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## ADSORPTION OF MOLYBDATE BY CLAY MINERALS I — KAOLINITE

*Adsorption of molybdate by kaolinite was investigated at 25°C in a 0.01 mol dm<sup>-3</sup> sodium chloride background medium at pH 3 to 8 and initial molybdenum concentrations ranging from 0.5 to 150 µgcm<sup>-3</sup>. Short term distribution equilibrium is attained in less than 10 hours and remains undisturbed for at least 48 hours. A maximum of adsorption is observed at pH = 3.8. The adsorption isotherm for pH = 4.6, the natural pH of kaolinite suspensions in 0.01 mol dm<sup>-3</sup> NaCl, fits well a Langmuir equation with a limiting value of 1.63 mg Mo/g kaolinite. For equilibrium Mo concentration in solution lower than 3 µg cm<sup>-3</sup>, i.e., the range normally found in the soil solution, the isotherm can be approached by a straight line and adsorption conveniently characterised by a distribution coefficient  $K_d = 160 \pm 4 \text{ cm}^3 \text{ g}^{-1}$ ; this is independent of the clay/solution ratio, Na,Cl-kaolinite shows a similar behaviour for the same low concentration range, but with higher adsorption.*

## 1 — INTRODUCTION

Clay minerals are potentially important in controlling the fixation and mobility of molybdenum in soils. Studies on the adsorption of molybdenum by the frequently occurring clay minerals, kaolinite, montmorillonite and illite are however scarce for kaolinite and lacking for the other two. Jones [1], in a comparative study of the adsorption of molybdenum by clay minerals and by iron and aluminium oxides, has investigated the adsorption of molybdate on kaolinite for a fixed initial molybdenum concentration and varying pH. Theng [2] has studied the adsorption isotherm of molybdate and its dependence on pH for a clay fraction of a Taita soil, reported to consist mainly of kaolinite and illite.

Adsorption isotherms provide a convenient means for describing adsorptive behaviour and have actually been used to predict the fertilizer requirements of soils [3]. They can yield (i), an equation which makes it possible to summarize adsorption by using a few numbers rather than by referring to a curve, and (ii), information about the nature of the adsorption process itself. However, since the isotherm is a macroscopic concept consistent with different mechanisms at the molecular level, such information must be supplemented with data concerning, e.g. rates of diffusion of exchangeable ions through the adsorbent, kinetics of the exchange reaction, and spectroscopy of the species at the adsorbent surface [4].

On the other hand, adsorption phenomena may present long term features differing from the short term behaviour, due to slow reaction between adsorbent and adsorbate. This has been observed and studied in particular in the case of the adsorption of phosphate by soils [5,6,7,8].

In the present work we investigate the short term adsorption of molybdate on kaolinite with the purpose of describing it with a minimal set of parameters; special attention is devoted to the range of molybdenum

concentrations usually found in the soil solution.

## 2 — EXPERIMENTAL

Light kaolin, (I) was obtained from BDH. X-ray diffraction analysis of this material showed besides the characteristic lines of kaolinite at 0.715 and 0.375 nm, weak lines at 1.0 and 0.496 nm indicating only a few per cent illite. Sedimentation analysis in hexametaphosphate medium yielded the following particle size distribution: 50-20  $\mu\text{m}$ , 5.9 %; 20-2  $\mu\text{m}$ , 0.8 %; 2-0.5  $\mu\text{m}$ , 65.0 %; < 0.5  $\mu\text{m}$ , 28.1 %. The specific BET ( $\text{N}_2$ ) area was  $13 \text{ m}^2 \text{ g}^{-1}$ . Na,Cl — kaolinite was prepared from (I) according to the method described by Posner and Quirk [9]. Otherwise, analytical grade reagents and deionized water were employed.

