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Cu and Pb Adsorption on Some Bentonitic Clays

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Cu^{2+} and Pb^{2+} adsorption isotherms were measured on some clay samples obtained from various regions of Turkey. Also specific surface areas of clays were determined from adsorption data of ortho-phenanthroline(OP). The adsorptions of ions and OP were studied using the batch equilibration technique as a function of adsorbate concentration. The adsorption data, over the whole range of concentrations used, follow the Langmuir adsorption isotherm. The retention capacities of the adsorbates and the cation exchange capacities of the clays were determined. Plots of K_d, the distribution coefficient of ions between the solid and solution phases, vs. Γ, the surface density of adsorbed ions, showed that all the samples behave similarly, i.e. K_d sharply decreases with increasing values of Γ. The amount of Pb^{2+} adsorbed is about 3-4 times that of Cu^{2+} and the same adsorption capacity sequence was found for each ion.

Introduction

The ability of clay minerals to adsorb heavy metal cations is an important property in the context of the increasing contamination of aquatic environments and soils by toxic wastes[1]. Also sorption of metals on clays is becoming important for preparing "pillared" clay catalysts[2]. Laboratory studies of the adsorption of heavy metals by clays have mostly been carried out using montmorillonite and illite[3-8].

The sheet faces of montmorillonite species acquire an overall negative charge through isomorphous substitution, either of Al^{3+} for Si^{4+} in silica tetrahedra or of Mg^{2+} for Al^{3+} in alumina octahedra. This negative charge is balanced by mono and divalent cations which are called exchangeable cations. The exchangeable cations are only loosely held in the framework and can be removed or exchanged easily by washing with a solution of another cation. The ion exchange phenomenon is a special case of adsorption. In the adsorption of some heavy metal ions by montmorillonite there is evidence of two forms of bound metal. One form is reversibly desorbed by the addition of competing ions. The other form requires low pH values for release and is considered to have entered the crystal lattice[3].

Several factors influence the adsorbability of ions on clays, including salt concentration, pH of the solution, degree of loading on the adsorber, presence of ligands and complex formation.

A wide range of methods is available for the determination of the specific surface areas of clays[9]. In general the methods are of different reliability and accuracy. Vapor phase adsorption methods, in particular the use of nitrogen or rare gases at low temperatures, have been widely accepted as the most reliable.

Solute adsorption however, offers several advantages over vapor phase adsorption for determination of the specific surface. The experimental procedure is much simpler than in any method requiring vacuum apparatus. Among the methods used successfully is that based on ortho-phenanthroline(OP) adsorption from an aqueous solution. Lawrie[10], Bower[11], and De Bussetti et.al.[12] reported that this method gives reliable results for some clays such as montmorillonite, illite, and kaolinite. In this study, for the determination of the surface densities of retained ions, specific surface areas of clay samples have been found by using adsorption data of OP.

Experimental

Materials and Apparatus

In this study, four bentonitic clay samples rich in the montmorillonite mineral were used as adsorbents. The following clay samples were subjected to examination. Eskişehir Beylikova bentonite(EBB), Eskişehir Demirliköy bentonite(EDB), Eskişehir Yunusemre bentonite(EYB), Konya Beyşehir bentonite(KBB). Chemical and mineralogical analyses of the samples were carried out. The clay samples were ground, dried at 105° C (24hr.) and passed through a 200 mesh sieve.

Cu^{2+} and Pb^{2+} stock solutions were prepared from analytical-grade nitrate salts, and Merck analytical-grade ortho-phenanthroline hydrochloride, with the composition $C_{12}H_9N_2Cl.H_2O$, was used in this study.

A Perkin Elmer 400 Atomic Absorption Spectrophotometer(AAS) was used to analyze the cations and a Varian SuperScan 3 UV-Visible Spectrophotometer was used for OP analysis. An Orion 701 A digital pH-meter was used for pH measurements.

Cu^{2+} and Pb^{2+} Adsorption

In the adsorption experiments clay samples approximately 1 gram in weight were weighed accurately and put into volumetric flasks. 100 mL of salt solutions at different concentrations were added to each of the samples. When a clay sample is placed in contact with the salt solution, it increases the solution's pH. Also the hydrolysis of cations affects the pH of the solution. Preliminary experiments and the solubility products of hydroxides of worked cations showed that the solutions have to be adjusted to the definite initial pH values using HNO_3 and KOH before equilibrium. Therefore the precipitation of hydroxides can be prevented during adsorption. Initial pH values were determined to be pH 5 and pH 4 for the Cu and Pb experiments, respectively. The clay-solution systems were then equilibrated for 48 hours by occasionally shaking at 25° C. The clay suspensions were centrifuged, the supernatant liquid was separated and filtered and cations were determined using AAS. The amounts of metal ions retained by the adsorbents were calculated by the difference between the initial and final (equilibration) concentrations of ions in each solution.

OP Adsorption

The adsorption of OP by the clay samples was carried out by adding 25ml of OP solutions of different concentrations (1-16 $mmol.L^{-1}$) to 0.15 g of adsorbent in volumetric flasks. The flasks were shaken for 30 min. and left for 24 hr. with occasional shaking at 25° C. Filtration followed and the filtrates were analyzed for OP.

