ADSORPTION OF Cd AND Zn ON MONTMORILLONITE IN THE PRESENCE OF A CATIONIC PESTICIDE

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ABSTRACT: The adsorption of Cd and Zn on a standard montmorillonite (SAZ-1) in the presence of the cationic pesticide chlordimeform, both in solution (simultaneous adsorption) and when the pesticide is previously adsorbed on the clay (successive adsorption) has been studied. The adsorption of Zn decreases when the chlordimeform concentration increases in both simultaneous and successive adsorptions, following the sequence: chlordimeform-free solutions > successive > simultaneous. In the adsorption of Cd the sequence is different: successive > chlordimeform-free solutions > simultaneous, indicating that a small amount of pesticide adsorbed favours Cd adsorption. In all cases, the apparent affinity of the metal for adsorption on montmorillonite, on the basis of distribution coefficients, K_D, is higher for lower metal surface coverage, and decreases largely with the amount of the metal adsorbed. This indicates the existence of high affinity sites on the clay, probably those of variable charge edge regions. The contribution of edge and interlamellar positions to adsorption of Zn and Cd on SAZ-1 has been studied.

The persistence of agrochemicals and heavy metals in soils depends mainly on the adsorption-desorption reactions that take place with their components. From the point of view of adsorption, clay minerals are the most important inorganic components in soil (Christensen, 1989). Their importance comes not only from their abundance but also from the high specific area and exchange capacity values, and, for some clay minerals, from their appreciable internal surface which is accessible to large organic molecules.

Heavy metals are significant pollutants in groundwaters and soil systems; their mobility, and consequent toxicity, can be enhanced or hindered by addition of organic materials (manure, fertilizers, pesticides, sewage sludges) affecting the interactions of metals with the soil surfaces (Bejarano & Madrid, 1992; Morillo *et al*., 1994; Undabeytia *et al*., 1994). This paper attempts to focus on the effect of the presence of an organic cation, the pesticide chlordimeform, on the adsorption of the heavy metals Cd and Zn on a standard montmorillonite.

MATERIALS AND METHODS

The clay used was a montmorillonite from Arizona SAZ-1 (Van Olphen & Fripiat, 1979), supplied by the Clay Minerals Society. Its cation exchange capacity (CEC) is 123.5 mEq/100g, of which 100.8 mEq is due to Ca^{2+}, 19.2 mEq to Mg^{2+}, 2.6 mEq to Na^+ and 0.9 mEq to K^+. This clay (SAZ) was treated several times with 1 M LiCl solution until reaching saturation. Excess salts were removed by placing samples in dialysis tubing in an excess of distilled deionized water, until a negative test for chloride was obtained by the $AgNO_3$ method. The dried sample was then heated for 48 h at 300°C; this will be referred to as SAZ-Li.

Technical grade chlordimeform, (N′-(4-chloro-2-methylphenyl)-N,N-dimethyl-methanoimidamide), supplied by Schering Agro, S.A., was used. This pesticide is soluble in water (50% by wt.) and ionizes completely, giving the cation chlordimeform and anion chloride.

Simultaneous adsorption experiments were done in triplicate in polypropylene centrifuge tubes, by

shaking 0.1 g of original clay mineral for 24 h at $20 \pm 1°C$ with 20 ml of solutions containing chlordimeform (0.1, 0.3, 0.5 and 1.0 mM) and a heavy metal, Cd or Zn (5, 10, 20 and 30 ppm). All the experiments were carried out in a 0.01 N NaCl medium to keep the ionic strength constant. The adsorption of metals from pesticide-free solutions was also determined under the same conditions. The heavy metal adsorbed was calculated as the difference between its concentration before and after reaching equilibrium. Cadmium and Zn concentrations in equilibrium solutions were determined by atomic absorption spectrometry.

The successive adsorptions (adsorption of metal on montmorillonite, previously treated with chlordimeform) were carried out by mixing 0.1 g of clay mineral with 0.01 N NaCl solutions containing various chlordimeform concentrations (0.1, 0.3, 0.5 and 1.0 mM). The samples were shaken for 24 h at $20 \pm 1°C$. After reaching equilibrium, the suspensions were centrifuged, the supernatant separated and the chlordimeform adsorbed was spectrophotometrically determined at 240 nm. The solid samples were washed twice with 20 ml of distilled water and then treated with Zn or Cd solutions (5, 10, 20 and 30 ppm) in 0.01 N NaCl medium for another 24 h at $20 \pm 1°C$.