One gramme portions of kaolinite were placed in 250  $\text{cm}^3$  polythene bottles and vigorously shaken for one minute with adequate volumes of  $0.01 \text{ mol dm}^{-3}$  sodium chloride. Aliquots of  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  standard stock solutions were added to the suspensions. The bottles were shaken for 24 hours at 120 15 cm-strokes per minute in a waterbath at  $25.0 \pm 0.5^\circ\text{C}$ . 10  $\text{cm}^3$  samples were then taken for pH measurements and the bottles replaced upright, fully immersed, in the waterbath for a further half an hour period. Finally, the supernatants were first centrifuged and then filtered through a  $0.4 \mu\text{m}$  polycarbonate membrane filter. It was checked that no significant loss of molybdenum occurred during the filtration step.

For adsorption measurements at pH values other than the natural pH (4.6) of kaolinite suspensions in  $0.01 \text{ mol dm}^{-3}$  sodium chloride,  $0.01 \text{ mol dm}^{-3}$  HCl or NaOH were added to the suspensions in order to approximate the pH sought. A period of 24 hours was allowed for acid-base equilibration, and the final pH recorded prior to the addition of molybdate.

Molybdenum was determined in the filtrates by flameless atomic absorption at 313.3 nm

with a slit setting of 0.7 mm. The detection limit (1% absorption,  $A=0.004$ ) was  $0.5 \text{ ng cm}^{-3}$  corresponding to 10 pg molybdenum per fire, as 20  $\text{mm}^3$  injections were used. By suitable dilution of the samples their absorbances were kept within the range where linearity is observed and memory effects are negligible. Blanks corresponded to about 5 to 10 % of the measured absorbances. The average of three readings was taken for each solution; the variation coefficient of the mean was 2 %.

## 3 — RESULTS AND DISCUSSION

### a) Equilibration time

The influence of time of contact between solution and solid phase on the extent of adsorption was investigated for several initial molybdenum concentrations and for contact times from 0.5 to 48 hours. Figure 1 shows a typical equilibration curve: adsorption of molybdenum rises steeply to about 60 % of its final value in less than 1 hour, then continues with a decreasing rate and reaches a plateau in about 10 hours; the plateau extends up to 48 hours at least. Equilibration times of 24 hours are therefore adequate.

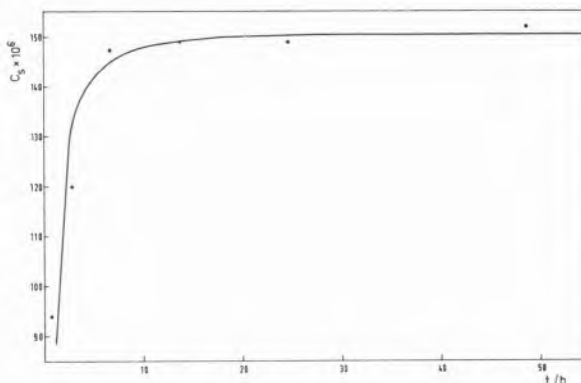


Fig 1

Effect of time of contact on the adsorption of molybdenum, 1 g kaolinite;  $100 \text{ cm}^3$   $0.01 \text{ mol dm}^{-3}$  NaCl;  $C_0(\text{Mo}) = 2.5 \mu\text{g cm}^{-3}$ .

### b) Clay/solution ratio

The influence of the clay/solution ratio on adsorption was investigated in the range 5-50 grams of kaolin per litre of solution and for an initial molybdenum concentration equal to  $2.5 \mu\text{g cm}^{-3}$ . This corresponded to  $0.3\text{-}1.7 \mu\text{g cm}^{-3}$  molybdenum in the aqueous phase at equilibrium.

From mass balance considerations the following relationship can be established

$$C_s = \frac{C_o}{\frac{m}{V} + \frac{1}{K_d}} \quad (1)$$

where  $C_o$  is the initial Mo concentration in solution in  $\mu\text{g cm}^{-3}$ ,  $C_s$  the equilibrium Mo concentration in the solid phase, also in  $\mu\text{g cm}^{-3}$ ,  $m$  is the mass of adsorbent (g) and  $V$  the volume ( $\text{cm}^3$ ) of solution,  $K_d = \frac{C_s}{C_e}$  is in general a function of  $C_e$ ; the equilibrium concentration in the liquid phase.

