SORPTION OF TRACE QUANTITIES OF CADMIUM BY SOILS WITH DIFFERENT CHEMICAL AND MINERALOGICAL COMPOSITION

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Abstract. Cadmium sorption experiments were performed using four soil separates of different chemical and mineralogical composition, adding Cd solutions with initial concentrations ranging from 15 to 150 μg l^{-1}. At the soils pHs, the sorption isotherms were a mixture of a constant partition isotherm with a high affinity one. Also, more than 90% of the initially added Cd was sorbed by all four soils. These results indicate a high affinity of these soils for trace amounts of Cd. The effect of pH was, in general, to decrease the amount of sorbed Cd as the pH decreased. The sorption isotherms were linear at all pH's. Also, the data fitted the Freundlich's sorption isotherm in all cases, but not Langmuir's. Freundlich's k values were found to be a good index of the relative Cd sorption affinities of the four soils at all the pH's used. It was found that the structural and chemical nature of the soils sorbent complex was a more important parameter than the CEC when studying the sorption of these trace amounts of Cd by soils.

1. Introduction

The current interest in the soil chemistry of Cd, as well as other heavy metals, is a direct result of the growing pollution of soils by industrial and urban wastes. Crop plants can absorb and accumulate toxic amounts of this metal and have already resulted in severe health problems for human beings and animals (Friberg *et al.,* 1971; Lagerwerff, 1972; Page, 1974; Page and Bingham, 1973).

There is very little information available on the chemistry of Cd in soils. Probably due to instrumental limitations, most researchers have investigated systems with Cd concentrations much higher than those normally found in soil solutions (Bittell and Miller, 1974; John, 1971; Lagerwerff and Brower, 1972; Levi-Minzi *et al.,* 1976; Santillán-Medrano and Jurinak, 1975). These concentrations have been reported as being in the order of 10 μg l^{-1} and less (Page, 1974). The conclusions reached working with Cd concentrations higher than those normally found in soil–water systems can be very helpful to an understanding of the Cd chemistry in soils. Nevertheless, these conclusions are not easy to extrapolate to lower Cd concentrations in solution where Cd in microamounts is competing for soil sorption sites with macroamounts of Ca, Mg, K and Na present in soil solutions. Also, there is the possible existence of high energy, very specific Cd sorption sites in some soil materials, which operate for very low concentrations of the metal in solution (García-Miragaya and Page, 1976).

These reasons make it desirable to try to study the soils sorption of Cd from solutions with concentrations of a few μg l^{-1}. With the recent development of flameless atomic absorption spectrophotometry, it is possible now to study the sorption chemistry of Cd by soils using Cd concentrations in solution of 100 μg l^{-1} and less.

The objective of this work was to study the partition of Cd between the solid phase of several soils of differing chemical and mineralogical composition, and an aqueous phase, using Cd solution concentrations similar to those found in natural soil–water systems.

2. Material and Methods

2.1. SOILS

Table I presents several selected chemical and mineralogical properties of the soils used. These data show the contrasting chemical and mineralogical properties of the soils. Imperial soil is a montmorillonitic soil with a high CEC. Olivenhaim is micaceous-vermiculitic. Boomer has kaolinite and goethite, and the organic soil has 16.3% organic matter and a mixed mineralogy. Since the silt and clay fractions of soils are physico-chemically most active, they were separated by wet sieving as follows: A given amount of soil sample was put into a beaker, and sufficient distilled water was added to make a suspension of the soils. The suspensions were passed through a sieve with openings of 74 μm, the samples collected in a beaker and the excess water removed by drying at 100°C. The CEC of the soils was determined by saturation with 1N—CaCl$_2$, washing with 1×10^{-3} N—CaCl$_2$ and replacement of Ca with three 1N—NaNO$_3$ washings. Calcium was determined by atomic absorption. Iron oxides were extracted by the Mehra and Jackson (1960) procedure and Fe was determined by atomic absorption in the extracts. X-ray diffraction analyses of the samples were made following Whittig (1965).