In all cases, the pH of the equilibrium solutions was 6.5 ± 0.1. The adsorption isotherms were obtained by plotting the amount of metal adsorbed, in μmol/g, *vs.* the equilibrium concentration, in μmol/l.

RESULTS AND DISCUSSION

The adsorption isotherms of the heavy metals Zn and Cd on SAZ are shown in Fig. 1. Both correspond to L-type isotherms according to Giles *et al.* (1960). The Zn^{2+} is adsorbed in larger amounts than Cd^{2+}, since chloride anions from the background electrolyte act as a complexing ligand towards Cd, giving rise to the formation of several complexes. The distribution of Cd-Cl species in solution for a 0.01 NaCl concentration is 50.25% Cd^{2+}, 47.74% $CdCl^+$, 2% $CdCl_2$ (Lindsay, 1979). In our system, the Zn-Cl species are negligible (the most abundant species is $ZnCl^+$, at only 2.62%). Cadmium adsorption decreases for two reasons: the first one is the lesser affinity of the clay surface for the $CdCl^+$ and $CdCl_2$ complexes than for cadmium aquo-ion; the second is the higher ionic potential of Zn than that of Cd. Thus Zn^{2+} adsorption will be
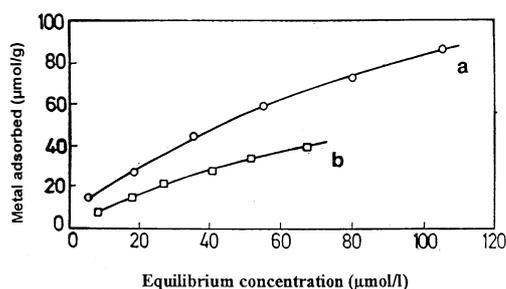

FIG. 1. Adsorption isotherms of Zn ($\bigcirc$) and Cd ($\square$) on SAZ.

favoured over Cd^{2+} by cationic interchange.

Figures 2 and 3 show the adsorption isotherms of Zn and Cd on SAZ from chlordimeform-free solutions in comparison with simultaneous and successive Zn adsorption at various chlordimeform concentrations. The Zn and Cd adsorption decreases
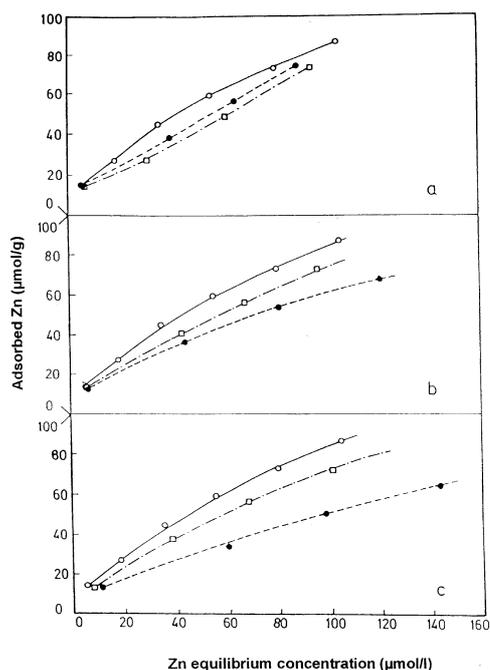