OP was determined colorimetrically[10] from the color developed with ferrous iron in the presence of the reducing agent hydroxylamine hydrochloride and acetate buffer at pH 3.5. For spectrophotometric absorbance readings, a 508 nm analytical wavelength was used. The amounts of OP adsorbed were calculated from the initial and final concentrations.

The surface area of each adsorbent was calculated from the retention capacity, assuming that each molecule of OP occupies an area of 60A^{02}. This calculation assumes that each OP molecule lies flat on the surface.

Results and Discussion

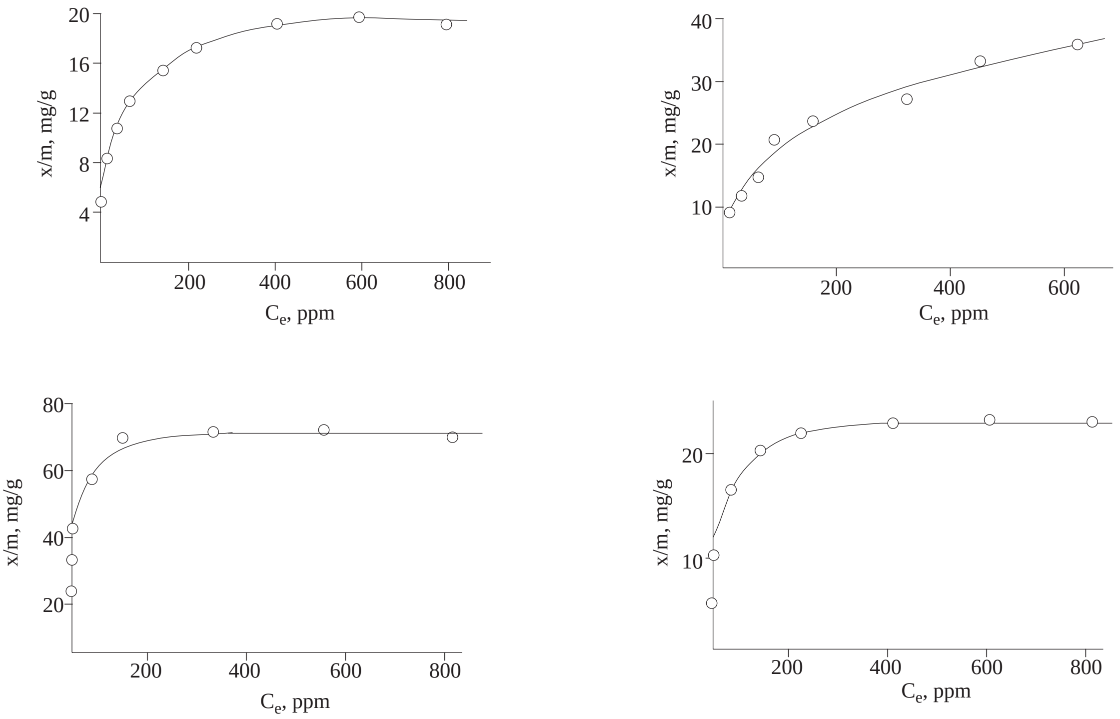
There have been numerous studies on the sorption of heavy metals from aqueous solutions by clay minerals. Some studies have shown that the adsorption is described by the Freundlich adsorption isotherm[8,13,14], but some adsorption isotherms follow the Langmuir equation[5,15–18].

The retention data in this study were analysed according to the Langmuir equation:

$$\frac{C_e}{(x/m)} = \frac{1}{k.b} + \frac{C_e}{b} \tag{1}$$

where C_e is the equilibration concentration of metal ion or OP remaining in the solution. x/m is the quantity of metal ion or OP adsorbed per unit weight of adsorbent. b and k are Langmuir constants. These constants are retention capacity (b), and bonding energy constant (k).

Straight lines were fitted to the points by the method of least squares, where the slope of the regression line is $1/b$, the intercept is $1/k.b$ and k = slope/intercept. The linear regression lines obtained had highly significant correlation coefficients (r), indicating a very good fit to the Langmuir equation. The adsorption isotherms and Langmuir lines for each adsorbate are shown in Figures 1-6. Langmuir constants and correlation coefficients are given in Tables 1 and 2 for metal ions and OP, respectively.



(c) **(d)**

Figure 1. Adsorption isotherms of Cu^{2+} on a) EBB, b) EDB, c) KBB, d) EYB.