TABLE I

Selected chemical and mineralogical properties of the soil separates (fraction < 74 μm, except for the organic soil where the whole soil was used)

Soil	CEC (me/100 g)	%Fe$_2$O$_3$	%OM	Mineralogy
Organic	33.8	—	16.30	Mont.»Kaol.»Mica, Quartz, Felds.
Imperial (Vertic Torrifluvent)	60.0	1.07	0.72	Mont.»Kaol., CaCo$_3$
Olivenhaim (Ultic Palexeralf)	25.0	1.07	1.80	Verm., Mica $\simeq$ Kaol.
Boomer (Ultic Haploxeralf)	23.8	8.29	1.50	Kaol. > Goeth.

All data, except the OM content and mineralogy of the organic soil, were determined by the authors. The OM content and mineralogy of the organic soil were taken from Pratt and Bair (1962). All the soil samples were collected in California.

2.2. SORPTION EXPERIMENTS

Duplicate samples of each soil separate weighing approximately 0.025 g were placed in 50 ml plastic centrifuge tubes. Twenty ml of $CdCl_2$ solutions ranging in concentration from 15 to 150 μg l^{-1} were added to the samples. Experiments to determine the time of equilibrium showed that after 1 h there was practically no change in the amount of Cd sorbed by the soil separates. The samples were shaken for 1 h, centrifuged at 10 000 rpm for 10 min, and Cd determined in the supernatant solution by Flameless Atomic Absorption Spectrophotometry (FAAS). The pH of the supernatant solutions was measured with a Beckman zeromatic – II, pH-meter Cadmium sorbed was calculated by the difference between the concentration of Cd in the original solution and the equilibrium solution. Blanks were run in each experiment. Cd concentrations being less than 0.1 μg l^{-1} in every case. To study the effect of pH on the sorption of Cd by these soils the procedure was similar. The only difference being that pH's of the solutions used for sorption experiments were adjusted to the desired values, with either HCl or NaOH solutions. In all the following sorption isotherms each point represents the average of two determinations.

3. Results and Discussion

Figure 1 shows the Cd sorption isotherms plots for the four soils used in the experiments at the soil's pH. The isotherms were linear and the intercepts of the equations adjusted by the least squares method were positive (except for the Olivenhaim soil, where it was slightly negative) (Table II). This indicates a high affinity of the soil sorbent complex for Cd at these very low concentrations. Their linearity indicates a constant partition coefficient. Thus, using Giles *et al.* (1960) classification of sorption isotherms these ones would be a mixture of a constant partition one with a high affinity isotherm. These findings coincide with those already reported for montmorillonite clay (García-Miragaya and Page, 1976). The high affinity of the soils is confirmed by the high percentage of sorbed Cd (> 90% in all four soils Table II). The sorption data were also well described by the Freundlich adsorption isotherm (Figure 2 and Table II). Plots of $C/(X/m)$ vs. C failed to produce straight lines indicating that the data did not follow the Langmuir isotherm. The order of sorption was Imperial (montmorillonitic) > Organic > Boomer (kaolinite – goethite) > Olivenhaim (micaceous – vermiculitic). It should be pointed out that the Imperial soil has a much higher pH (8.4) than the other three soils. This high pH increases appreciably the amount of Cd sorbed due to the increase in negative soil charge, less competition of Cd with H$^+$ for ion sorption sites, as well as the formation of moderate amounts of the Cd(OH)$^+$ species in solution (which could make up to 10 to 15% of the solution Cd at pH 8.4, according to Hahne and Kroontje, 1973). Since the soils charged surfaces could affect the hydrolysis reaction equilibrium (Frink and Peech, 1963; Ragland and Coleman, 1960), this distribution
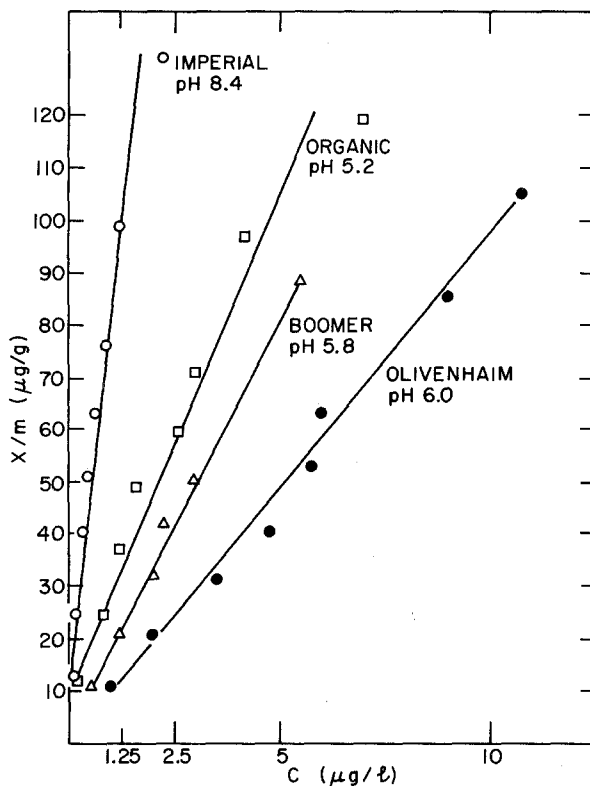
Fig. 1.   Sorption isotherms for the four soils.