FIG. 2. Adsorption isotherms of Zn on SAZ from chlordimeform-free solutions ($\bigcirc$) in comparison with simultaneous ($\bullet$) and successive ($\square$) adsorption of Zn, at various chlordimeform concentrations: 0.1 (a), 0.5 (b) and 1.0 (c) mmol/l.
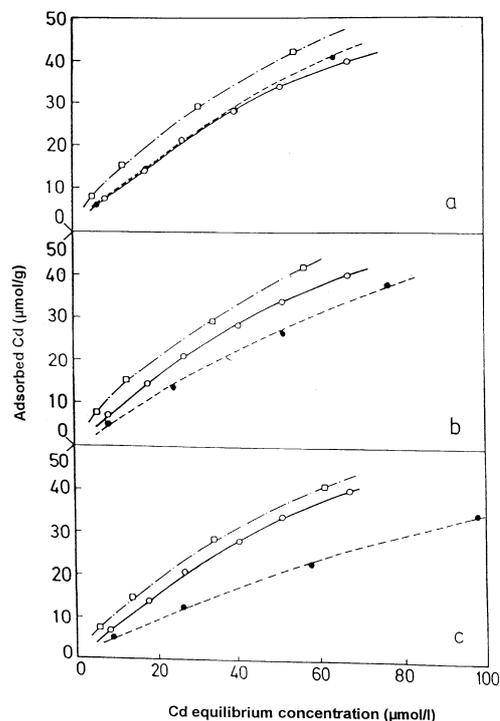
FIG. 3. Adsorption isotherms of Cd on SAZ from chlordimeform-free solutions (○) in comparison with simultaneous (●) and successive (□) adsorption of Cd, at various chlordimeform concentrations: 0.1 (a), 0.5 (b) and 1.0 (c) mmol/l.

when the metal is adsorbed simultaneously with the pesticide. The decrease in Zn and Cd adsorption on montmorillonite could be due to the competition between the metals and chlordimeform for permanent charge positions on the clay.

Adsorption of Zn is generally higher in successive than in simultaneous adsorption, probably due to the fact that in the former case, chlordimeform concentration in solution is very low when Zn adsorption takes place, since it is only a small part of that previously adsorbed on montmorillonite, which has been subsequently desorbed. Therefore, its competitive effect towards Zn is lower. The higher concentration of pesticide in the simultaneous adsorption will make this interchange more difficult. This is due to the competition with Zn for interlayer positions, leading to a lesser adsorption of Zn than in the case of the isotherms carried out in absence of chlordimeform (free

adsorption) or in the successive adsorption.

In the case of chlordimeform being adsorbed before metal adsorption (successive adsorption), the amount of pesticide adsorbed is 1.15, 7.38 and 16.60 mEq/100g when the chlordimeform concentrations used were 0.1, 0.5 and 1.0 mM, respectively. The greater amount of chlordimeform adsorbed (16.6 mEq/100g) is only 13.40% of the total CEC. For Zn successive adsorption, the amount of Zn adsorbed (Fig. 2) is lower than from the pesticide-free solutions, due to the adsorption of the organic cations being less reversible because of the strong interaction by electrostatic and Van der Waals forces, and hence the surface accessible to the metal adsorption is lower. However, the amount adsorbed (~ 70 μmol/g) is nearly independent of the chlordimeform concentration. Experiments carried out in our laboratory (data not included) indicate that less Zn is adsorbed on montmorillonite saturated with chlordimeform than on the original clay. As a consequence, Zn adsorption is not favoured when chlordimeform is previously adsorbed.

The great difference between Zn and Cd adsorption on montmorillonite in the presence of chlordimeform is in successive adsorption: for Cd, a higher metal adsorption is always observed when the pesticide has been previously adsorbed on the clay. It seems to be contradictory to the competitive effect between Cd and the pesticide when the concentration of the latter increases. No possible explanation has been found so far.

For both heavy metals (Figs. 2 and 3), the adsorption at the lowest metal concentration is practically the same for pesticide-free solutions, simultaneous and successive adsorption, independently of chlordimeform concentrations. This could indicate the existence of sites on the clay surface with a high preference for the metal. It has been suggested by several authors (Aualiitia & Pickering, 1987; Zachara & McKinley, 1993) that the sorption of metal ions on layer silicates can take place on to several types of surface site, with high energy sites performing in the lower range of surface coverage. Ziper *et al.* (1988) have also attributed the higher adsorption of Cd, with the edge/planar surface ratio increased, to the existence of high affinity sites. Thus, the retention of heavy metal ions on montmorillonite can be expected to occur mainly by two different mechanisms: adsorption on edge charge sites, and interchange with the cations

saturating the permanent charge planar positions.