Equation (1) can be given the form

$$\frac{C_o}{C_s} = \frac{m}{V} + \frac{1}{K_d} \quad (2)$$

implying a linear dependence of  $\frac{C_o}{C_s}$  on  $\frac{m}{V}$  if  $K_d$  is constant. Figure 2 shows that this is indeed the case. The observed slope, 0.96, agrees with the theoretical value, 1, and the intercept yields  $K_d = 131 \text{ cm}^3 \text{ g}^{-1}$ . A better estimation of  $K_d$  because no extrapolation is involved, can be obtained by averaging the experimental  $C_s/C_e$  ratios, which yields  $K_d = 139 \pm 16 \text{ cm}^3 \text{ g}^{-1}$ .

Thus, for molybdenum equilibrium concentrations in solution up to  $1.7 \mu\text{g cm}^{-3}$  at least the adsorption equilibrium can be described by a distribution coefficient which does not

depend on the clay/solution ratio nor on molybdenum concentration.

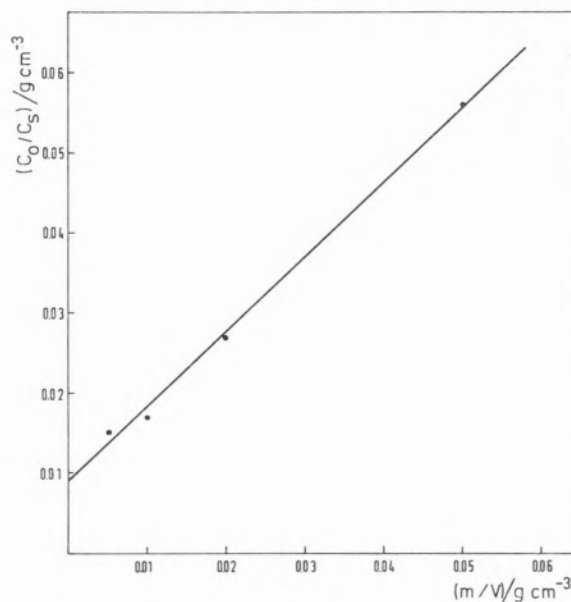


Fig. 2

Confirming that Mo adsorption does not depend on clay/solution ratio.

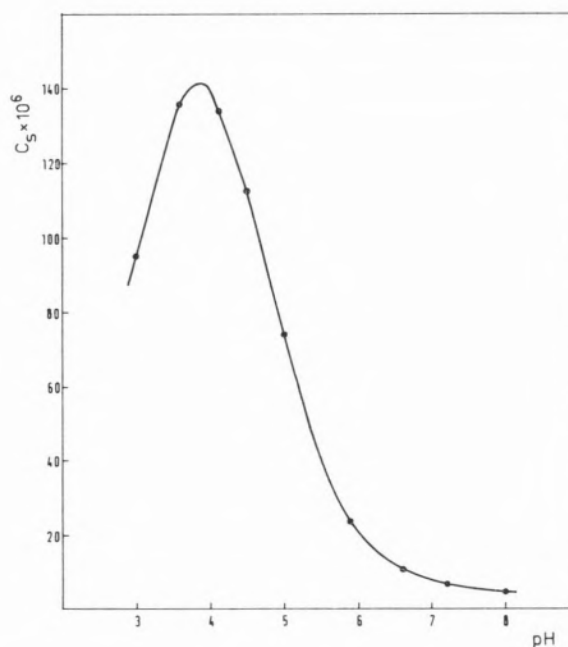


Fig. 3

Dependence of Mo adsorption pH. 10 g kaolin/dm<sup>3</sup>;  $C_o(\text{Mo}) = 2 \mu\text{g cm}^{-3}$ ;  $0.01 \text{ mol dm}^{-3} \text{ NaCl}$  medium.

