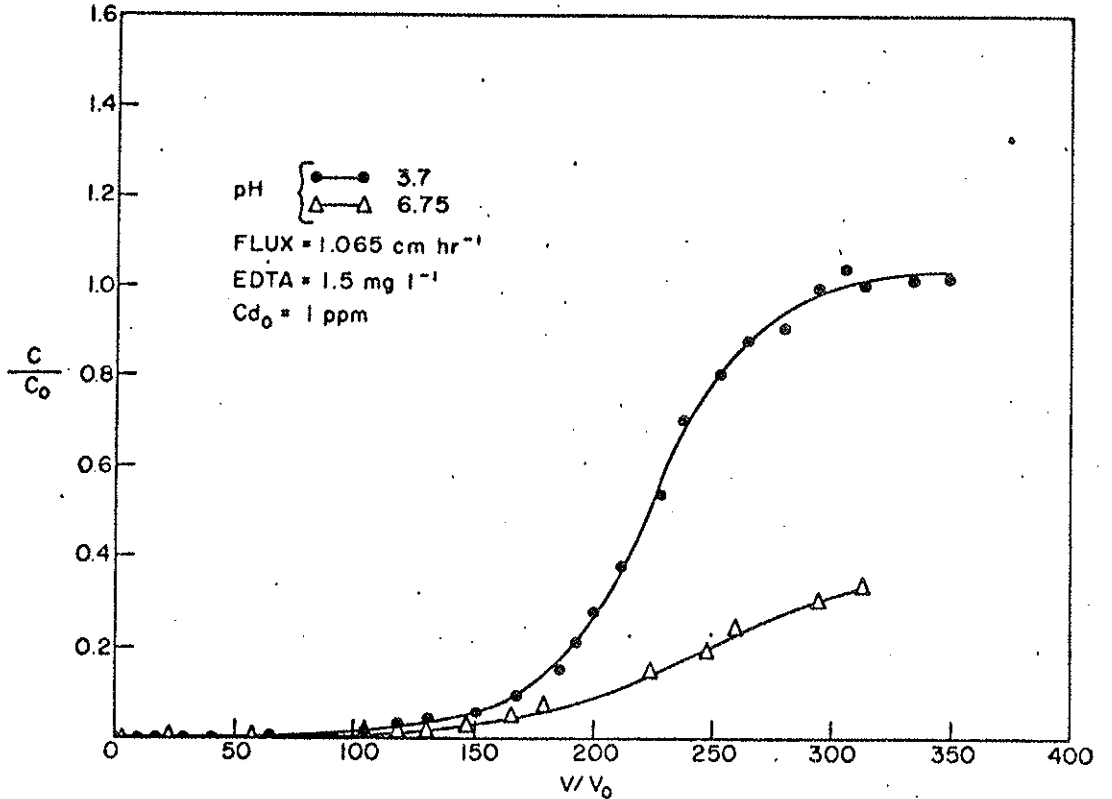


Figure 18. Effect of pH on the Cadmium breakthrough curve.

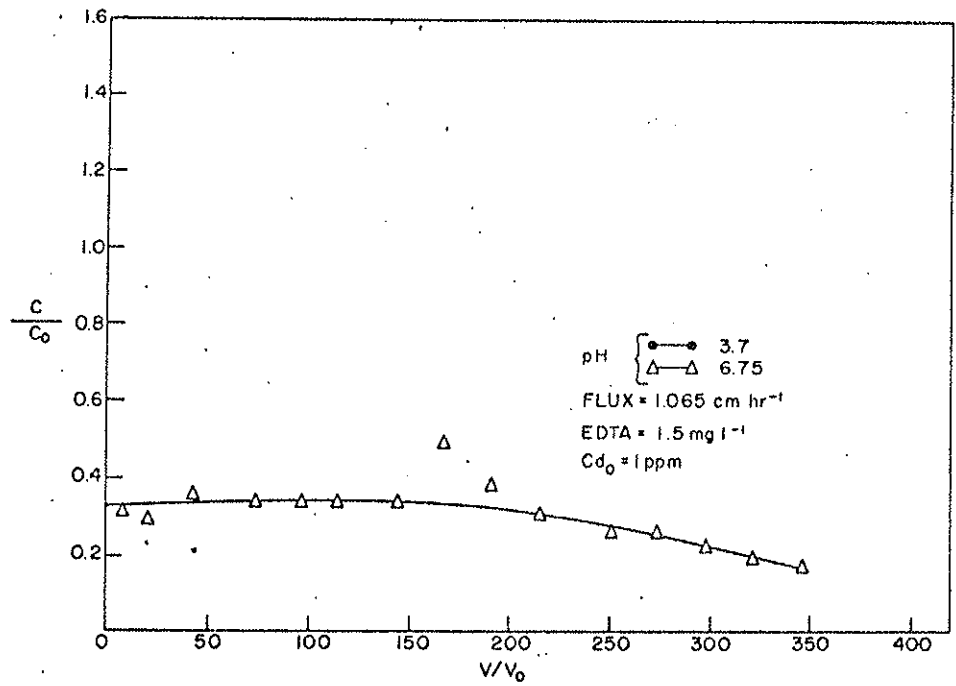


Figure 19. Effect of pH on the Cadmium desorption curve for a flux of 1.065 cm hr^{-1} , 1.5 mg l^{-1} EDTA and initial Cadmium concentration of 1 ppm. Column #11 has a pH of 3.7 and column #14 has a pH of 6.75.

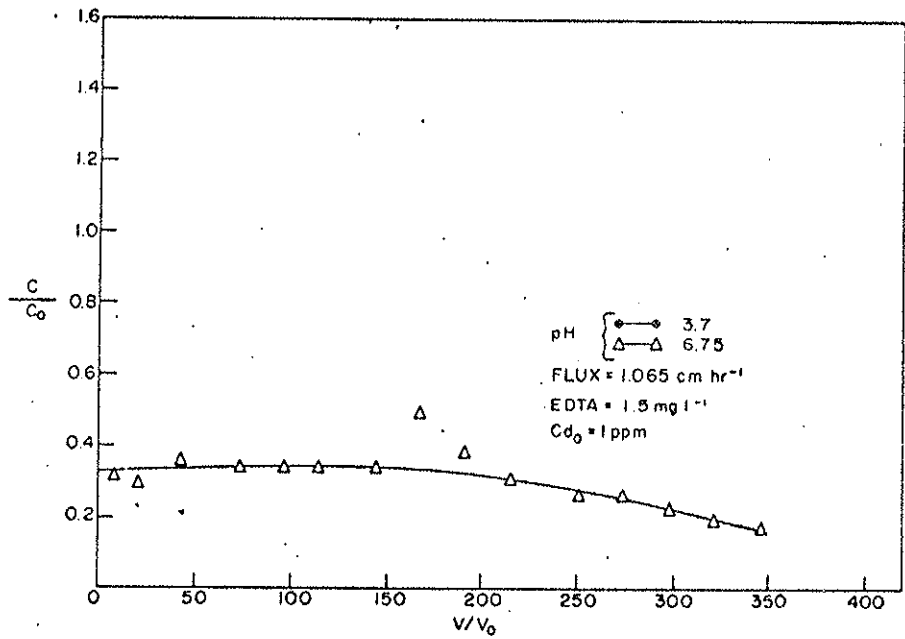


Figure 20. Effect of pH on Cadmium ion desorption. Column #14 (pH 3.7) Cadmium ion concentration was much greater than 1 ppm, so a curve is not illustrated here.

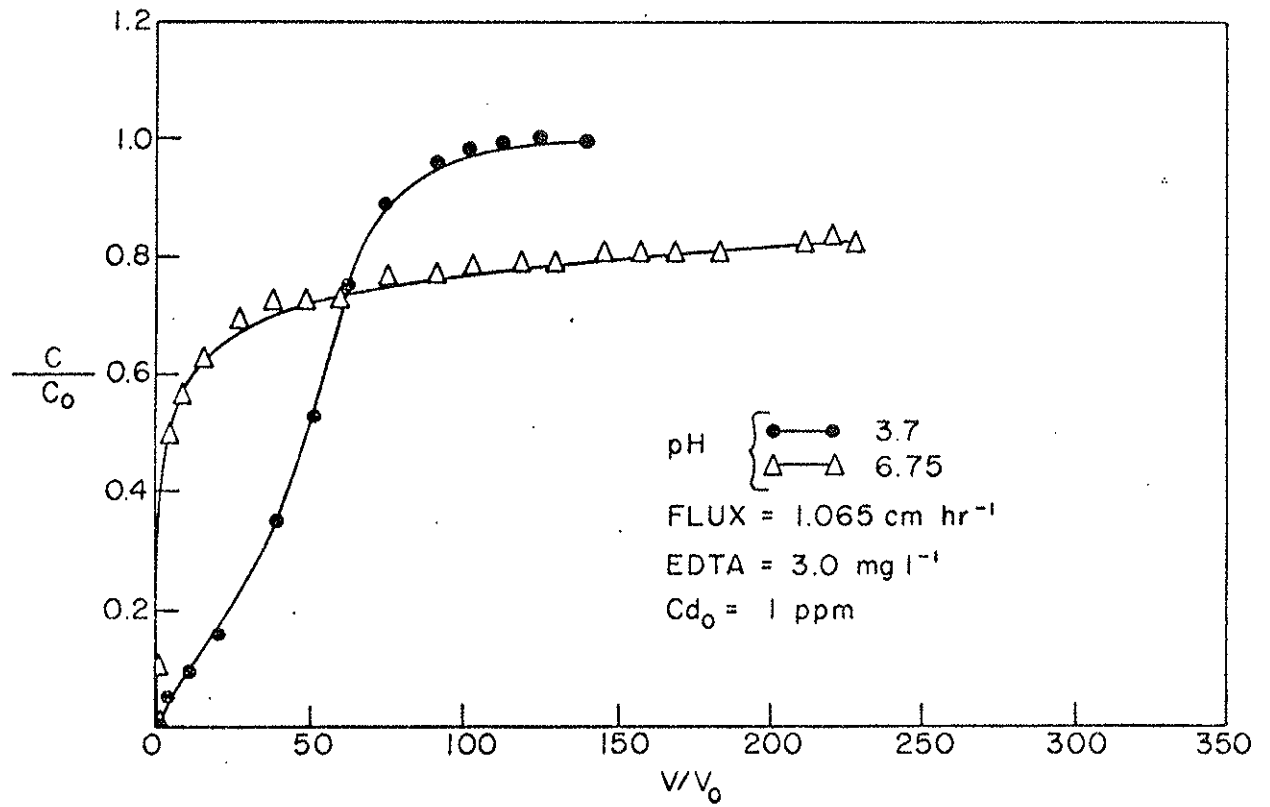


Figure 21. Effect of pH on Cadmium breakthrough curves for a flux of 1.065 cm hr⁻¹, 3.0 mg l⁻¹ EDTA and initial Cadmium concentration of 1 ppm. Column #5 has a pH of 3.7 and column #6 has a pH of 6.75.

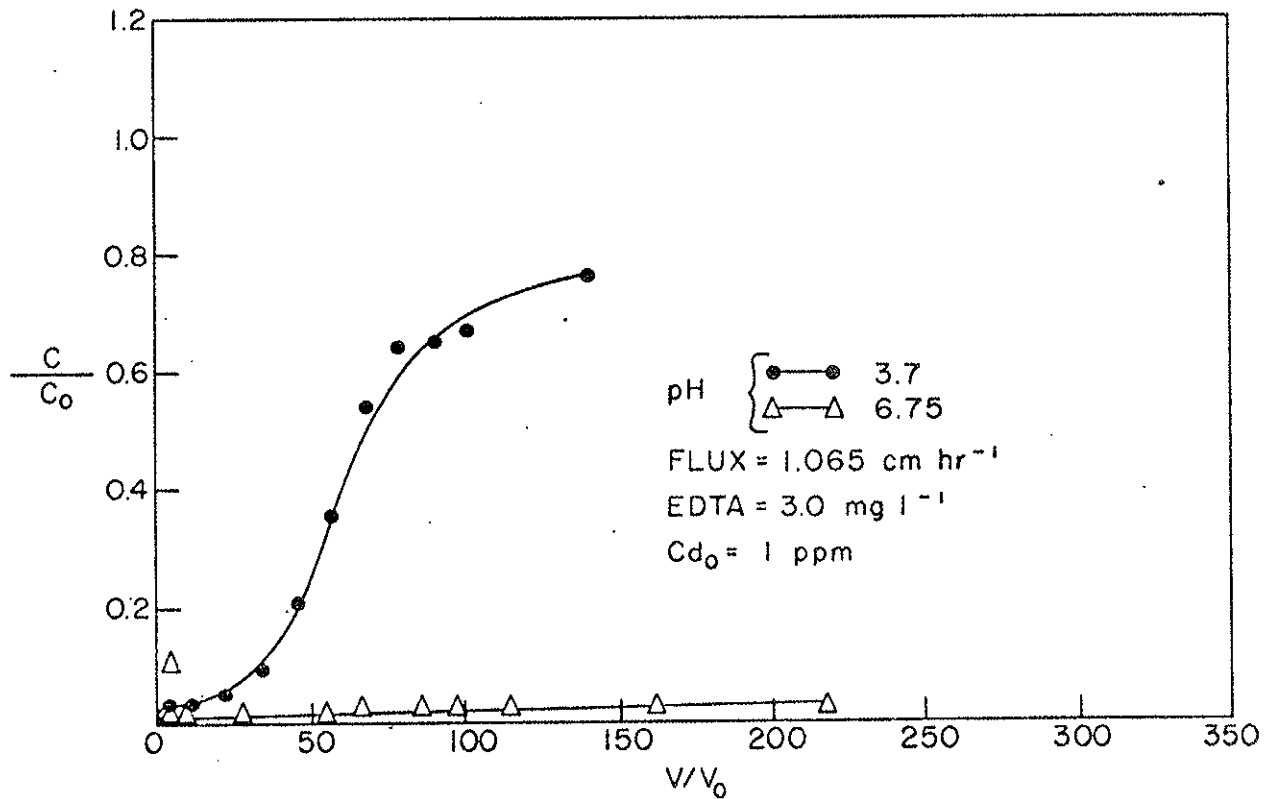


Figure 22. Effect of pH on Cadmium ion breakthrough curve.