TABLE II

Linear and Freundlich equations for the four soil separates

Soil	Linear Equation	Correlation Coefficient
Imperial pH 8.4 ± 0.1	$x/m = 23.08 + 54.27\,C$	$r = 0.967$[a]
Organic pH 5.2 ± 0.1	$x/m = 17.64 + 15.99\,C$	$r = 0.978$[a]
Boomer pH 5.8 ± 0.1	$x/m = 3.43 + 15.52\,C$	$r = 0.997$[a]
Olivenhaim pH 6.0 ± 0.1	$x/m = -0.17 + 9.67\,C$	$r = 0.995$[a]

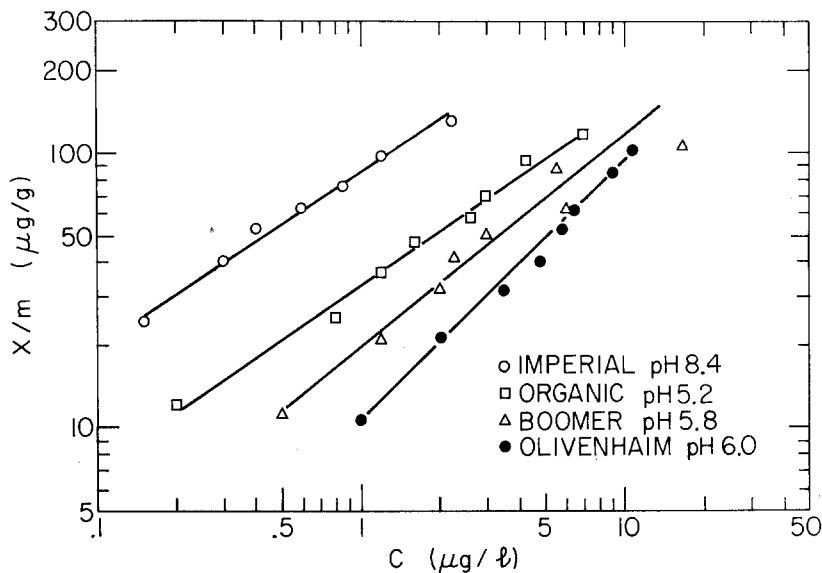| Soil	Freundlich Equation	Correlation Coefficient	Freudlich's k
Imperial pH 8.4 ± 0.1	$\log x/m = 1.94 + 0.72 \log C$	$r = 0.983$[a]	87.1
Organic pH 5.2 ± 0.1	$\log x/m = 1.53 + 0.66 \log C$	$r = 0.994$[a]	33.9
Boomer pH 5.8 ± 0.1	$\log x/m = 1.31 + 0.63 \log C$	$r = 0.978$[a]	20.4
Olivenhaim pH 6.0 ± 0.1	$\log x/m = 1.02 + 0.95 \log C$	$r = 0.995$[a]	10.5

[a] = Significant at the 0.001 level.

Fig. 2. Freundlich isotherms for the four soils.

should be taken as approximate. The same order was also followed by the intercepts of the straight line equations as well as by the Freundlich's k (Table II). Both parameters can be considered as indicators of the degree of affinity of the surfaces for Cd.