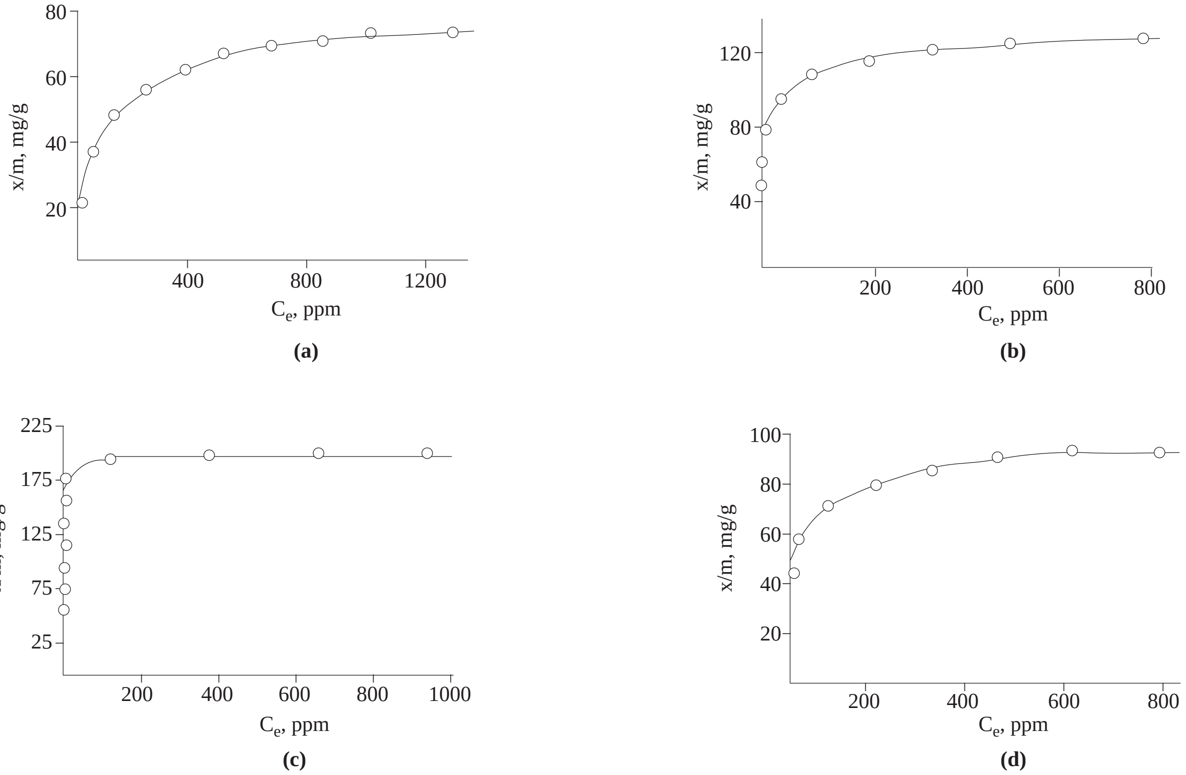


Figure 2. Adsorption isotherms of Pb^{2+} on a) EBB, b) EDB, c) KBB, d) EYB.

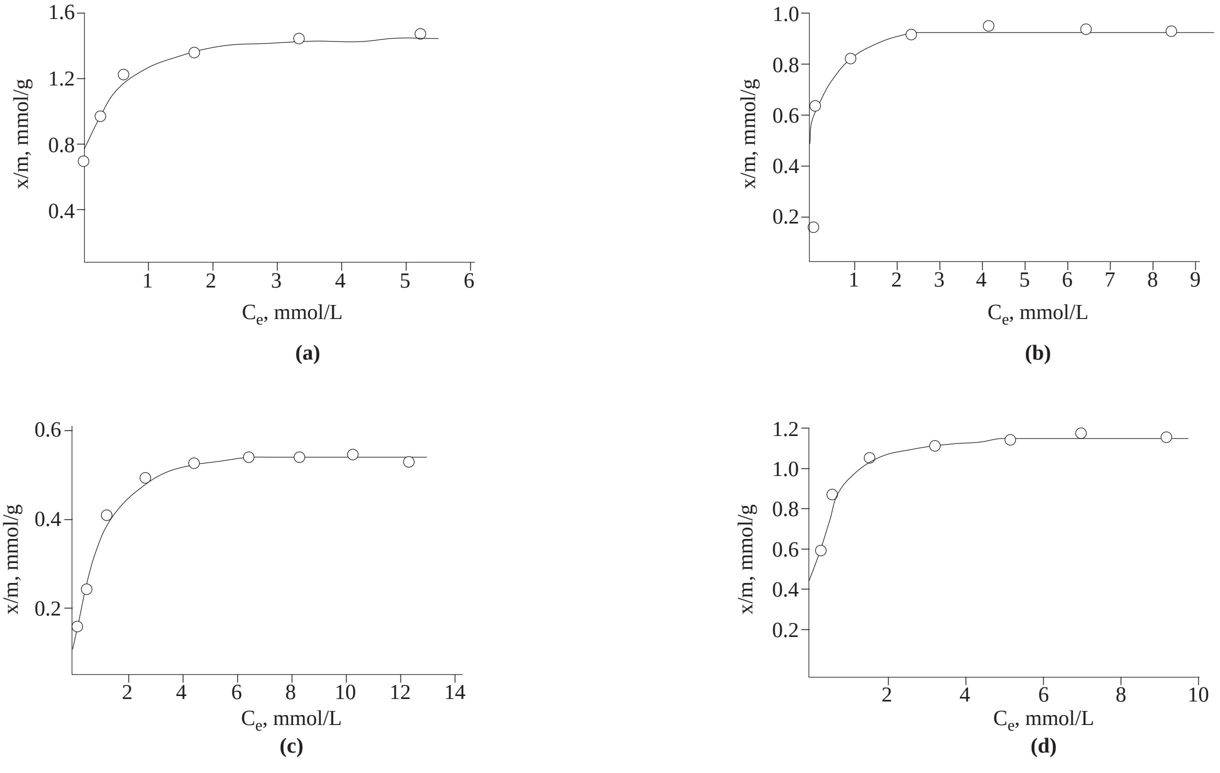


Figure 3. Adsorption isotherms of OP on a) EBB, b) EDB, c) KBB, d) EYB.