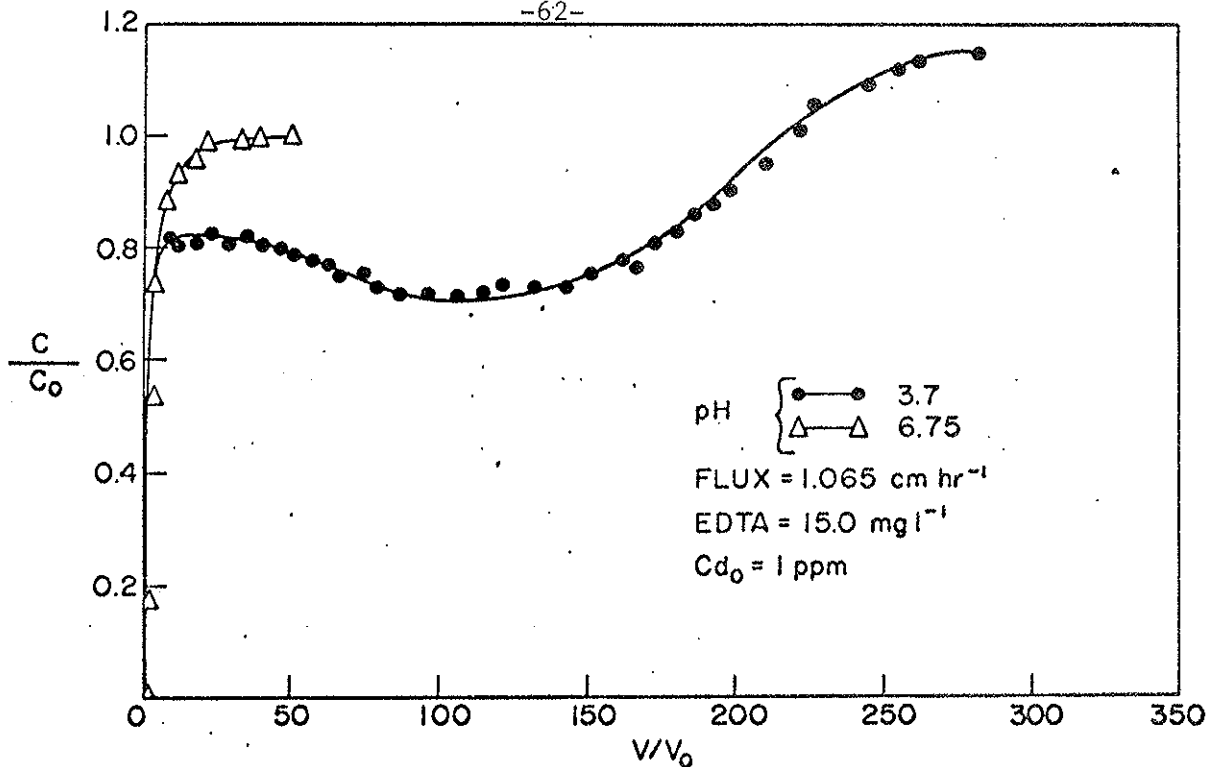


Figure 23. Effect of pH on Cadmium breakthrough for a flux of 1.065 cm hr⁻¹, 15 mg l⁻¹ EDTA and 1 ppm initial Cadmium concentration. Column #12 is pH 3.7 and column #15 is pH 6.75.

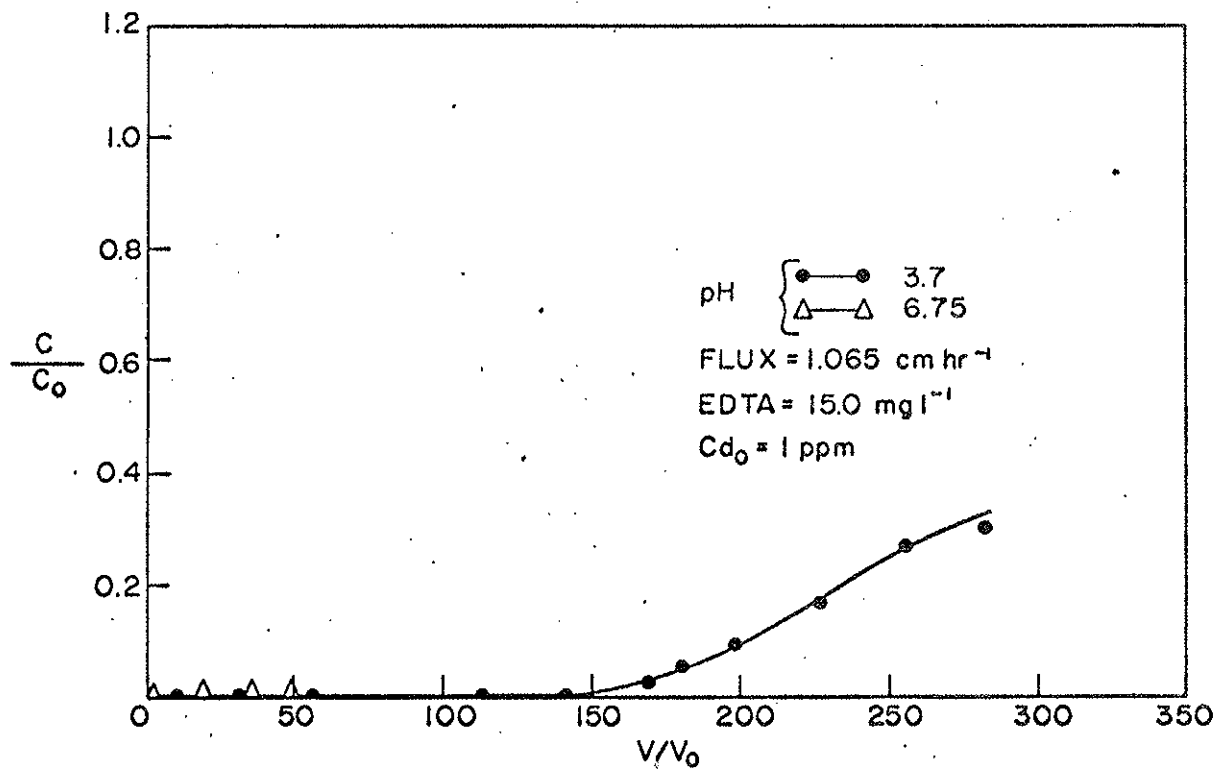


Figure 24. Effect of pH on Cadmium ion breakthrough.

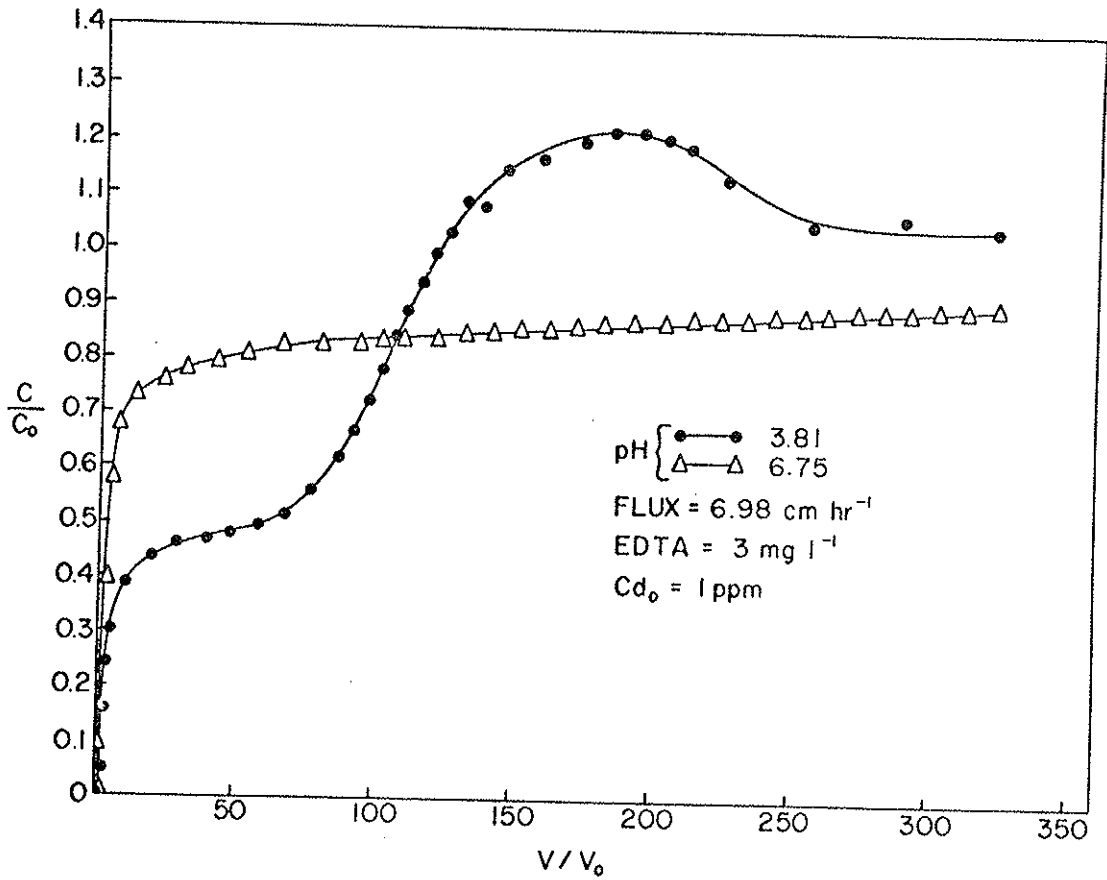


Figure 25. Effect of pH on breakthrough of Cadmium for a flux of 6.98 cm hr⁻¹, 3 mg l⁻¹ EDTA and initial Cadmium concentration of 1 ppm. Column #4 has a pH of 3.81 and column #7 has a pH of 6.75.

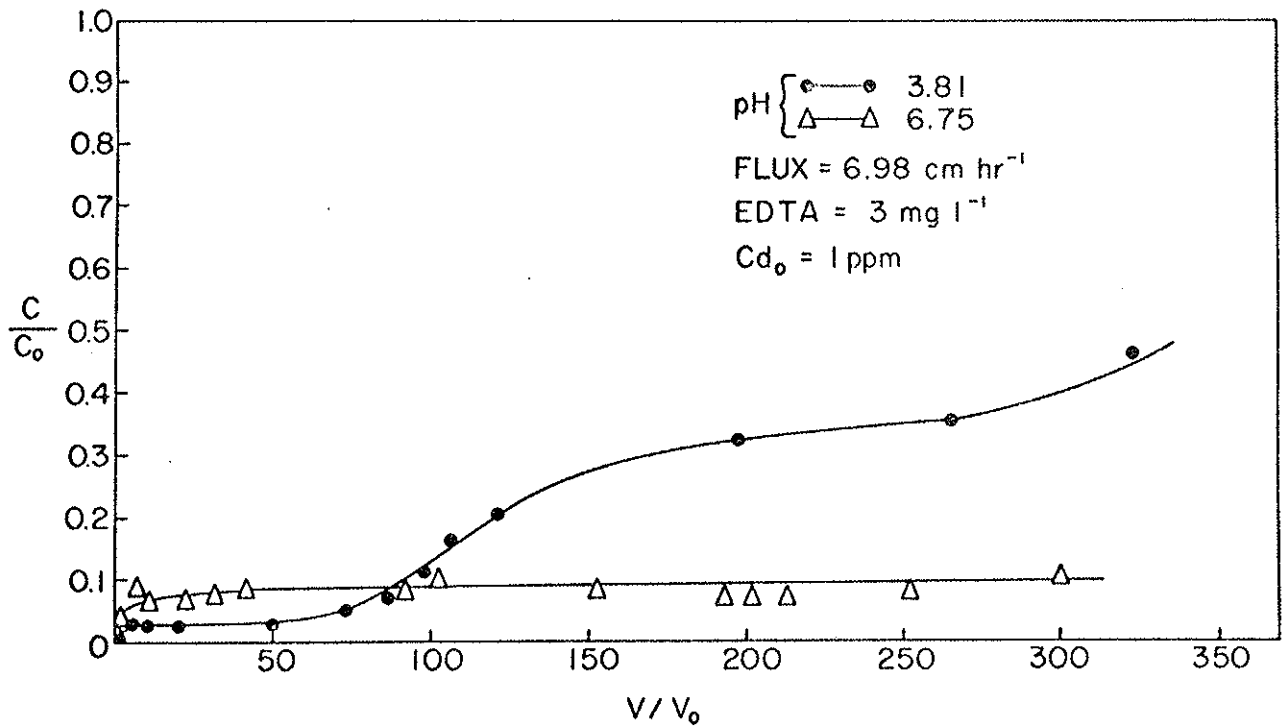


Figure 26. Effect of pH on breakthrough of Cadmium ion.

Breakthrough Curves, Group Two: The soil is Hanford sandy loam and the influent Cadmium concentration is 100 ppb.