EFFECT OF pH

The pH effect on the sorption of trace amounts of Cd by the different soils is shown in Figure 3. In general, there was a decrease in the amount of Cd sorbed as the pH decreased. This was to be expected, due to the effect of increasing concentration of H^+ and Al in solution, both of which compete with Cd for ion sorption sites on the soil sorbent surfaces, as well as the concomitant decrease of negative charge of the same surfaces. One exception was the Imperial soil (montmorillonitic) where there was the expected reduction on the amount sorbed at pH's 6.7 and 6.2 (with respect to the amount sorbed at pH 8.4), but then there was an unexpected increase in Cd sorption at pH 3.7, where the sorption isotherm was practically similar to the one at pH 8.4 (Figure 3a). One plausible explanation for this finding can be deducted from the mineralogy of this soil, where montmorillonite predominates. Montmorillonite, being unstable at pH 3.7, starts decomposing and some fresh, finally divided, probably amorphous, highly reactive materials (like silicic acid or mixtures of Al and silicic acid) produced by decomposition of the montmorillonite, are reacting with trace amounts of Cd in a very specific fashion, and therefore increasing the Cd sorption at lower pH's. This explanation is consistent with the findings of Tiller (1967), who working with montmorillonite, found an increase in the sorption of Zn

(chemically similar to Cd) when silicic acid was added to the system. Later on, he also found the same behavior with Ni and Co (Tiller, 1968). Also a similar behavior has been found in experiments of Cd sorption on montmorillonite clay (García-Miragaya, 1975). Nevertheless, the authors think that more detailed experimental work is necessary for the further clarification of this controversial and interesting point.
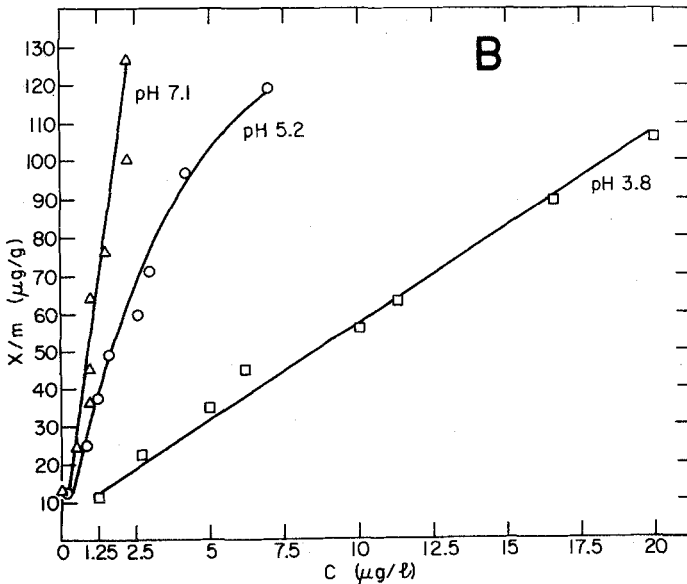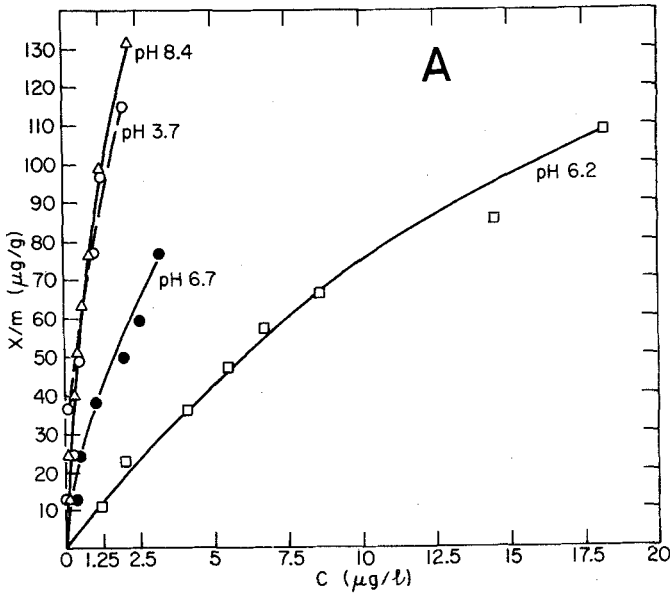
Except for the Imperial soil pH 8.4 sorption isotherm, the soil pH's of all the other sorption experiment were below 7.1. Taking Hahne and Kroontje's (1973) hydrolysis distribution diagrams, we can conclude that Cd was present almost exclusively as the Cd^{+2} species in all the experiments. In the Imperial soil pH 8.4
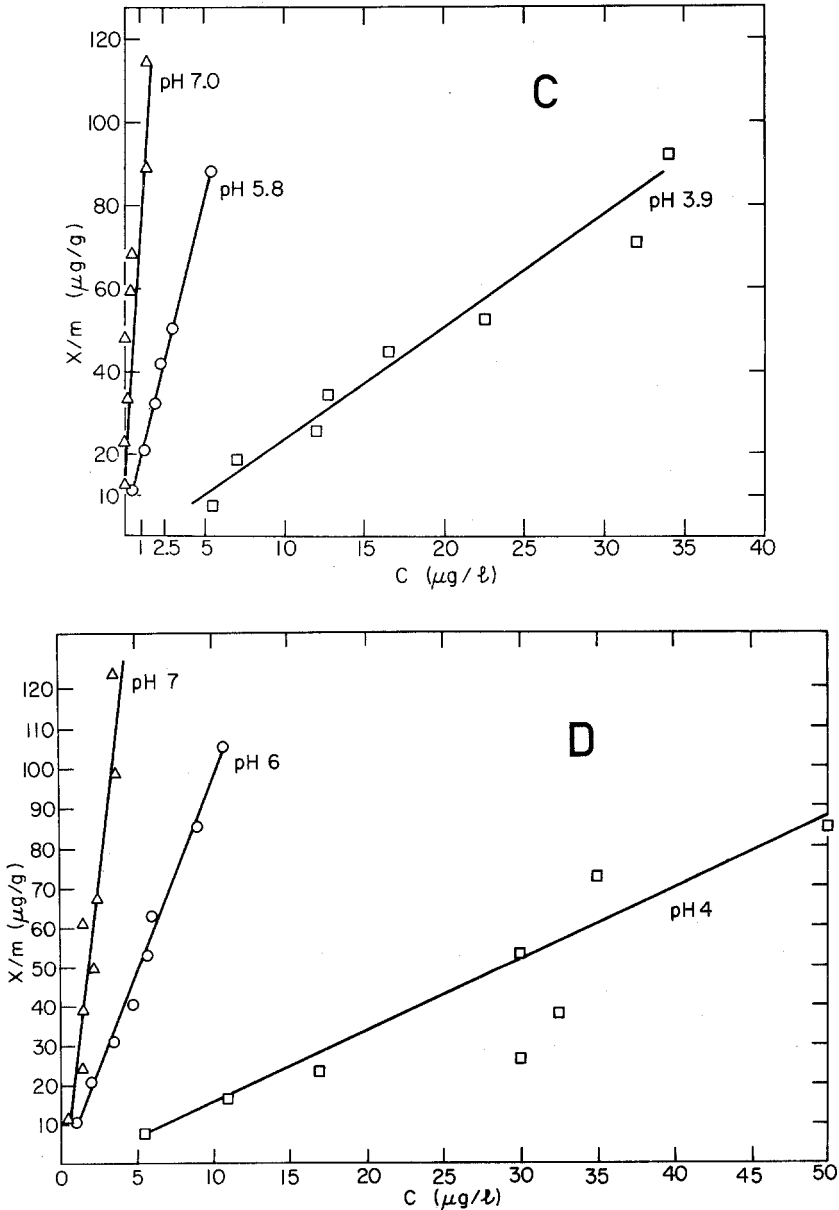