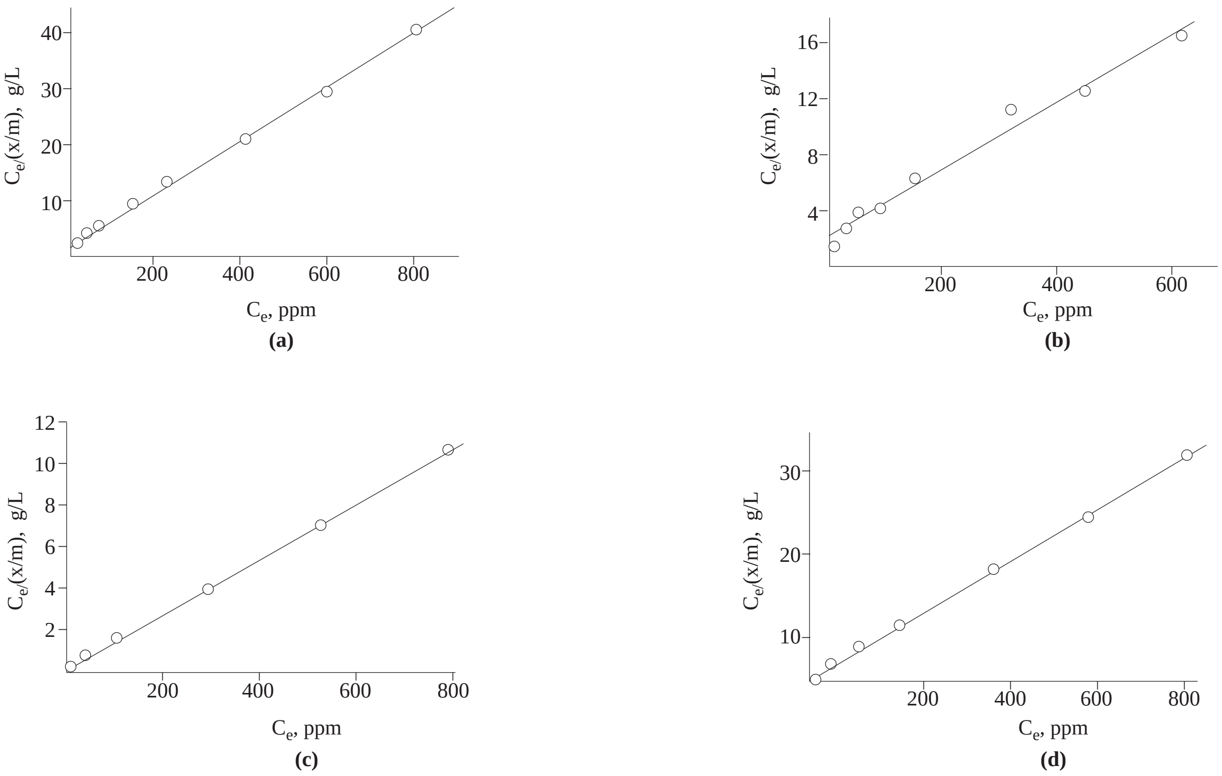


Figure 4. Langmuir lines for Cu^{2+} on a) EBB, b) EDB, c) KBB, d) EYB.