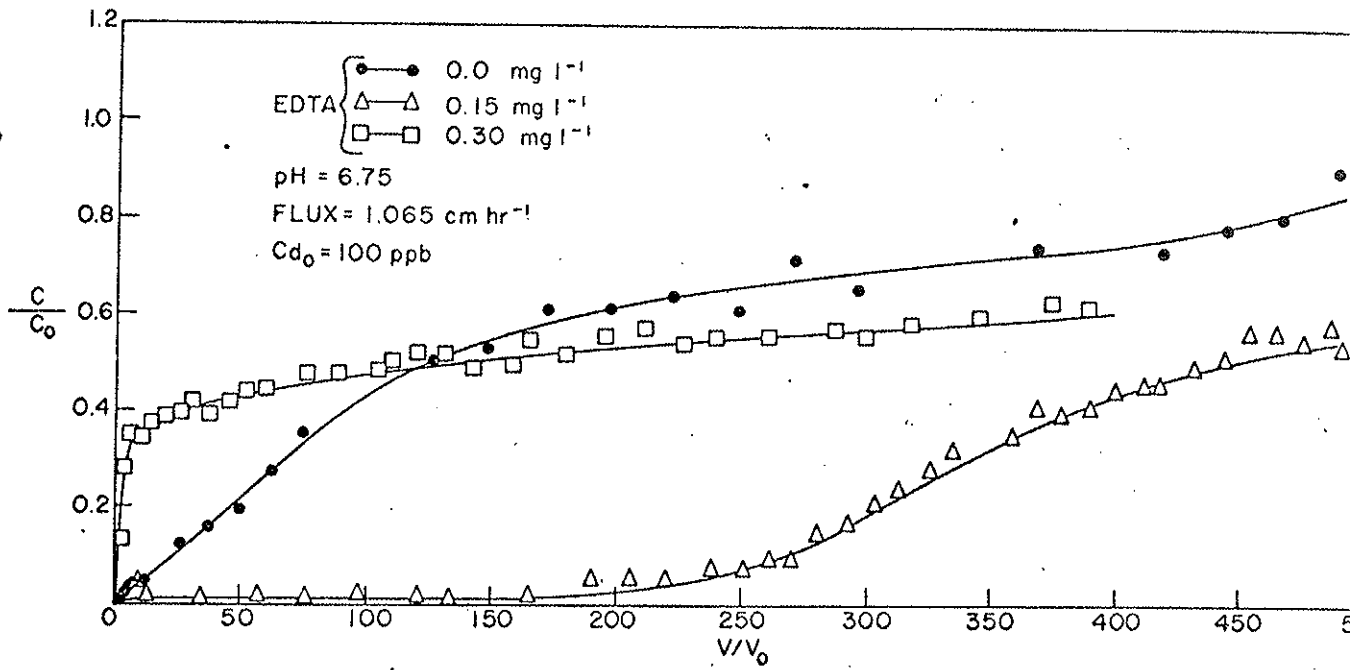


Figure 27. Effect of EDTA concentration on Cadmium breakthrough for a flux of 1.065 cm hr^{-1} , pH of 6.75 and initial Cadmium concentration of 100 ppb. EDTA concentrations of 0.0, 0.15 and 0.30 mg l^{-1} correspond to columns 24, 19 and 8, respectively.

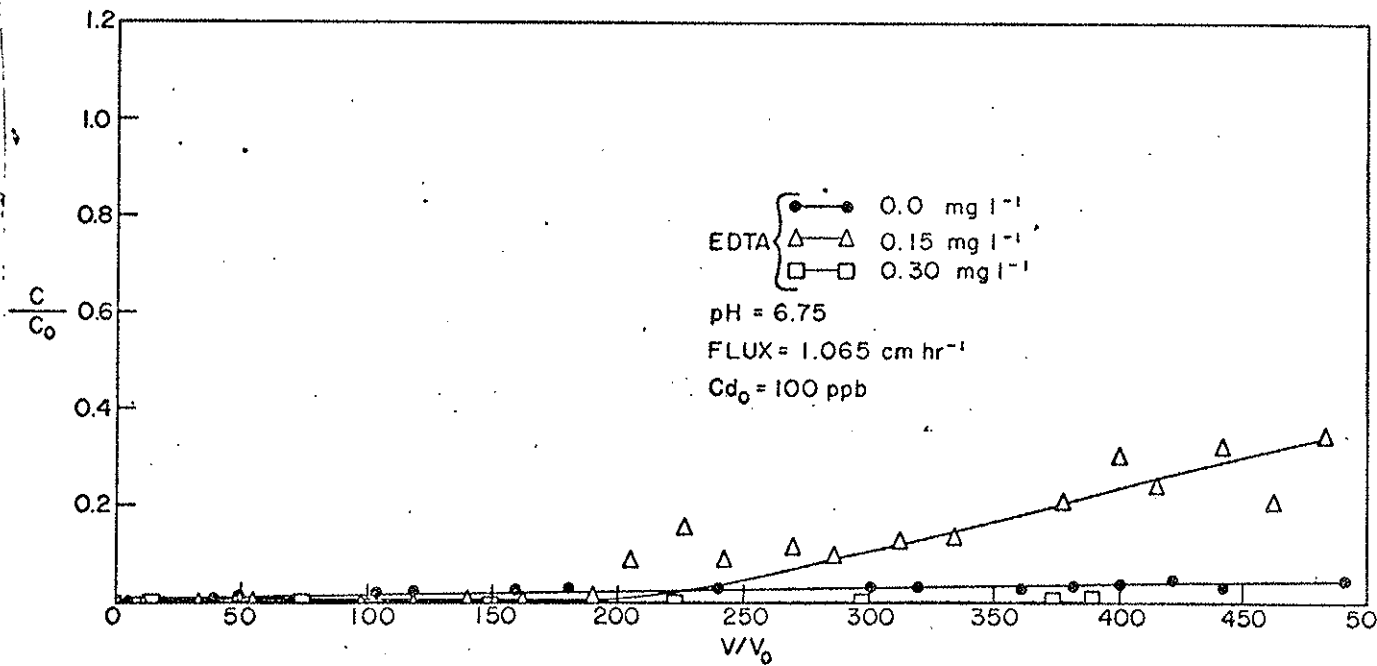


Figure 28. Effect of EDTA concentration on Cadmium ion breakthrough.

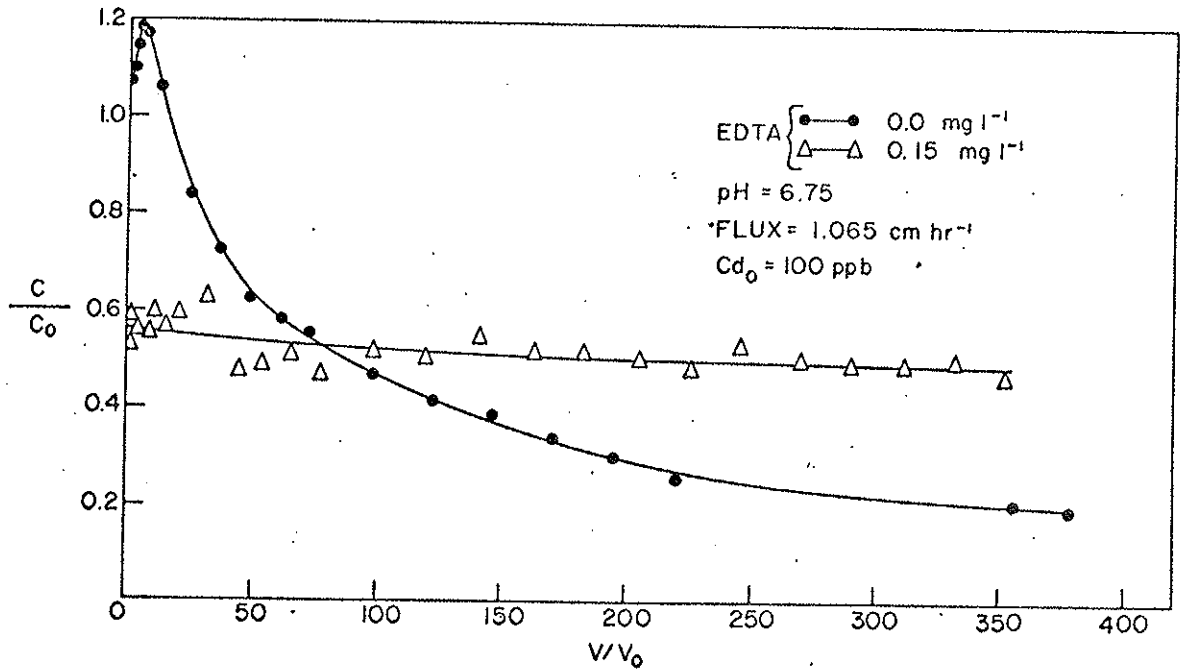


Figure 29. Effect of EDTA concentration on Cadmium desorption for a flux of 1.065 cm hr⁻¹, pH of 6.75 and initial Cadmium concentration of 100 ppb. Column #24 has 0.0 mg l⁻¹ EDTA and column #19 has 0.15 mg l⁻¹ EDTA.

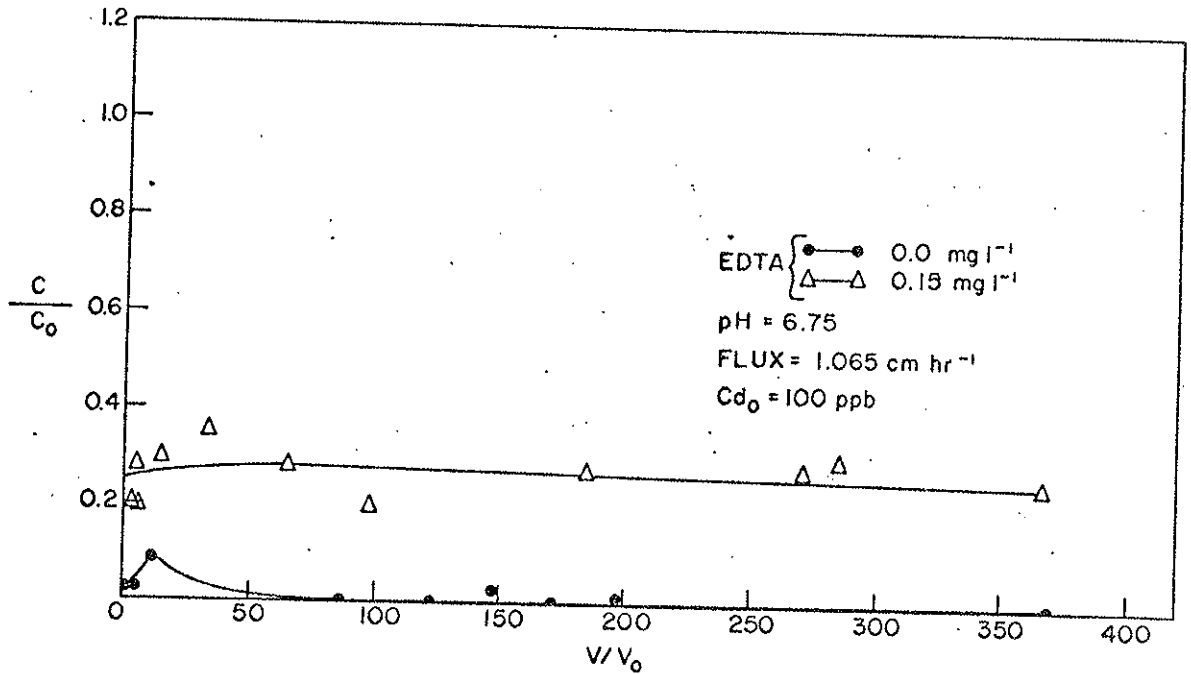


Figure 30. Effect of EDTA concentration on Cadmium ion desorption.

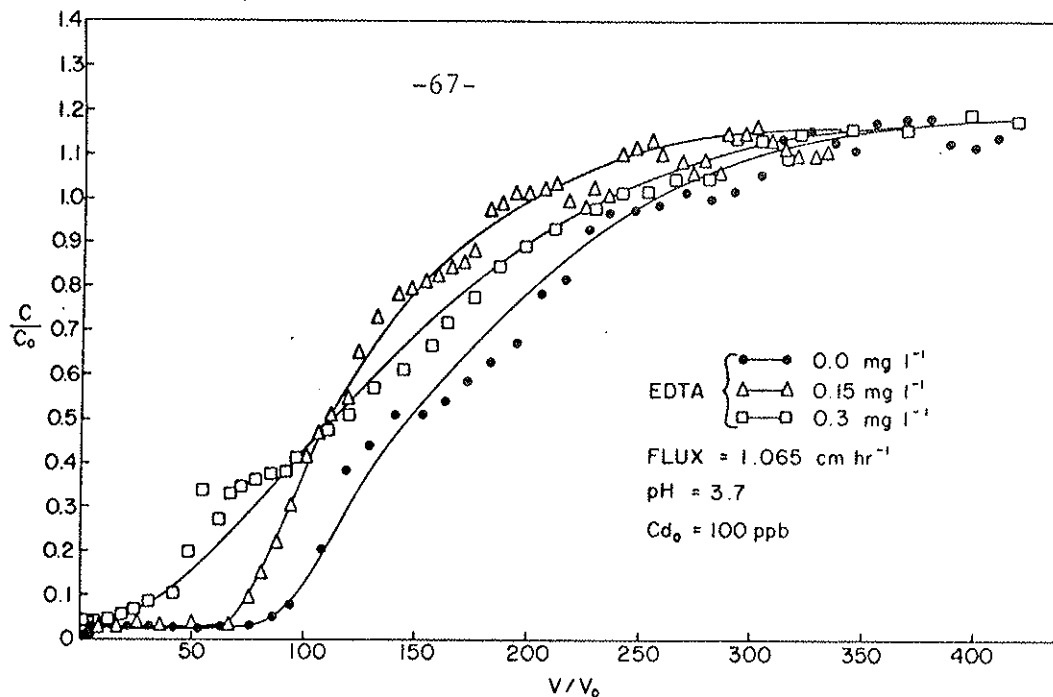


Figure 31. Effect of EDTA concentration on breakthrough of Cadmium for a flux of 1.065 cm hr⁻¹, pH of 3.7 and initial Cadmium concentration of 100 ppb. EDTA concentrations of 0.0, 0.15 and 0.3 mg l⁻¹ correspond to columns 21, 17 and 16, respectively.