Fig. 3. (a) pH effect on the sorption of Cd by Imperial soil; (b) pH effect on the sorption of Cd by Organic soil; (c) pH effect on the sorption of Cd by Boomer soil; and (d) pH effect on the sorption of Cd by Olivenhaim soil.

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case, around 10 to 15% of Cd was present as the $Cd(OH)^+$ species and the rest as Cd^{+2}. Since the soil charged surfaces can affect the hydrolysis products distribution, this last observation will apply mainly to the Cd solutions before sorption by the soil, and only approximately at the Cd in the equilibrium solution. Nevertheless, the difference is probably too small to be of importance, specially at pH 7.1 and below.

The sorption isotherms were linear for all pH's (Table III). Also, they followed the Freundlich isotherm presented in the form of $\log x/m = \log k + 1/n \log C$ (Table III). It is useful to indicate at this point that the Freundlich's k (which are interpreted

TABLE III

Linear and Freundlich equations for the four soil separates at different pH's (initial Cd concentrations from 0.015 to 0.15 ppm)

Soil	Linear Equation	Correlation Coefficient	
Imperial			
pH 8.4 ± 0.1	$x/m = 23.08 + 54.27\,C$	$r = 0.967$[a]	
pH 6.7 ± 0.1	$x/m = 12.23 + 19.96\,C$	$r = 0.986$[a]	
pH 6.2 ± 0.1	$x/m = 14.38 + 5.29\,C$	$r = 0.983$[a]	
pH 3.7 ± 0.1	$x/m = 26.26 + 49.32\,C$	$r = 0.971$[a]	
Organic			
pH 7.1 ± 0.1	$x/m = 5.43 + 48.43\,C$	$r = 0.965$[a]	
pH 5.2 ± 0.1	$x/m = 17.64 + 15.99\,C$	$r = 0.978$[a]	
pH 3.8 ± 0.1	$x/m = 9.27 + 4.85\,C$	$r = 0.997$[a]	
Boomer			
pH 7.0 ± 0.1	$x/m = 30.18 + 53.01\,C$	$r = 0.918$[a]	
pH 5.8 ± 0.1	$x/m = 3.43 + 15.52\,C$	$r = 0.997$[a]	
pH 3.9 ± 0.1	$x/m = -2.26 + 2.56\,C$	$r = 0.981$[a]	
Olivenhaim			
pH 7.0 ± 0.1	$x/m = -6.95 + 30.98\,C$	$r = 0.934$[a]	
pH 6.0 ± 0.1	$x/m = -0.17 + 9.67\,C$	$r = 0.995$[a]	
pH 4.0 ± 0.1	$x/m = -4.40 + 1.69\,C$	$r = 0.910$[a]	

Soil	Freundlich Equation	Correlation Coefficient	Freundlich's k
Imperial			
pH 8.4 ± 0.1	$\log x/m = 1.94 + 0.72 \log C$	$r = 0.983$[a]	87.1
pH 6.7 ± 0.1	$\log x/m = 1.53 + 0.69 \log C$	$r = 0.985$[a]	33.9
pH 6.2 ± 0.1	$\log x/m = 1.07 + 0.79 \log C$	$r = 0.989$[a]	11.7
pH 3.7 ± 0.1	$\log x/m = 1.91 + 0.39 \log C$	$r = 0.954$[a]	81.3
Organic			
pH 7.1 ± 0.1	$\log x/m = 1.71 + 1.03 \log C$	$r = 0.966$[a]	51.3
pH 5.2 ± 0.1	$\log x/m = 1.53 + 0.66 \log C$	$r = 0.994$[a]	33.9
pH 3.8 ± 0.1	$\log x/m = 1.00 + 0.77 \log C$	$r = 0.998$[a]	10.0
Boomer			
pH 7.0 ± 0.1	$\log x/m = 1.95 + 0.53 \log C$	$r = 0.959$[a]	89.1
pH 5.8 ± 0.1	$\log x/m = 1.31 + 0.63 \log C$	$r = 0.978$[a]	20.4
pH 3.9 ± 0.1	$\log x/m = 0.15 + 1.18 \log C$	$r = 0.969$[a]	1.4
Olivenhaim			
pH 7.0 ± 0.1	$\log x/m = 1.35 + 1.14 \log C$	$r = 0.960$[a]	22.4
pH 6.0 ± 0.1	$\log x/m = 1.02 + 0.95 \log C$	$r = 0.995$[a]	10.5
pH 4.0 ± 0.1	$\log x/m = 1.24 + 1.02 \log C$	$r = 0.944$[a]	17.0

[a]Significant at the 0.001 level.

as an index of sorption affinity between the sorbent and the sorbate) were a good consistent index showing the different relative affinities for Cd of the several soils at the various pH's of the experiments. On the other hand, the intercepts of the linear equations varied in a non-consistent way, their usefulness seems to be mainly as a qualitative index of the high affinity of the soil surfaces for these trace amounts of Cd.