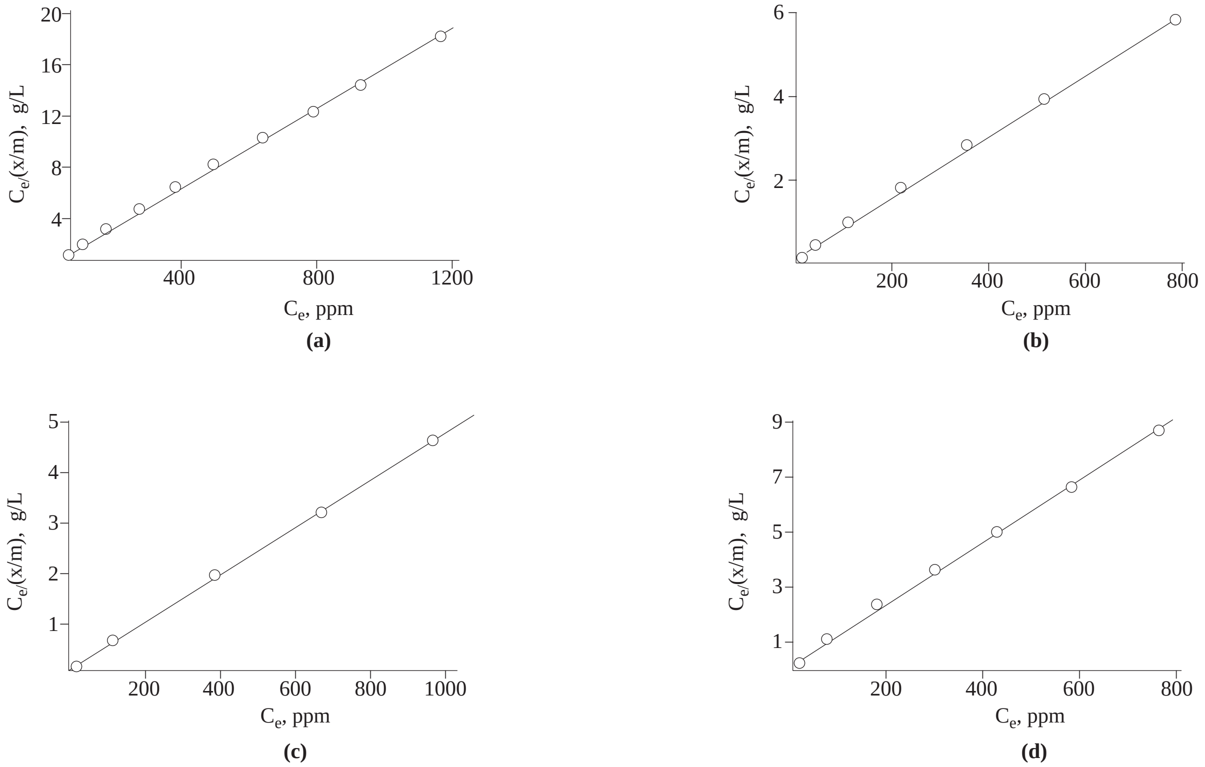


Figure 5. Langmuir lines for Pb^{2+} on a) EBB, b) EDB, c) KBB, d) EYB.

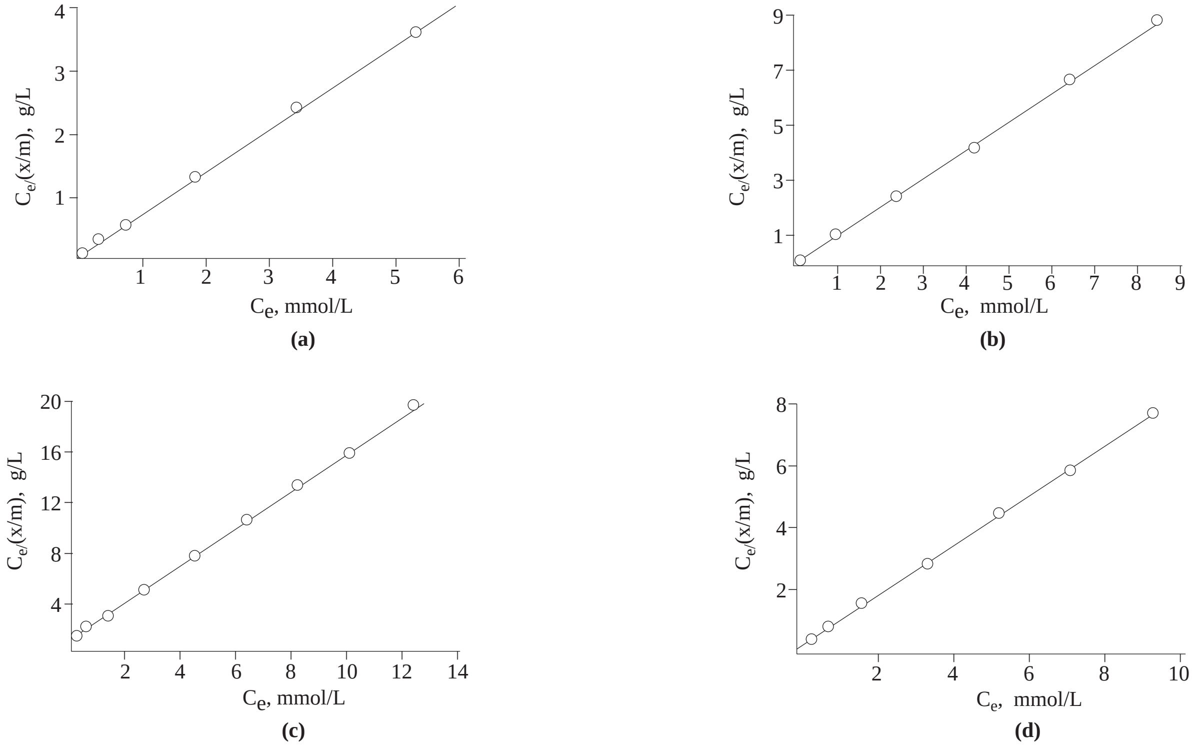


Figure 6. Langmuir lines for OP on a) EBB, b) EDB, c) KBB, d) EYB.