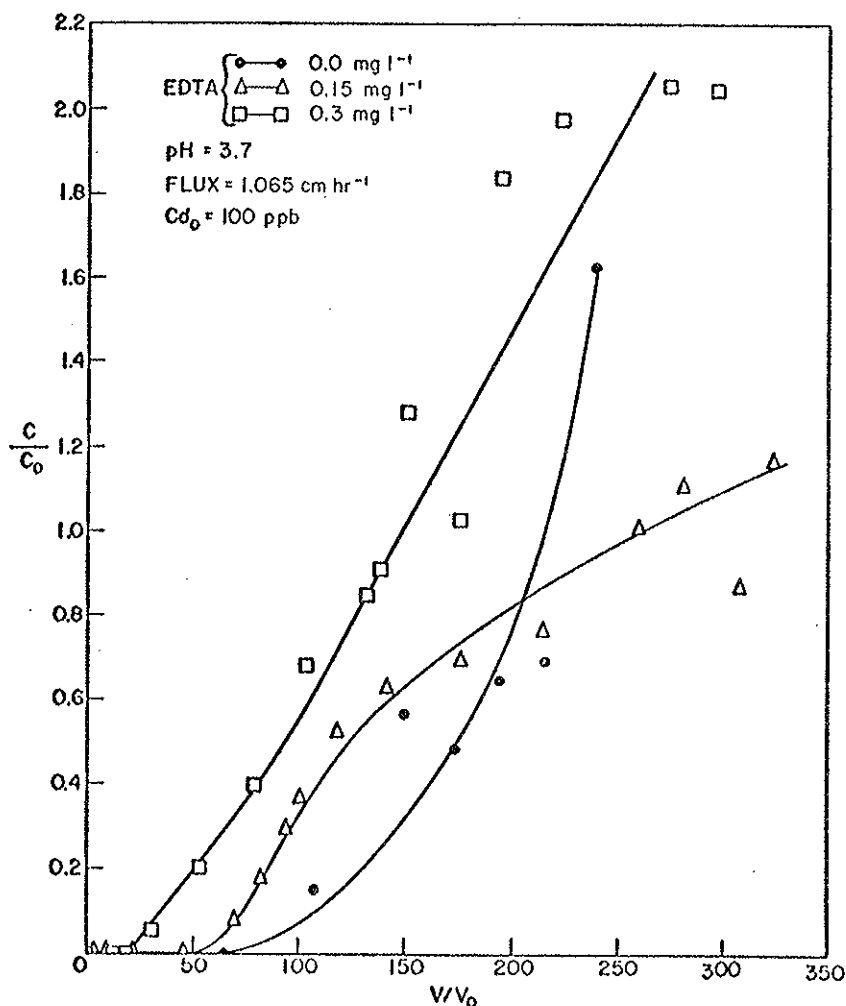


Figure 32. Effect of EDTA concentration on breakthrough of Cadmium ion.

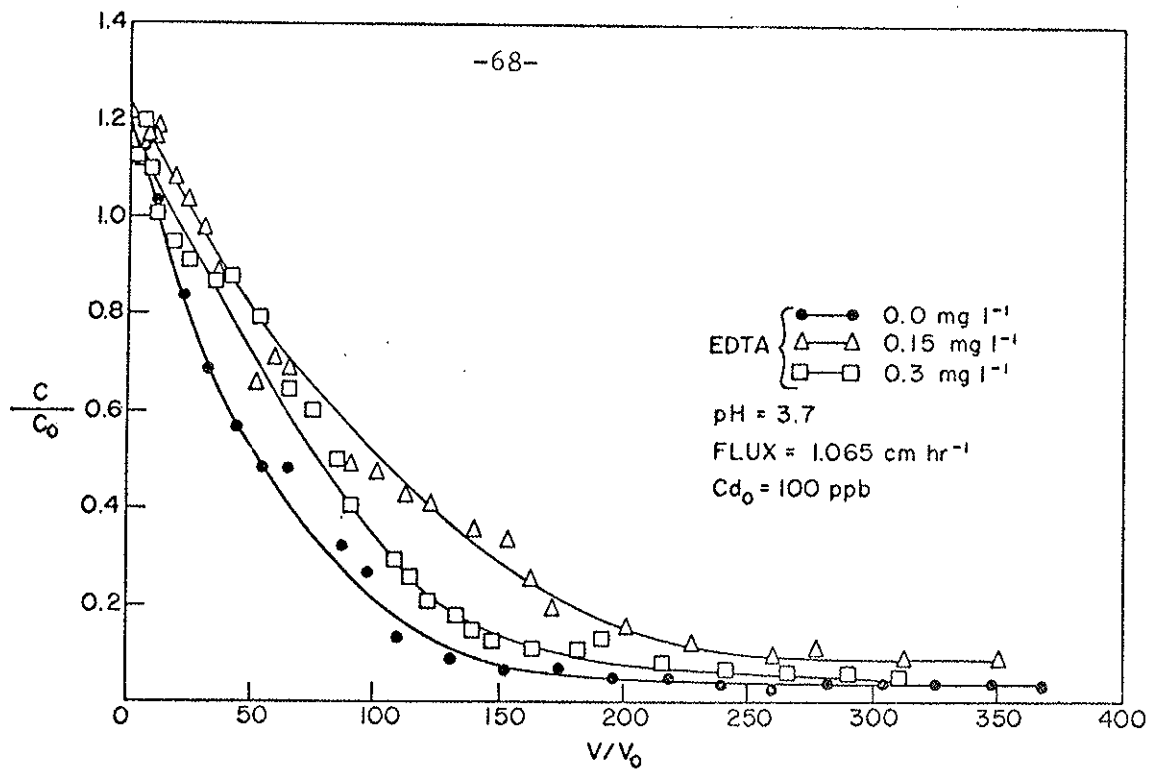


Figure 33. Effect of EDTA concentration on Cadmium desorption for columns having a pH of 3.7, flux of 1.065 cm hr⁻¹ and initial Cadmium concentration of 100 ppb. EDTA concentrations of 0.0, 0.15 and 0.3 mg l⁻¹ correspond to columns 21, 17 and 16, respectively.

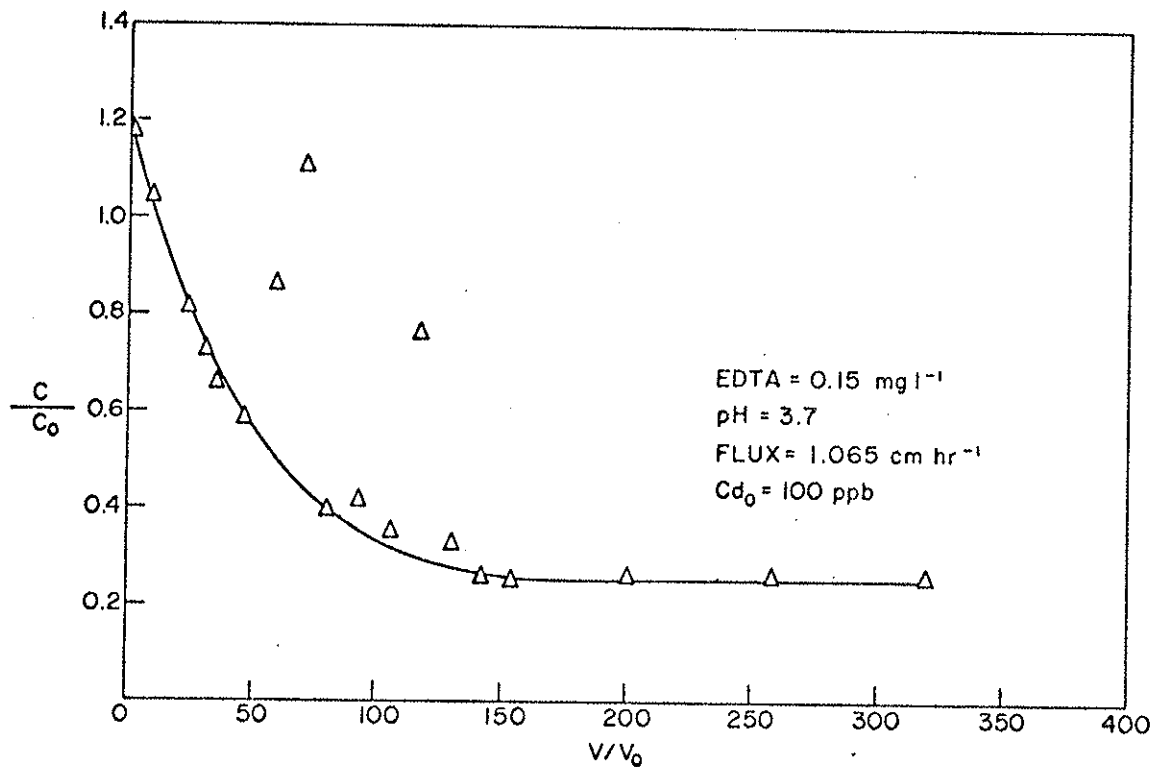


Figure 34. Cadmium ion desorption curve for column #17. Cadmium ion concentrations were much greater than $C/C_0 = 1$ for columns #16 and #21, so the data are not illustrated here.

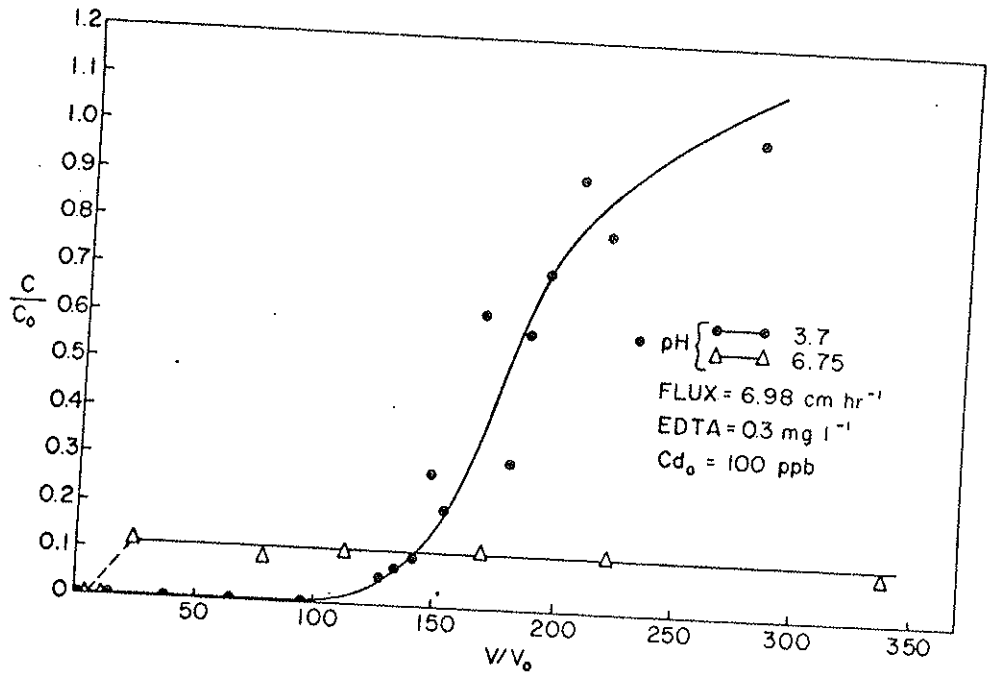


Figure 35. Effect of pH on breakthrough of Cadmium for a flux of 6.98 cm hr⁻¹, 0.3 mg l⁻¹ EDTA and initial Cadmium ion concentration of 100 ppb. Column #18 is pH 3.7 and column #9 is pH 6.75.

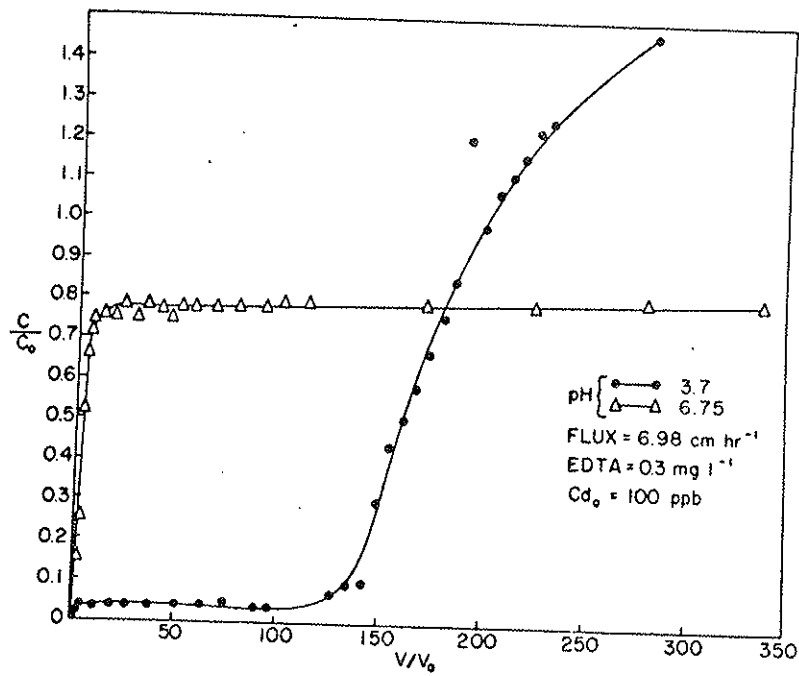


Figure 36. Effect of pH on breakthrough on Cadmium ion.