When we compare the soils sorption isotherms at similar pH's, that is, when we eliminate pH as a variable on the sorption process, the differences in the amounts of Cd sorbed will be due mainly to the different chemical and mineralogical composition of the soils sorption complex. Comparing the isotherms at pH ~ 6 the sorption order was organic soil > Boomer > Olivenhaim > Imperial (Figure 4a; Table III). At pH 4.0 the order of sorption was essentially the same as that at pH 6.0 (Figure 4c; Table III), with the exception of the Imperial soil where Cd sorption increased at this lower pH. The possible cause of this unexpected behavior has been already pointed out before in this section. At pH 7.0 the sorption order was Boomer > Organic > Olivenhaim > Imperial (Figure 4b and Table III). As it can be seen
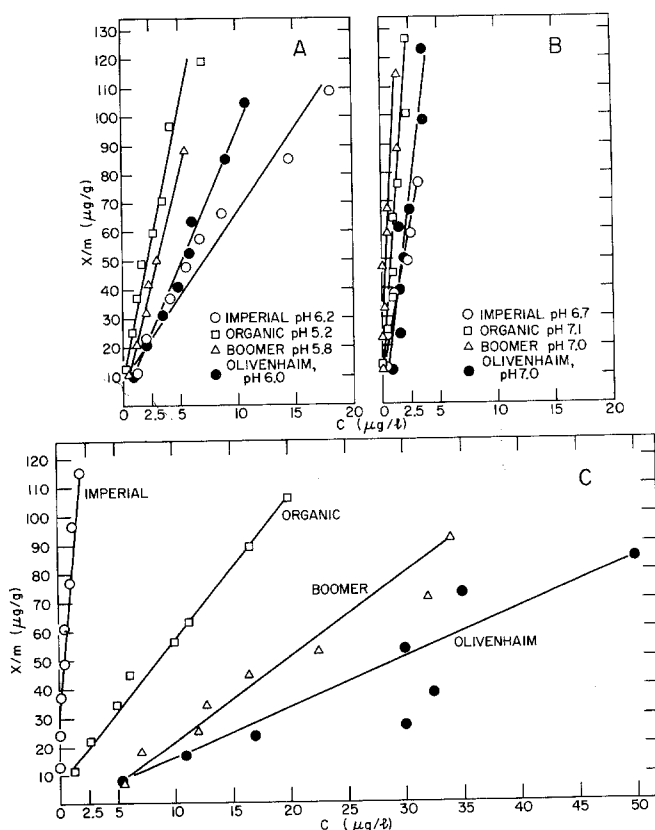

Fig. 4. Sorption isotherms for the four soils at different pH's: a – pH ~ 6.0; b – pH ~ 7.0; and c– pH ~ 4.0.

from these data the Organic and Boomer (kaolinite, goethite) soils sorbed more Cd than the other two soils Imperial (montmorillonite) and Olivenhaim (vermiculitic-micaceous), these results suggest that organic matter and iron oxides have a higher affinity for trace amounts of Cd than 2:1 layer silicates. At pH 7.0 the Boomer soil sorbed more Cd than the Organic one, while at pH 6.0 the order was the opposite. The increase in Cd sorption with increment in pH is due to the formation of new sorption sites, together with the diminishing of the competition of H with Cd for soil sorption sites. The mechanisms responsible for the charge increase of the iron oxide between pH 6.0 and 7.0 (mainly the adsorption of potential determining OH^- or/and dissociation of Fe—OH groups at the oxide surface) seem to be more effective increasing the Cd sorption capacity between these pH's than those of the organic matter (mainly dissociation of carboxylic, phenolic and enolic groups). As a result, at pH 7.0 the Boomer soil (kaolinite, goethite) sorbed more Cd than all the other soils in the range of concentrations used in these experiments. This observation is in agreement with Jenne's (1968) hypothesis of the high sorptive affinity of iron oxides for heavy metals in general. Furthérmore, if we consider that the CEC of the Boomer soil (kaolinite, goethite) was lower than that of Olivenhaim (vermiculite-mica) and much lower than that of the Imperial (montmorillonitic) soil (Table I), and nevertheless sorbed more Cd than both at pH's 6.0 and 7.0. We can conclude that the iron oxides have a higher affinity for these trace quantities of Cd that the 2:1 layer silicates, at those pH's. On the other hand at the lower pH there was the highly unexpected behavior of the montmorillonitic soil (Imperial at pH 3.7). All these facts tend to indicate that the structure and chemical nature of the soil sorbent complex are more important parameters to be considered when studying the sorption of trace quantities of Cd than their CEC.

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