## c) pH

The dependence of molybdenum adsorption on pH is shown in figure 3. A maximum of adsorption is observed for  $\text{pH} = 3.8$ , i.e. near the  $\text{pK}$  of the  $\text{HMoO}_4^-$  ion [10] as required by the theory of Hingston et al. [11,12]. Essentially the same curves have been reported by Jones [1] for kaolinite under similar conditions ( $20 \text{ g clay/dm}^3$ ,  $C_0 = 2 \text{ } \mu\text{g cm}^{-3}$ ) and by Theng [2] for the clay fraction of a Taita soil containing mainly kaolinite and illite ( $2.5 \text{ g clay/dm}^3$ ,  $C_0 = 2.5 \text{ } \mu\text{g cm}^{-3}$ ,  $0.2 \text{ mol dm}^{-3} \text{ NaCl}$  medium).

## d) Pre-treatment of the adsorbent

Kaolinite in the Na,Cl homoionic form adsorbs more molybdenum than the untreated clay (Fig. 4), indicating that less accessible sites have been exposed by the pre-treatment of the adsorbent. The differences are significant enough to deserve further investigation.

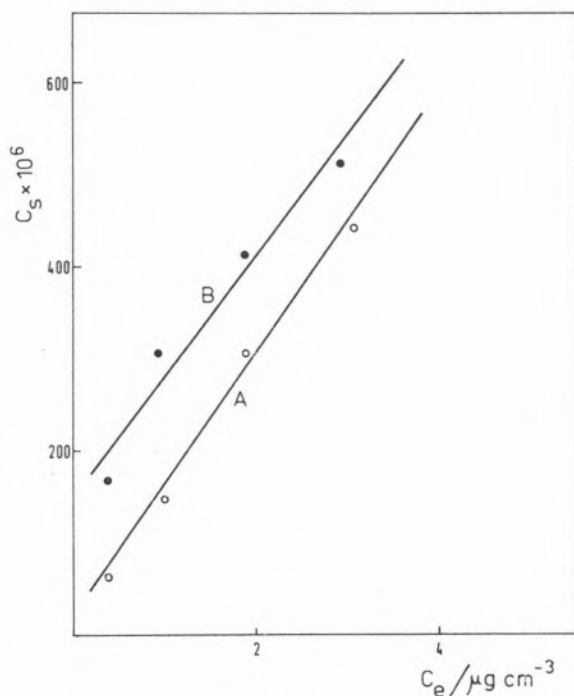


Fig. 4

Effect of the pre-treatment of kaolinite on the adsorption of molybdenum. A — untreated kaolinite; B — Na,Cl-kaolinite,  $10 \text{ g clay/dm}^3$ .

## e) Molybdenum concentration

Figure 5 shows the adsorption isotherm for equilibrium molybdenum concentrations in solution up to  $100 \text{ g cm}^{-3}$ , at  $\text{pH} 4.6$  and for a clay/solution ratio equal to  $10 \text{ g dm}^{-3}$ . The curve is of the L type (Giles classification [13]), indicating a moderately high affinity between molybdate and adsorbent.

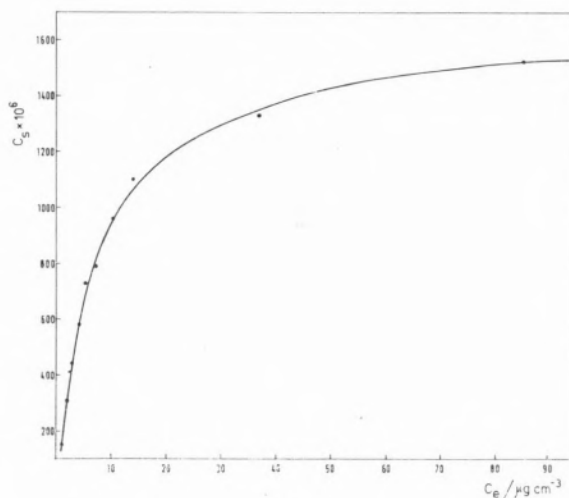


Fig. 5

Adsorption isotherm for molybdate on kaolinite at  $298 \text{ K}$  in  $0.01 \text{ mol dm}^{-3} \text{ NaCl}$  medium.