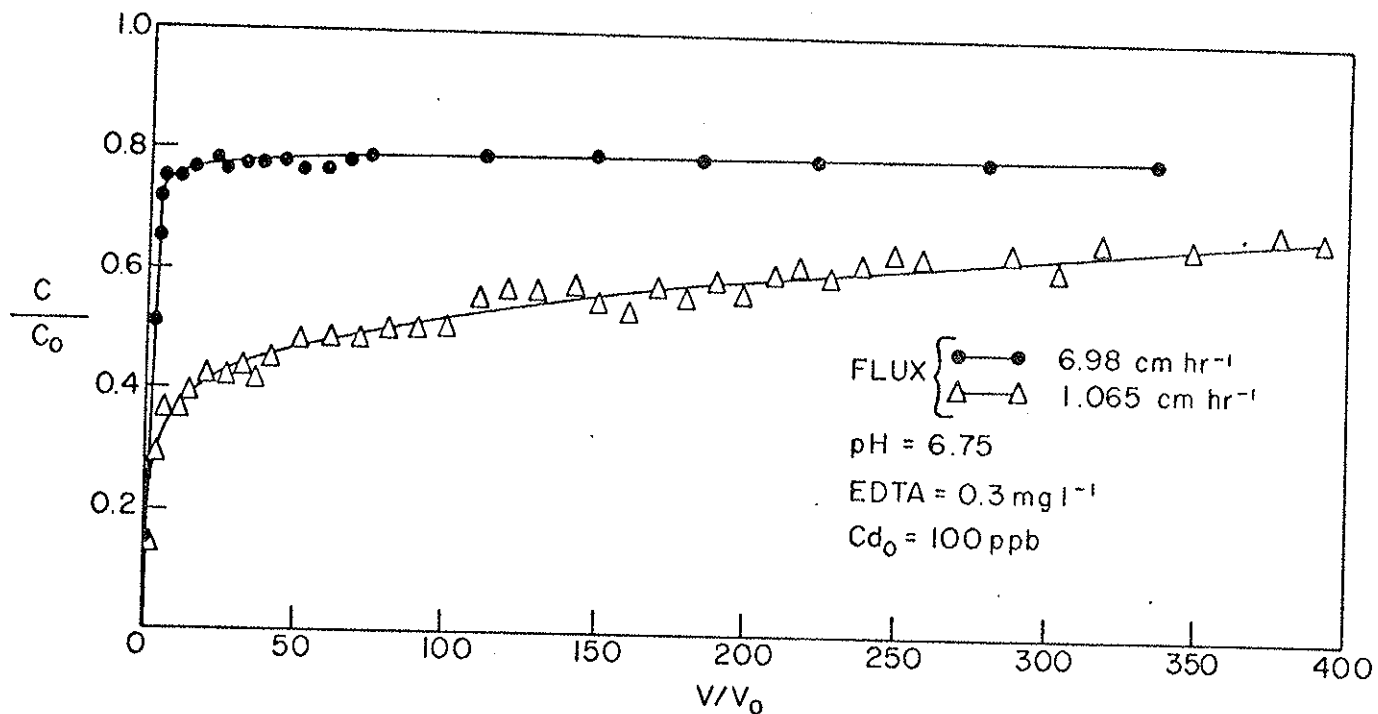


Figure 37. Effect of flux on Cadmium breakthrough for columns having pH of 6.75, 0.3 mg l⁻¹ EDTA and 100 ppb initial Cadmium concentration. Fluxes of 6.98 and 1.065 correspond to columns 9 and 8, respectively.

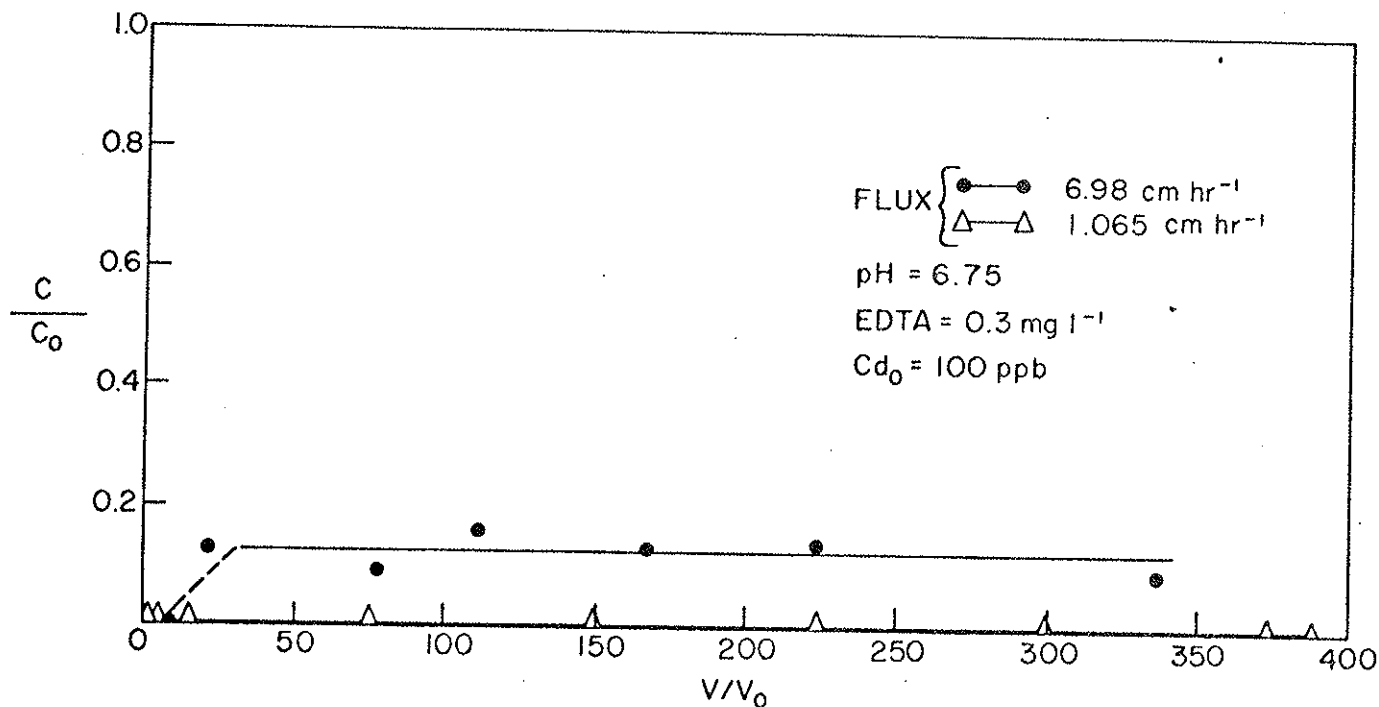


Figure 38. Effect of flux on Cadmium ion breakthrough.

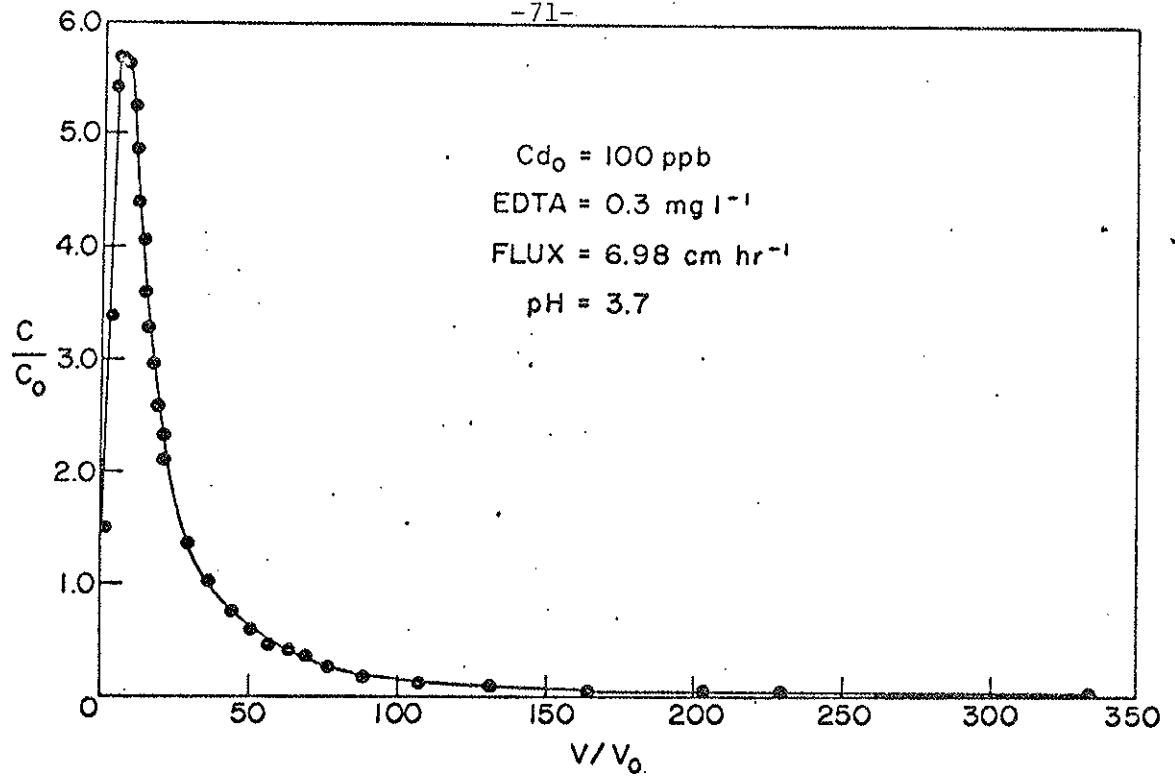


Figure 39. Breakthrough curve of desorption Cadmium from column #18.

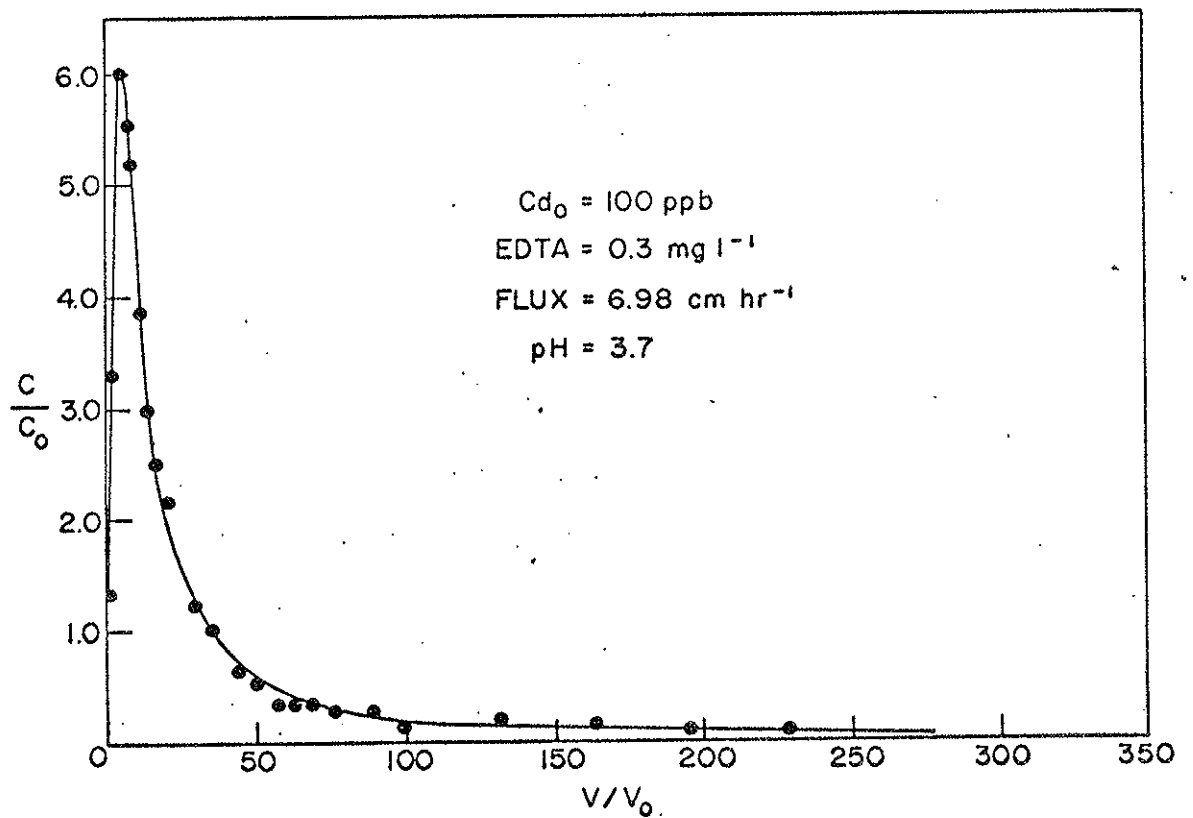


Figure 40. Cadmium ion desorption from column #18. The high correlation between these two curves shows that the effluent is entirely ionic Cadmium.

Breakthrough Curves, Group Three: This group shows the breakthrough of Cadmium for Yolo soil and compares the results with Hanford soil.

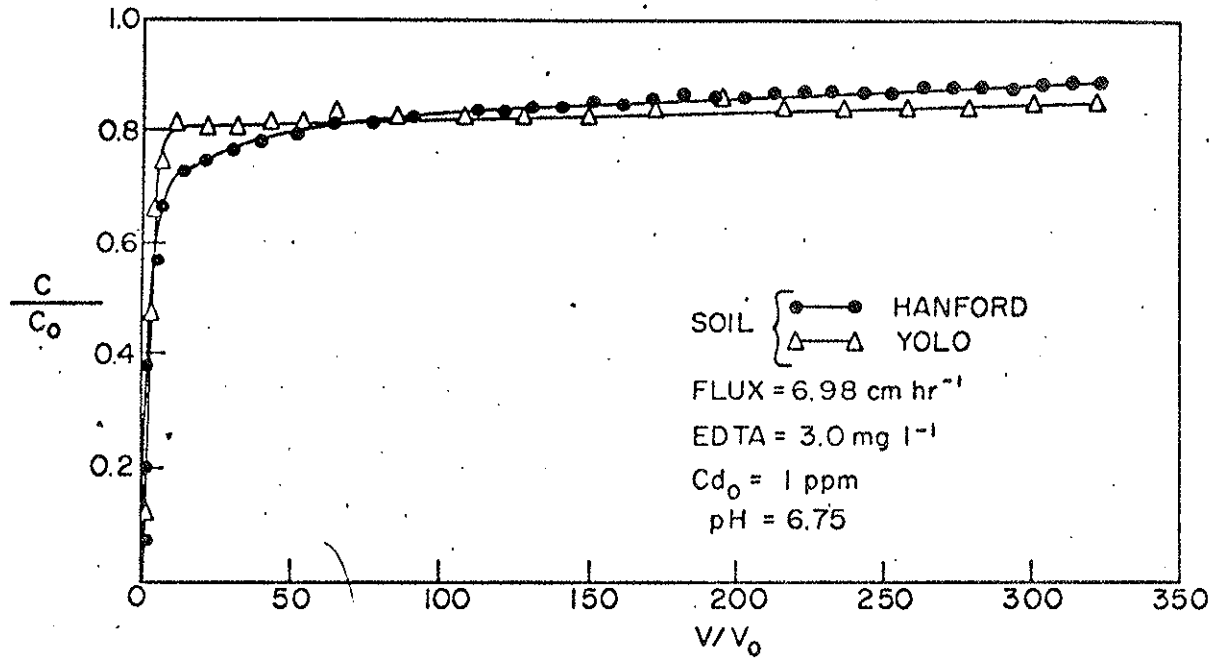


Figure 41. Effect of soil type on Cadmium breakthrough for columns having pH 6.75, 6.98 cm hr⁻¹ flux, 3.0 mg l⁻¹ EDTA and initial Cadmium concentration of 1 ppm.