Madrid *et al*. (1991), observed that the number of high preference sites for Zn adsorption on montmorillonite increases with the pH, and suggested that they are located in variable charge regions. We tested the influence of solution pH on Cd adsorption to the edge positions. For this purpose, Cd adsorption experiments were carried out on Li⁺-fixed montmorillonite at pH 5 and 6.5 (the same as in adsorption experiments on SAZ), with ionic strength 0.01 N NaCl (SAZ-Li). This presents the phenomenon known as the Hoffmann-Klemen effect: an irreversible collapse of the *c*-axis and hydration capacity, and a loss of exchangeable Li⁺, as shown from cation exchange capacity measurements (Trillo *et al*., 1993; Alvero *et al*., 1994). The SAZ-Li eliminates almost completely the effect of interlayer sites in relation to adsorption, and hence cation adsorption results mainly from edges, with a minor contribution from external planar sites (Ziper *et al*., 1988).

Figure 4 shows that Cd adsorption on SAZ-Li at pH 6.5 (Fig. 4b) is higher than at pH 5 (Fig. 4c). As can be observed from Cd adsorption isotherms on SAZ and SAZ-Li at pH 6.5 (Figs. 4a and 4b, respectively), edge positions on the clay play an important role in Cd adsorption, since the amount of Cd adsorbed on edge positions is ~20 µmol/g, practically half of the amount adsorbed on SAZ (39 µmol/g) at the higher Cd concentration used. However, the amount of Cd adsorbed on edge positions in SAZ-Li at pH 6.5 should not be assumed to be the real Cd adsorption on edge positions in SAZ at the same pH, as in this case there are also interlamellar positions competing with those for Cd adsorption. Moreover, there could be some adsorption at interlamellar sites which were not eliminated on SAZ-Li.

This behaviour can also be seen by using the distribution coefficient, K_D, which is a simple and useful parameter to measure the affinity adsorbent-adsorbate. This cofficient, K_D, is defined as

$$K_D M = \frac{\Pi[\text{clay-}M]}{\Pi[\text{sol-}M]}$$

where $\Pi[\text{clay-}M]$ is the product of the concentrations of M species (Zn or Cd) adsorbed on the clay in µEq/g, and $\Pi[\text{sol-}M]$ is the product of the various species of M in the equilibrium solution (in µEq/g). For Zn, K_D has been calculated assuming that the metal is present in solution and on the clay

as Zn^{2+}, and not as the species $ZnOH^+$, since, from its equilibrium constant and at the pH of our system (6.5), the proportion of $ZnOH^+$ will be 9%, and hence its influence should be expected to be small. The $ZnCl^+$ species in solution is also negligible (2.62%). For Cd, the species which have been considered for K_D calculations are Cd^{2+} (50.25%) and $CdCl^+$ (47.44%). The hydrolysis species are negligible at the equilibrium pH; only at pH above 7.5 do they contribute significantly to the total Cd in solution (Lindsay, 1979).

In Figs. 5 and 6, K_D values for Zn and Cd adsorption on montmorillonite have been represented as a function of the amount of metal adsorbed, for simultaneous (Figs. 5a and 6a) and successive adsorptions (Figs. 5b and 6b). In all cases, K_D values (that is, affinity adsorbent-adsorbate) are high for the low amount of metal adsorbed, but decrease with increasing metal surface coverage on the clay. This indicates the existence of high- and low-affinity adsorption sites on the clay, as mentioned above. Moreover, in simultaneous adsorption of Zn (Fig. 5a) and Cd (Fig. 6a), a decrease in the K_D value is seen when the chlordimeform concentration increases, indicating that the apparent metal affinity for the clay decreases in the presence of chlordimeform. This
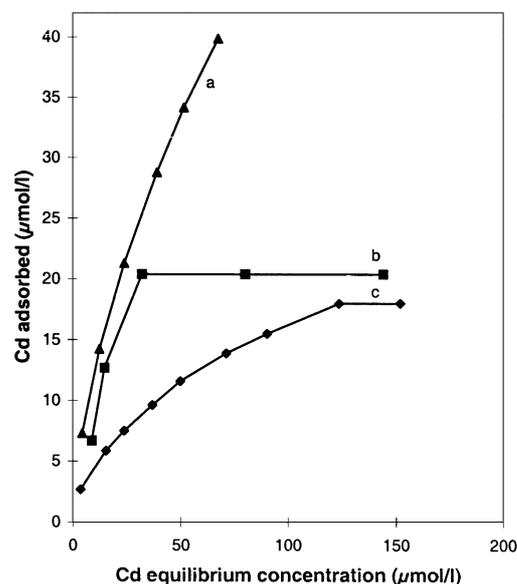