Table 1. Langmuir equation data for Cu and Pb retention

Ion	Sample	b, mg/g	k, L/mg	r
Cu	EBB	20.2922	0.0342	0.9989
	EDB	40.7830	0.0110	0.9904
	EYB	23.8607	0.0948	0.9997
	KBB	72.4113	0.1872	0.9999
Pb	EBB	77.8210	0.0130	0.9988
	EDB	132.1004	0.0865	0.9994
	EYB	97.8474	0.0470	0.9990
	KBB	204.9180	0.5851	1.0000

Table 2. Langmuir equation data for OP retention

Sample	b, mmol/g	k, L/mmol	r
EBB	1.4807	7.9183	0.9997
EDB	0.9464	18.9975	0.9998
EYB	1.1905	4.2812	0.9999
KBB	0.6654	1.6152	0.9995

The specific surface area, (S) in $m^2.g^{-1}$ is given by the formula,

$$S = X_m \cdot N \cdot A/n \tag{2}$$

where X_m is the monolayer capacity in moles per gram (= retention capacity, b), N is the Avogadro number, A is the area of surface occupied by each OP molecule in a sq.meter, and n is the number of OP in micelle.

Kinetic and light scattering studies show that OP is adsorbed as a micellar unit composed on average of 3.5 molecules/micelle[12]. The surface area occupied by such a unit is expected to be less than 3.5 times the area of one molecule of OP.

Specific surface areas and cation exchange capacities of the clays are given in Table 3. Cation exchange capacities were determined using the ammonium saturation method.

Table 3. Surface area and cation exchange capacity of clays

Sample	SSA, m^2/g	CEC, meq/100g
EBB	153	78.00
EDB	98	73.95
EYB	123	61.54
KBB	69	31.15

The adsorbability of Pb^{2+} onto each clay sample is more than that of Cu^{2+} (Table 1). The amount of Pb^{2+} adsorbed is about 3-4 times that of Cu^{2+}. The adsorption capacity sequence of clay samples for each ion has been found to be KBB > EDB > EYB > EBB.

The data in Tables 1 and 3 show that the Cu^{2+} and Pb^{2+} retention capacities of the studied clays were inversely related to the CEC of the clays.

There are contradictory results about the dependence of the adsorption of heavy metals to CEC in the literature. For example, Shuman[5] and Navrot et.al.[18] showed that the retention capacity is positively correlated to the CEC. John[15], on the other hand, failed to find any such correlation. Reddy and Perkins[19], found an inverse relation between CEC and Zn fixation. Helios-Rybicka[8], found that neither the CEC nor the specific surface area of clay minerals has any significant effect on the amount of sorption.

It seems reasonable to assume that the montmorillonite adsorbed heavy metals on two classes of site: on one, cation-exchange behavior is followed, and on the other the adsorption behavior is similar to that on hydrous oxide gels of aluminum and iron. The latter sites correspond to the edges and broken bonds of the montmorillonite.[7,20].

In the sorption of Cu^{2+} ions by Ca-bentonite the majority of the adsorption sites are considered to be lattice OH groups located at crystal defects and edges[3]. The involvement of surface OH groups available for deprotonation in the specific sorption process is supported by some IR evidence[21].

The adsorption of heavy metals on montmorillonite cannot be explained in terms of simple ion-exchange mechanism and CEC cannot be considered to be the sole predicting parameter. When considering the sorption of heavy metals on clay minerals, the role played by hydrated iron oxides and hydroxides must be taken into account[5,22].