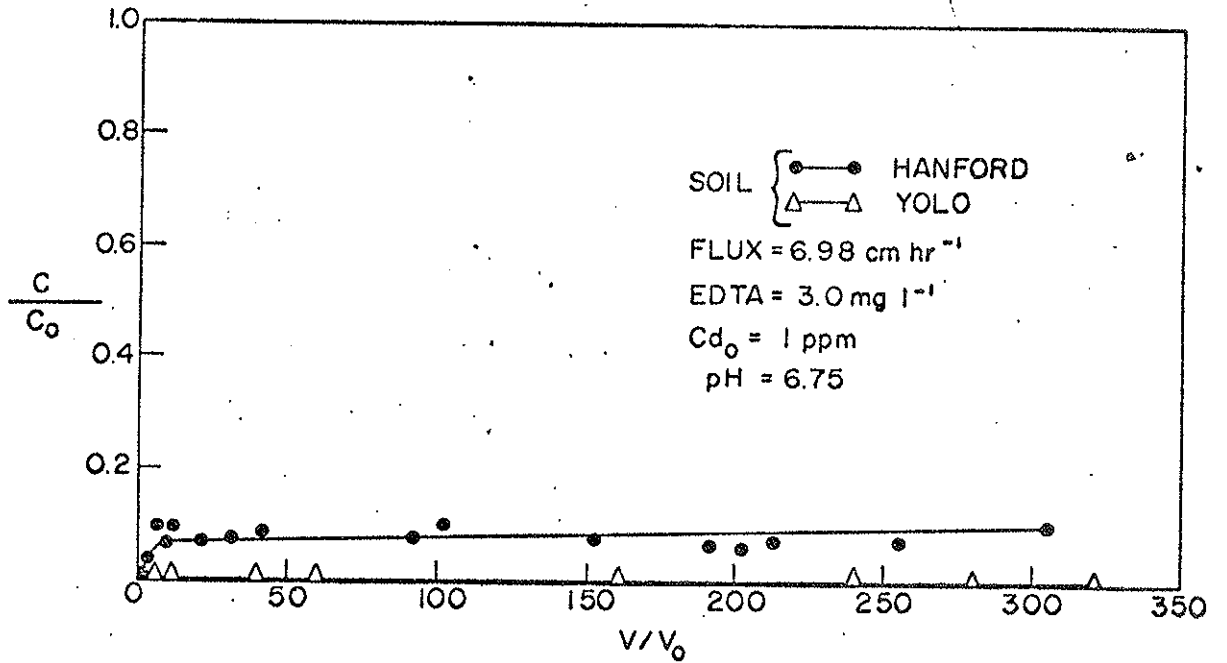


Figure 42. Effect of soil type on Cadmium ion breakthrough for above column conditions.

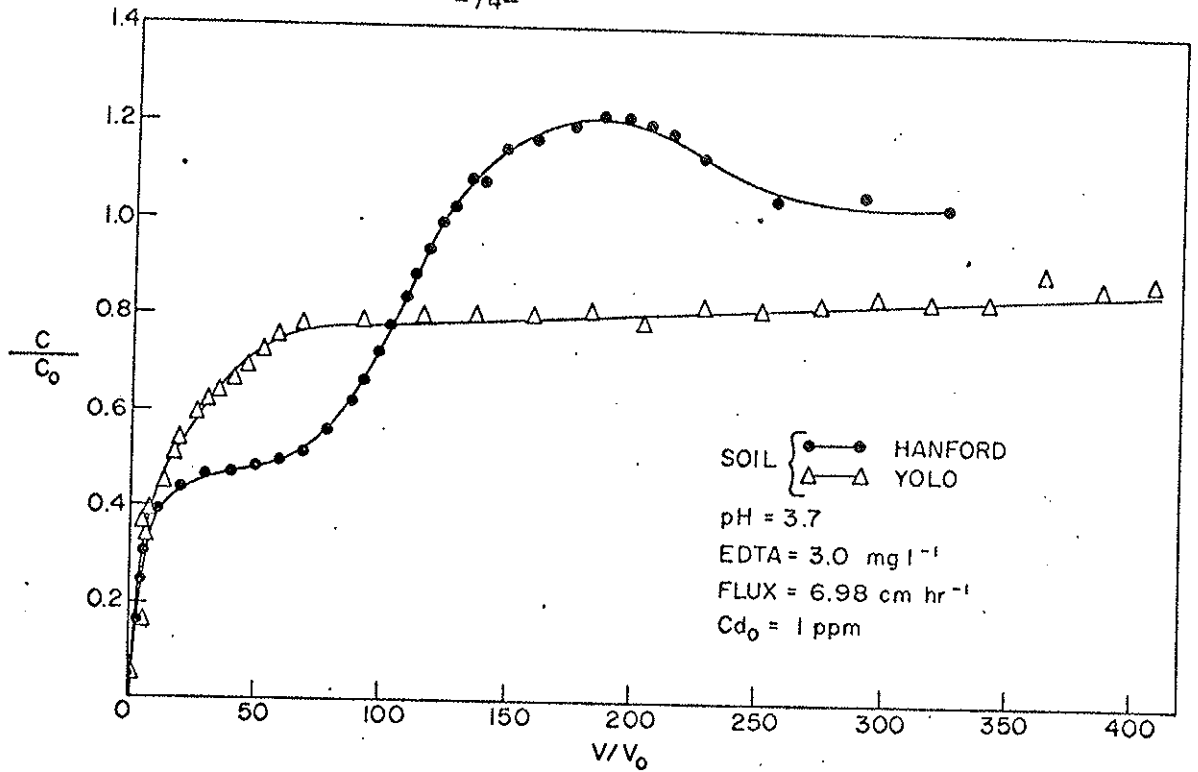


Figure 43. Effect of soil type on Cadmium breakthrough for a flux of 6.98 cm hr⁻¹, pH of 3.7, 3.0 mg l⁻¹ EDTA and initial Cadmium concentration of 1 ppm. Hanford and Yolo soils are columns 4 and 25, respectively.

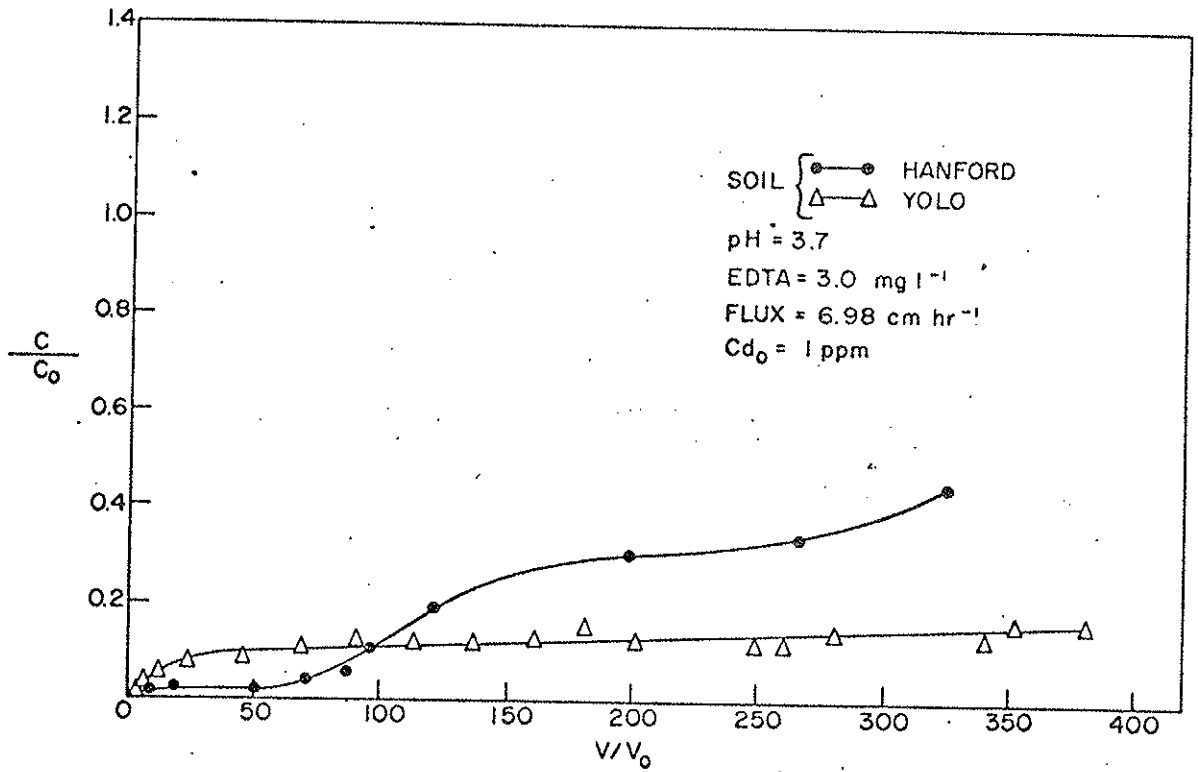


Figure 44. Effect of soil type on Cadmium ion breakthrough.

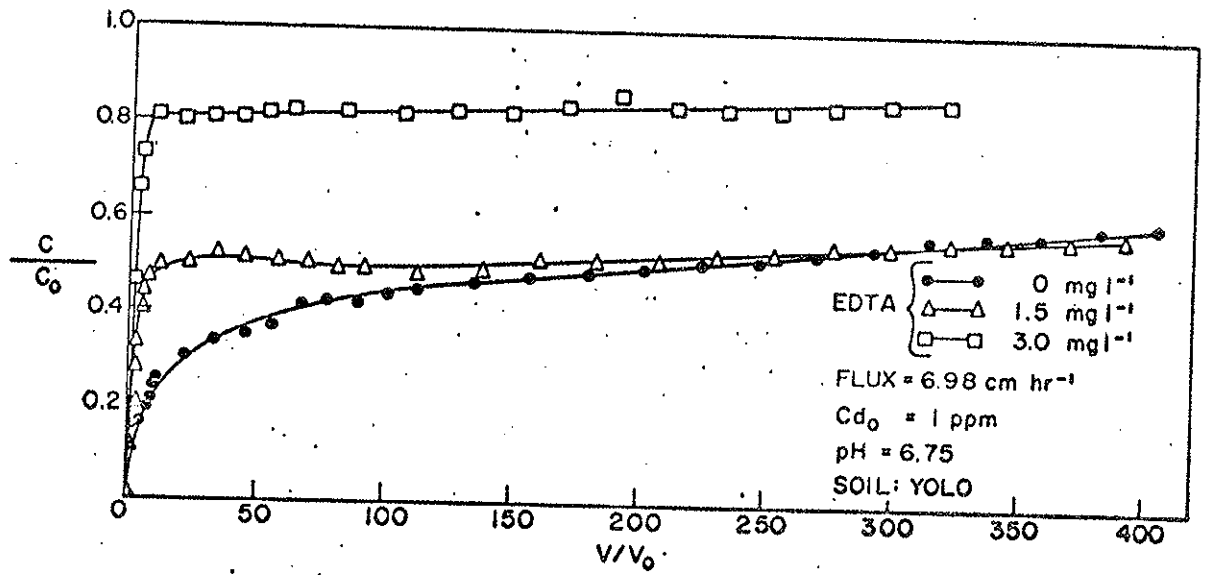


Figure 45. EDTA effect on Cadmium breakthrough for Yolo soil having influent pH of 6.75, flux of 6.98 cm hr⁻¹ and initial Cadmium concentration of 1 ppm.

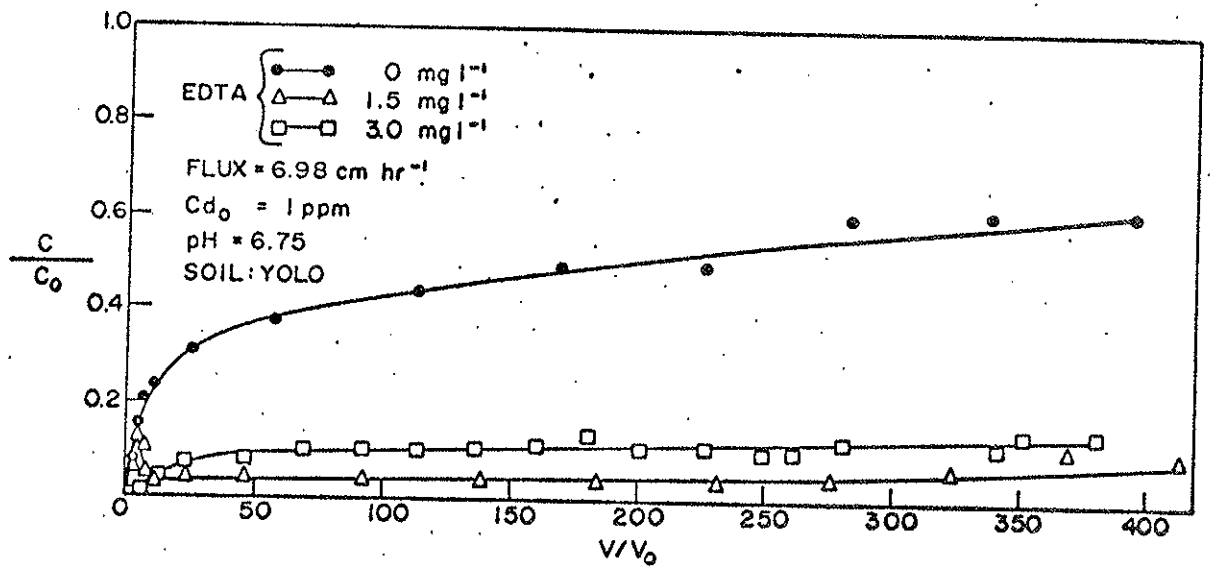


Figure 46. EDTA effect on ionic Cadmium breakthrough for the above column conditions.