It conforms to the Langmuir equation, (Fig. 6):

$$\frac{C_e}{C_s} = 0.594 \times 10^{-3} C_e + 5.24 \times 10^{-3} \quad (4)$$

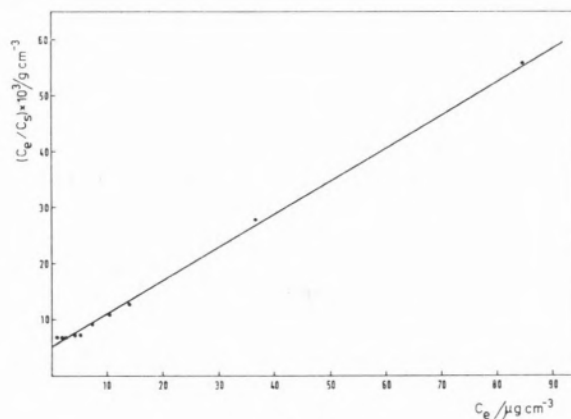


Fig. 6

Langmuir plot for the adsorption isotherm of fig 5.

For molybdenum equilibrium concentrations in solution lower than  $3 \mu\text{g cm}^{-3}$  the isotherm can be conveniently described by the straight line (Fig. 7)

$$C_s = 160C_e \quad (5)$$

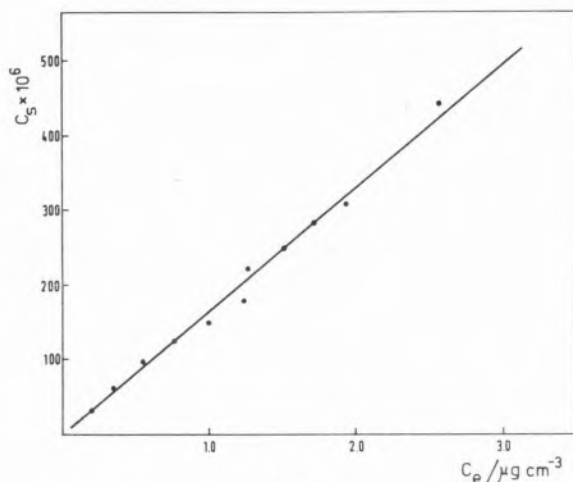


Fig. 7

Linear plot for adsorption isotherm of fig. 5 for  $C_e < 3 \mu\text{g cm}^{-3}$ .

and the adsorption equilibrium therefore characterized by a single parameter, the distribution coefficient  $K_d = 160 \pm 4 \text{ cm}^3 \text{ g}^{-1}$ . On the other hand, for  $C_e > 2 \mu\text{g cm}^{-3}$  a better Langmuir fit is given by the equation

$$\frac{C_e}{C_s} = 0.615 \times 10^{-3} C_e + 4.5 \times 10^{-3} \quad (6)$$

The differences between calculated and experimental  $C_s$  values amount to  $6 \pm 5 \%$  in the case of equation (5); for equation (6) the differences are  $3 \pm 2 \%$ , in better agreement with the variation coefficient for the experimental  $C_s$ ,  $2 \pm 1 \%$ .

Equation (6) indicates that saturation of the adsorbent by molybdate is achieved at  $1.63 \text{ mg Mo/g kaolinite}$ . Each molybdate ion may be attributed an individual area of  $0.3\text{--}0.4 \text{ nm}^2$ , considering the tetrahedral configuration of the ion and the O-O distance in sodium molybdate [14]. Thus, the total area

occupied by molybdate on saturated kaolinite amounts to  $3\text{--}4 \text{ m}^2$ ; this corresponds to about  $1/4$  of the total BET area of the adsorbent and may represent the area of the edge faces of the crystalites.

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