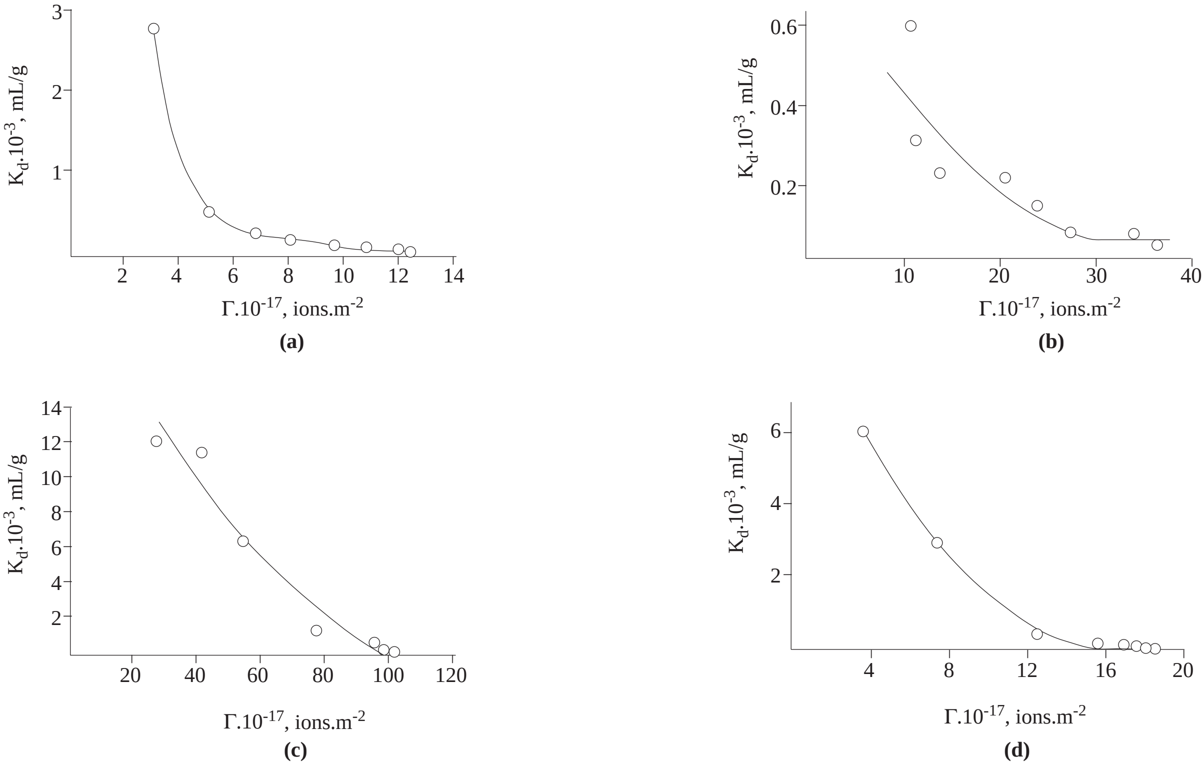
The pH of the solutions in this study was limited to less than 7 so that no precipitation of hydroxides of the studied cations would occur (initial pH values were adjusted to pH 5 and pH 4 for the Cu and Pb experiments before equilibrium, as mentioned in general procedure section). The pH has several effects on the adsorption process. At different acidities, the species present in the solution may be different. Some studies have shown that the adsorption of Cu, Pb and Co is pH dependent[3,21,23]. This phenomenon was interpreted in terms of structural hydroxyl groups of the clay or hydroxy-aluminum compounds. The pH may have an effect on the solid phase too; for example, the capacity of oxides and selectivity of ions towards oxides is known to be pH dependent[24]. Precipitation may also occur, especially in the high pH range. The solutions were adjusted to the required pH values using HNO_3, and KOH, and no buffering system was used in this study. This is because the choice of a buffering system is restricted by the need to avoid complex formation and to avoid strong adsorption of the buffering agent on the clay.

Also the dependence of the distribution coefficient of ions between the solid and solution phases (K_d) on the surface density of retained ions (Γ) are given in Figures 7 and 8 for each sample. These values are given as follows[18]:

$$K_d = \frac{(x/m)}{C_e}, \quad [mL.g^{-1}] \tag{3}$$

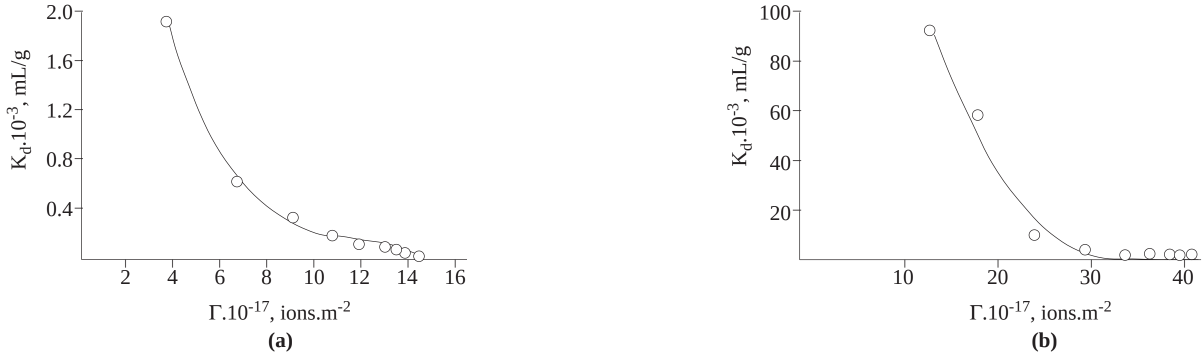
$$\Gamma = \frac{(x/m).N}{(\text{atomic weight}).S}, \quad [\text{ions}.m^{-2}]. \tag{4}$$

As the surface density increases K_d decreases, showing reduced affinity of the surface towards ions. At high surface coverages the adsorption is due to ion-exchange, where Pb^{2+} or Cu^{2+} compete mostly with exchangeable Ca^{2+} and Mg^{2+}, and K_d is relatively low[18,25–27]. At low surface coverages K_d reaches the values characteristic of the specific adsorption region on montmorillonite and is due to more specific sites, or possibly other mechanisms of retention.