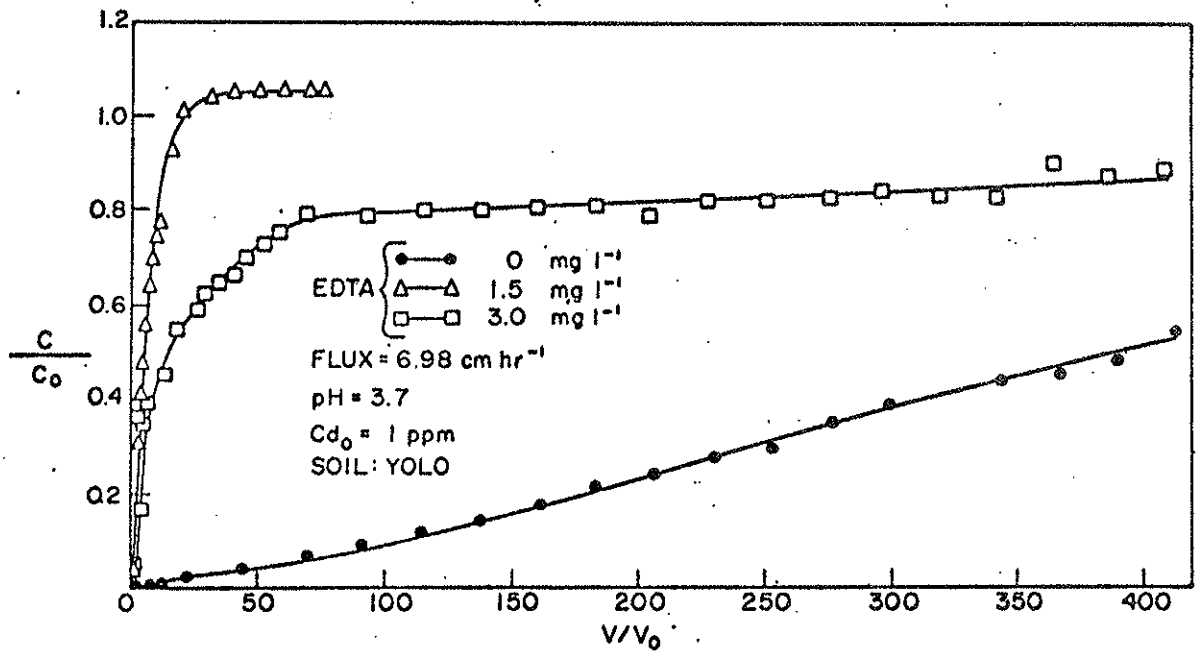


Figure 47. EDTA effect on total Cadmium breakthrough for Yolo soil columns having influent pH of 3.7, flux of 6.98 cm hr⁻¹ and influent Cadmium concentration of 1 ppm. The curve for 0 mg l⁻¹ EDTA continues linearly to 700 pore volumes.

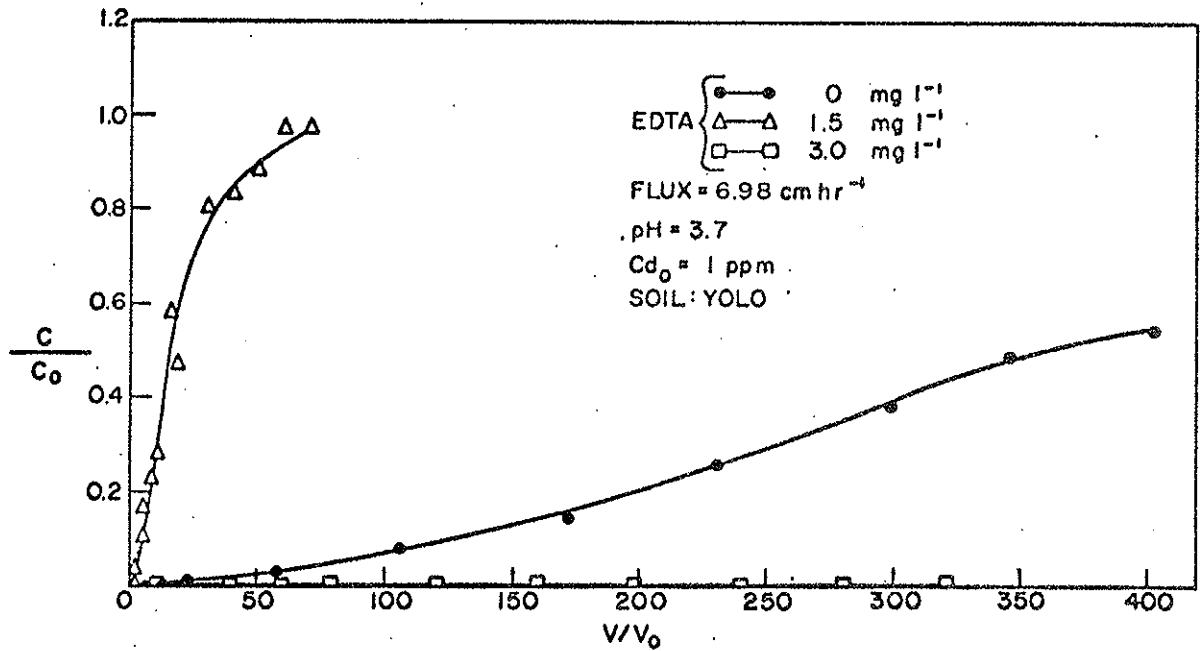


Figure 48. EDTA effect on ionic Cadmium breakthrough for Yolo soil columns having the conditions indicated above.

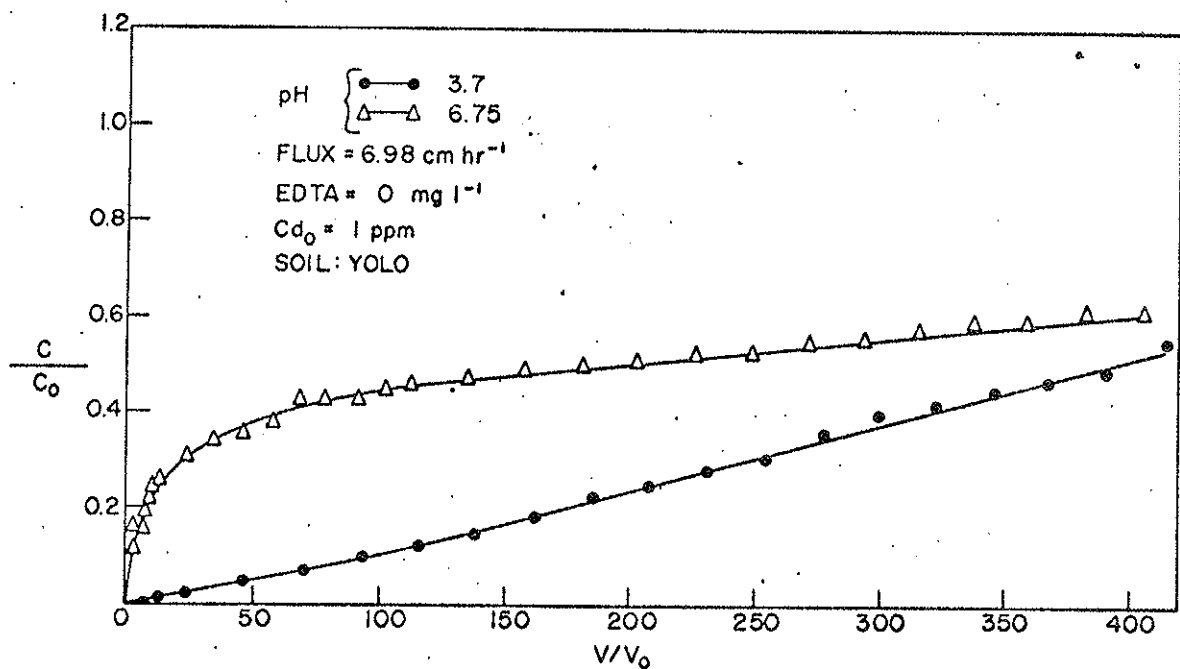


Figure 49. The effect of influent solution pH on Cadmium breakthrough for Yolo soil having 0 mg l⁻¹ EDTA, 6.98 cm hr⁻¹ flux and 1 ppm influent Cadmium concentration. The curves continue linearly to at least 600 pore volumes.

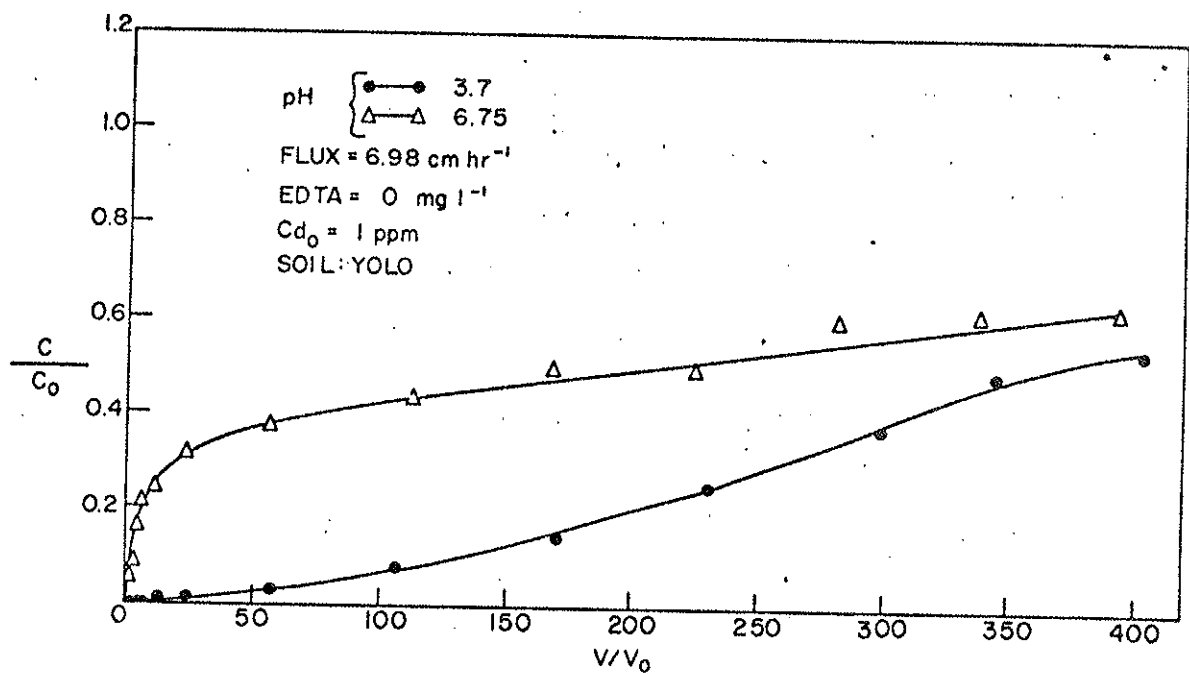


Figure 50. The effect of influent solution pH on ionic Cadmium breakthrough for Yolo soil having above conditions.

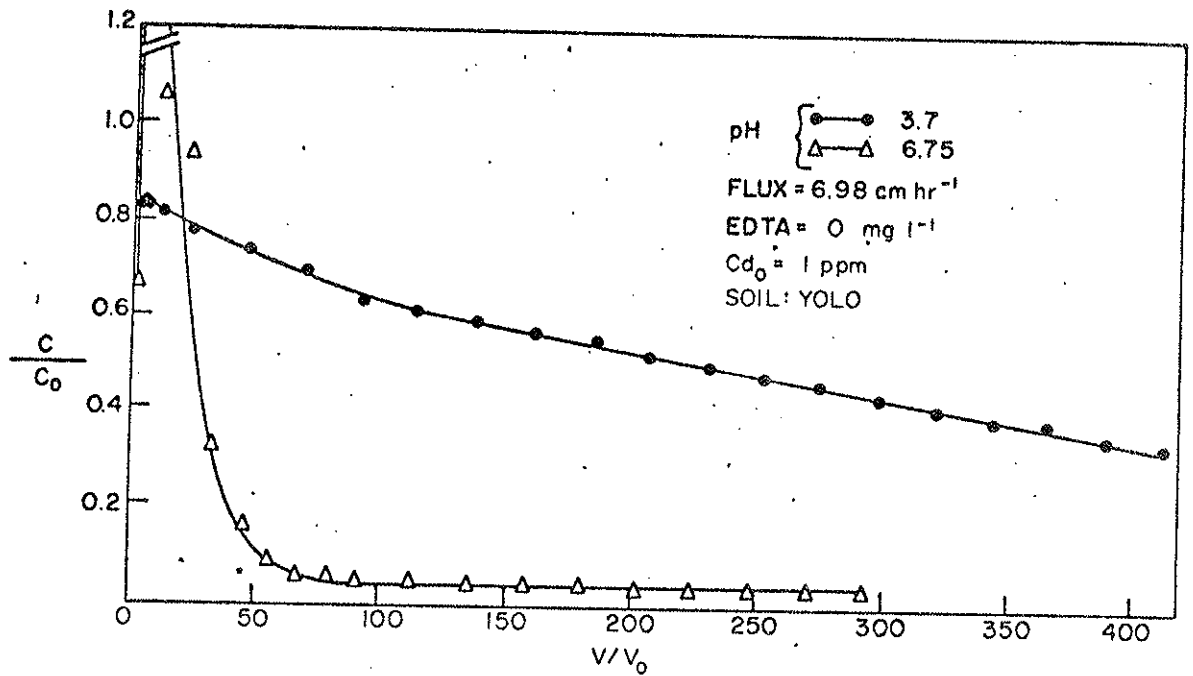


Figure 51. The effect of pH on Cadmium desorption for Yolo soil previously treated with 0.0 mg l⁻¹ EDTA and 1 ppm Cadmium at a flux of 6.98 cm hr⁻¹.