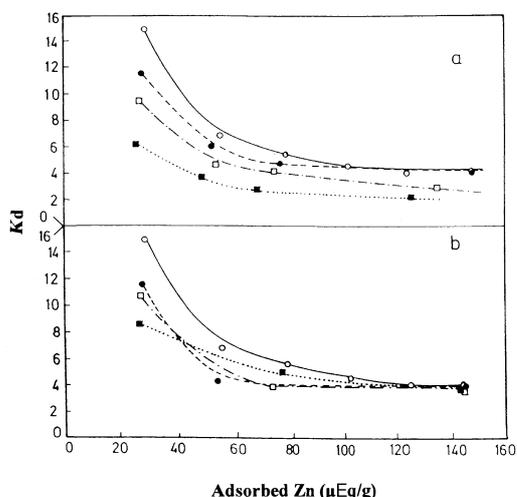FIG. 4. Cd adsorption isotherms on SAZ (a); and on SAZ-Li at solution pH 6.5 (b) and 5 (c).

FIG. 5. Zn K_D values as a function of the amount of Zn adsorbed in simultaneous (a) and successive (b) adsorption, at various chlordimeform concentrations: 0 (○), 0.1 (●), 0.5 (□) and 1.0 (■) mmol/l.

FIG. 6. Cd K_D values as function of the amount of Cd adsorbed in simultaneous (a) and successive (b) adsorption, at various chlordimeform concentrations: 0 (○), 0.1 (●), 0.5 (□) and 1.0 (■) mmol/l.

behaviour is also observed for K_D values in Zn successive adsorption (Fig. 5b), but is quite different for Cd successive adsorption (Fig. 6b). In this case, the apparent affinity of Cd adsorption is higher when the clay has been previously treated with the pesticide than in its original form.

On the other hand, in simultaneous adsorption of Zn (Fig. 5a) and Cd (Fig. 6a), the decrease in affinity is observed for both low and high amounts of metal adsorbed. In successive adsorption, however, the behaviour of the K_D curves is different for the high amounts of Zn and Cd adsorbed, since K_D converges towards a constant value for all the chlordimeform concentrations used. The reason could be that when the metal surface coverage on the clay is high, the high affinity sites have been filled, and only the interlayer positions are accessible. In such conditions, when the adsorption is simultaneous, the chlordimeform concentration in the equilibrium solution causes strong competition with the heavy metal that makes metal affinity decrease. In successive adsorption, however, the chlordimeform concentration present in the equilibrium solution is very low, because only a very small fraction of pesticide has been desorbed from the clay. The competition with the heavy metal is practically nil, and metal affinity for the planar positions is the same for each chlordimeform
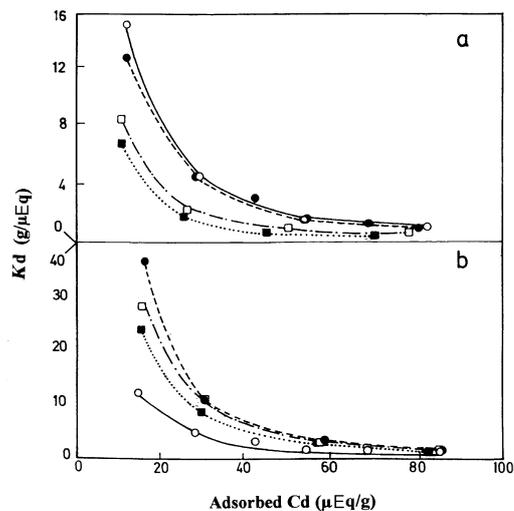
concentration used (Figs. 5b and 6b), and the same as when there is no chlordimeform previously adsorbed.

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