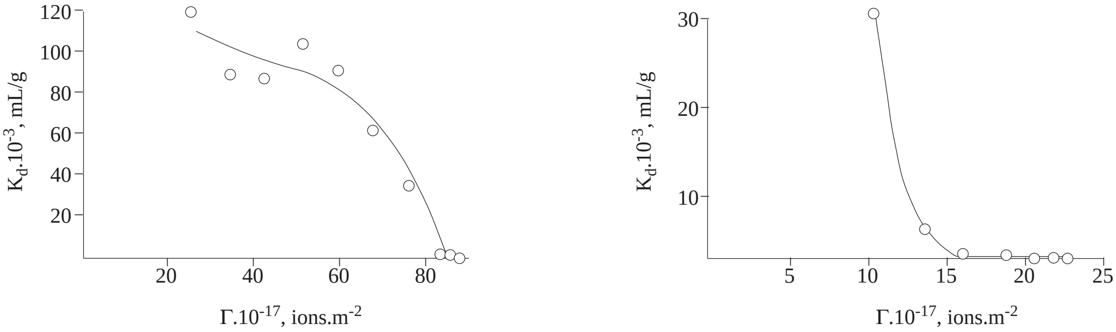


(a) **(b)** **(c)** **(d)**

Figure 7. Plots of K_d vs. Γ for Cu^{2+} a) EBB, b) EDB, c) KBB, d) EYB.



(a) **(b)**



(c) **(d)**

Figure 8. Plots of K_d vs. Γ for Pb^{2+} a) EBB, b) EDB, c) KBB, d) EYB.

Conclusion

From this study, the following conclusions were made:

1. The adsorption of Cu^{2+} and Pb^{2+} on bentonitic clay samples was found to conform with the Langmuir equation.
2. The amount of Pb^{2+} adsorbed is about 3-4 times that of Cu^{2+}.
3. The adsorption capacity sequence of clay samples for each ion has been found to be KBB $>$ EDB $>$ EYB $>$ EBB.
4. Cu^{2+} and Pb^{2+} retention capacities of studied clays were inversely related to the CEC and surface area values of the clays and these data suggest that the adsorption of heavy metals on bentonitic clays cannot be explained in terms of simple ion-exchange mechanism, and surface area cannot be considered to be a predicting parameter.

References

1. P.M. Huang, **The Handbook of Env. Chem.**, ed. by O. Hutzinger, **Vol.2** (1980).
2. T.J. Pinnavaia, M.S. Tzou, S.D. Landau, and R. Raythatha, **J. Molecular Catal.**, **27**, 195-212 (1984).
3. H. Farrah and W.F. Pickering, **Aust. J. Chem.**, **29**, 1177-1184 (1976).
4. H. Farrah and W.F. Pickering, **Water Air Soil Pollution**, **8**, 189-197 (1977).
5. L.M. Shuman, **Soil Sci. Soc. Am. Proc.**, **40**, 349-352 (1976).
6. R. Salim and B.G. Cooksey, **Plant and Soil**, **54**, 399-417 (1980).
7. Y. Egozy, **Clays and Clay Miner.**, **28**, 4 311-318 (1980).
8. E. Helios-Rybicka, **Miner. Pol.**, **14**, 57-63 (1983).
9. H. Van Olphen, "**Surface Area Determination**", Butterworths, London (1970).
10. D.C. Lawrie, **Soil Sci.**, **92**, 188-191 (1961).
11. C.A. Bower, **Soil Sci.**, **95**, 192-195 (1963).

12. S.G. De Bussetti, E.A. Ferreira, and A.K. Helmy, **Clays and Clay Miner.**, **28**, 2, 149-154 (1980).
13. A.C.M. Bourg and R.H. Filby, Proc. of the Intern. Conf. on Transport of Persistent Chemicals in Aquatic Ecosystems, Ottowa, Canada, II, 1-5 (1974).
14. E. Helios-Rybicka, **Clay Minerals**, **20**, 525-527 (1985).
15. M.K. John, **Can. J. Soil. Sci.**, **52**, 343-350 (1972).
16. R. Levi-Minzi, G.F. Soldatini, and R. Riffaldi, **J. Soil Sci.**, **27**, 10-15 (1976).
17. L.M. Shuman, **Soil Sci. Soc. Am. Proc.**, **39**, 454-458 (1975).
18. J. Navrot, A. Singer, and A. Banin, **J. of Soil Sci.**, **29**, 505-511 (1978).
19. M.R. Reddy and H.F. Perkins, **Soil Sci. Soc. Am. Proc.**, **38**, 229-231 (1974).
20. A. Maes and A. Cremers, **J. Soil Sci.**, **119**, 198-202 (1975).
21. E.E. Hildebrand and W.E. Blum, **Naturwissenschaften**, **61**, 169 (1974).
22. E. Helios-Rybicka and J. Schoer, **Mineralogia Polonica**, **13**, 1, 61-68 (1982).
23. P. Peigneur, A. Maes, and A. Cremers, **Clays and Clay Miner.**, **23**, 71-75 (1975).
24. K.A. Kraus, H.O. Phillips, T.A. Carlson, and J.S. Johnson, Progress in Nuclear Energy, IV, 28, Pergamon Press, Oxford, 3-16 (1960).
25. J. Garcia-Miragaya and A.L. Page, **Soil Sci. Soc. Amer. J.**, **40**, 658-663 (1976).
26. J. Garcia-Miragaya and A.L. Page, **Soil Sci. Soc. Amer. J.**, **41**, 718-721 (1977).
27. J.E. Bittel and R.J. Miller, **J. Env. Qual.**, **3**, 250-253 (1974).