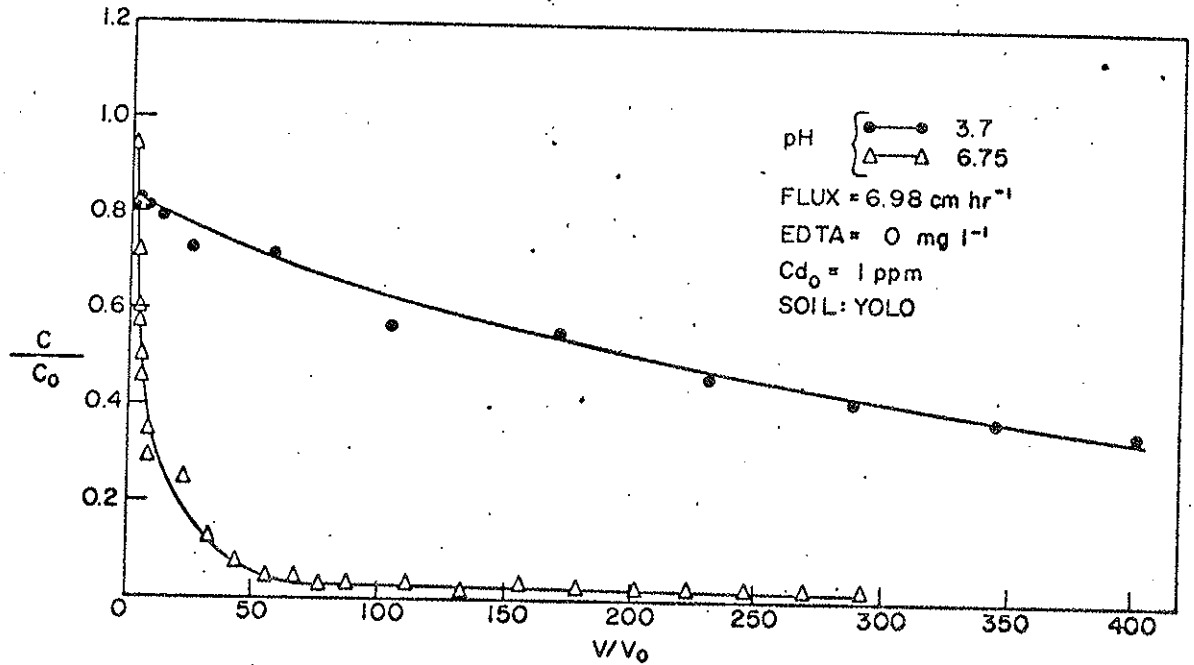


Figure 52. The effect of pH on Cadmium ion desorption for the column conditions indicated above.

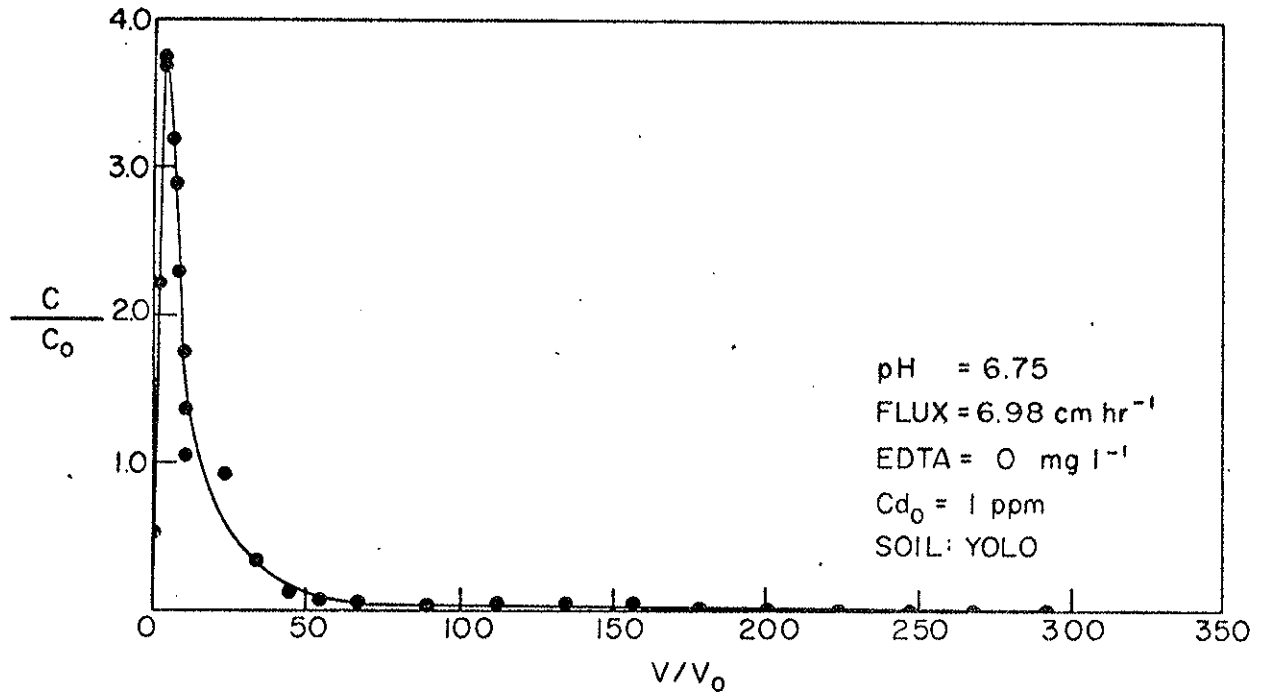


Figure 53. The Cadmium desorption curve for Yolo column which had previously been treated with an influent solution of pH 6.75, 0 mg l⁻¹ EDTA and 1.0 ppm Cadmium at flux 6.98 cm hr⁻¹. The small scale shows the complete curve which is partially shown on the preceding curve.

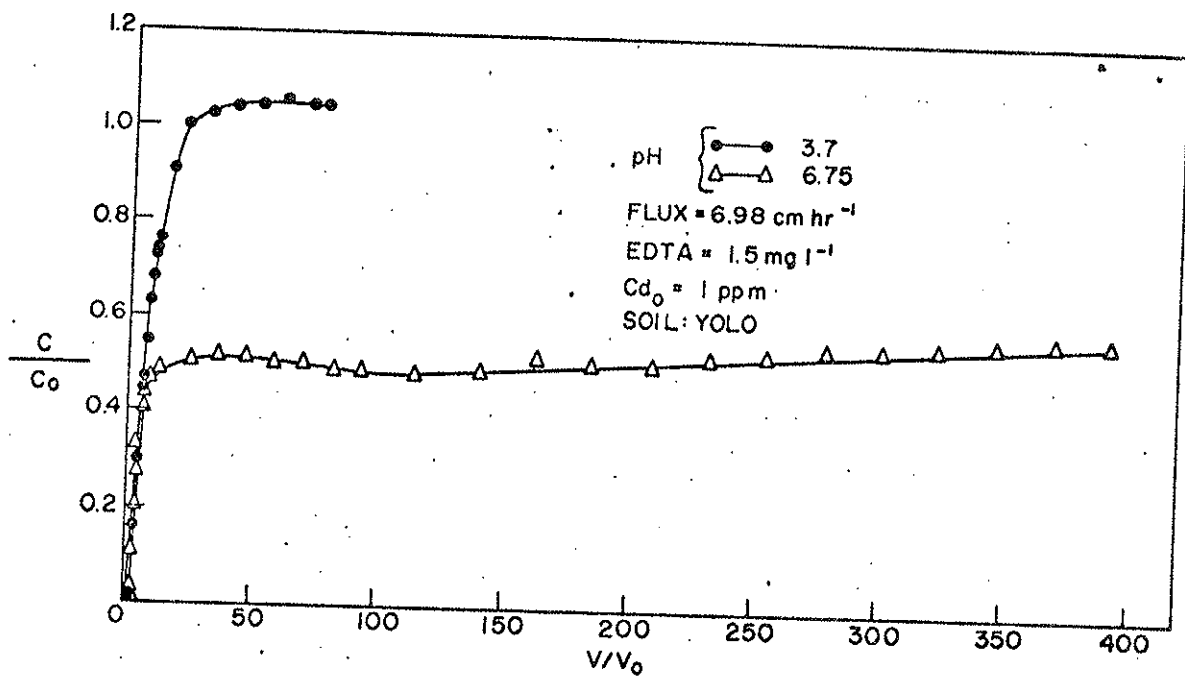


Figure 54. The effect of pH on Cadmium breakthrough for Yolo soil receiving 1.5 mg l⁻¹ EDTA, 1 ppm Cadmium and flux of 6.98 cm hr⁻¹. The pH 6.75 curve continues linearly up to 700 pore volumes.

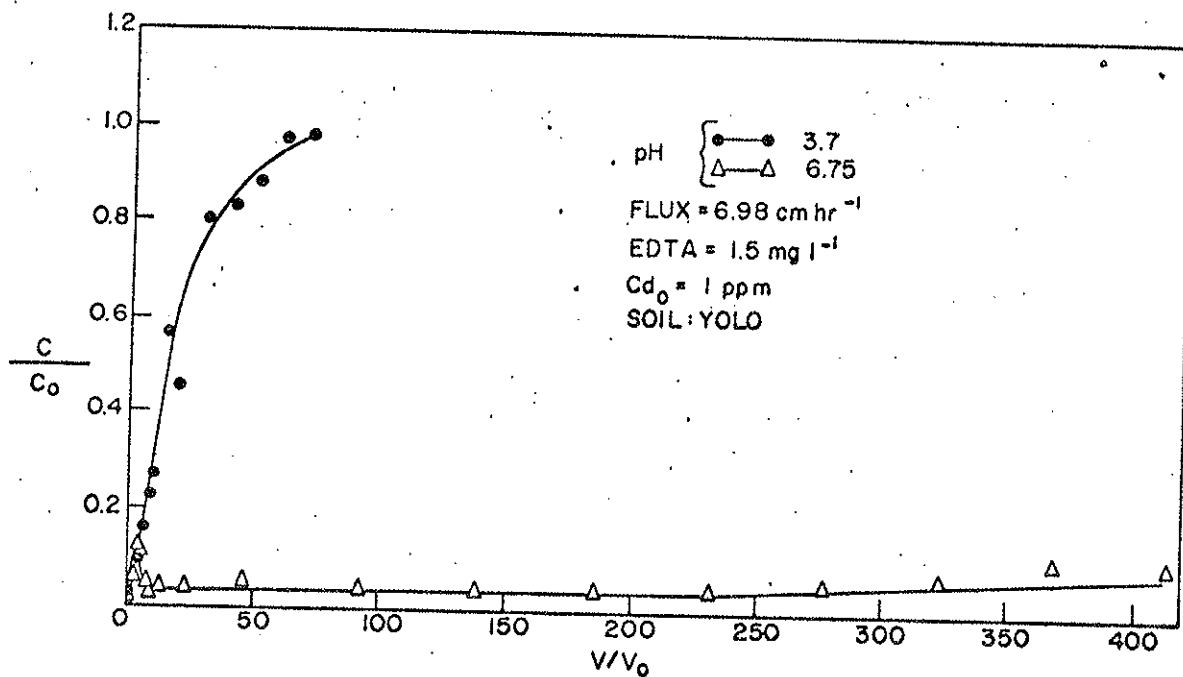


Figure 55. The effect of pH on ionic Cadmium breakthrough for Yolo soil having above conditions.

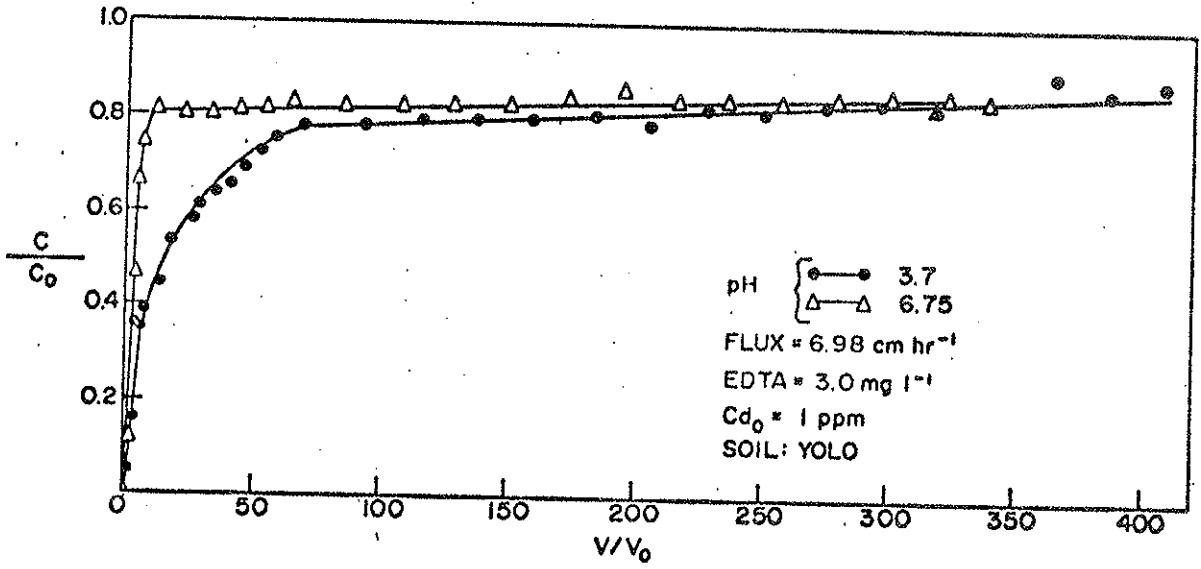


Figure 56. The effect of pH on Cadmium breakthrough for Yolo soil receiving 3.0 mg l⁻¹ EDTA, 1 ppm Cadmium and flux of 6.98 cm hr⁻¹.

III. PUBLICATIONS

Fujii, Roger. The Complexing and Adsorption of Cadmium in Soils in the Presence of EDTA and NTA. M.S. Thesis, University of California.

Mingelgrin, U. and J. W. Biggar. Copper Species in Aqueous Sewage Sludge Extract. (Submitted)

Mingelgrin, U. A General Model for the Adsorption of Trace Metals. (In preparation)