

EFFECT OF LIGANDS ON THE ELIMINATION OF LEAD IONS FROM WATER
BY ADSORPTION ON ALUMINIUM OXIDE

BY

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ABSTRACT

The effects of some organic and inorganic ligands and change of Ph on Pb(II) uptake at aluminium oxide/water interface are determined in model experimental systems. Some ligands(e.g., citric acid) form nonadsorbing complexes in solution and prevent the coordination of Pb(II) ions at the surface. Other ligands (e.g., glutamic acid) can be immobilized at the surface resulting in increasing the Pb(II) uptake. Since a good Pb(II) uptake (up to 99%) is achieved at pH values higher than 5, no pH adjustments have to be made for natural waters. The results suggest that the Pb(II) concentration in natural aqueous systems may be controlled by surface binding on hydrous aluminium oxide surface.

INTRODUCTION

Many trace metals(e.g.,Cu,Pb,Hg,Cd,Zn,Ag) are concentrated in sedimentary material in natural aquatic system⁽¹⁻⁸⁾. Removal of many trace elements is known to be related to adsorption or other surface association phenomena with hydrous metal oxides, clays or detrital organic matter⁽⁹⁻¹¹⁾. The distribution of trace metals among phases varies with the

identity of the trace metal, the solid phase and the chemical environment.

Many investigations have been devoted to the process by which the trace metals are transported and released at the sediment/ water interface. The form in which metals enter the sediment phase is important since it will determine the rate of redistribution within the sediment⁽⁹⁾ and affects the toxicity to deposit-feeding animals^(8,12) in the surface sediments.

Although many (natural and synthetic) complexing ligands are present in natural waters, most studies of adsorption of trace metals were carried out in simple systems in the absence of ligands. Davis and Leckie⁽¹³⁾ have investigated the effects of some ligands on Cu(II) and Ag(I) uptake by amorphous iron oxide. Mac Naughton and James⁽¹⁴⁾ investigated the effect of few inorganic ligands on the Hg(II) uptake by hydrous SiO₂. Vuceta and Morgan⁽¹⁵⁾ found that Cu(II) adsorption decreases in presence of some nonadsorbing ligands(e.g., citric acid and EDTA). Similar finding was reported by Osaki et al.⁽¹⁶⁾ regarding the effect of glycine, NTA and EDTA on the adsorption of Co²⁺ ions. This finding suggests a competition between the ligand and oxide surface for complexation of the metal ion. In these cases, the metal adsorption was dramatically decreased by the presence of a complexing ligand in the system at appropriate concentrations.

The present work was undertaken to determine the roles of several inorganic and organic ligands in altering the Pb(II) uptake on aluminium oxide surface. Although our experimental systems are simple in comparison to natural

waters, the effect of ligands and Ph on the adsorption properties of Al_2O_3 surface could be identified. However, this work tries to determine and compare the adsorptive properties of oxide surfaces modified by adsorbed ligands and free oxide surfaces .

EXPERIMENTAL

The commercial product aluminium oxide (Al_2O_3 90 active neutral for chromatography particle size 0.063–0.200 mm, 70–230 mesh ASTM MERCK) was used, Which consists predominantly of $\gamma-Al_2O_3$ ⁽¹⁷⁾ . All measurements were made in $NaNO_3$ solution at ionic strength of 0.001 M at 25° C. Lead nitrate, EDTA, NTA, salicylic acid, succinic acid, glutamic acid, ascorbic acid and tartaric acid (all BDH laboratory reagents) were used without further purifications.

Stock solutions of all these organic acids (10^{-2} – 10^{-3} M) and lead nitrate (0.5 g/L Pb^{2+}), 0.5 M $NaNO_3$, 0.1 M $NaCl$, 0.01 M Na_2SO_4 , 0.5 M $NaOH$ and conc. HNO_3 solutions were kept in 100 ml glass stoppered volumetric flasks. Each aqueous solution of total volume 50 millilitres was prepared such that the initial concentration of $[Pb^{2+}] = 10$ ppm, $[ligand]=10^{-2}$ – 10^{-4} M and $Al_2O_3=40$ mg/50 ml. All the Ph adjustments (Ph 2–6) were made by dilute HNO_3 or $NaOH$ solutions using SEIBOLD G 103 Ph-meter and a combined glass electrode. After an equilibration time of 24 hours using shaker (BURRELL Corp. Pittsburgh, PA.) at 25°C, each solution was filtered (to remove the solid phase Al_2O_3) and acidified by one drop of concentrated HNO_3 to avoid the hydrolysis of $Pb(II)$ ions. The concentration of the residual (unadsorbed) $Pb(II)$ ions remaining in each solution

was then determined by Perkin Elmer 2380 atomic absorption spectrophotometer using a Perkin Elmer electrodeless lead discharge lamp and air-acetylene gas at 283.3 nm and slit band width (SBW) of 0.7 nm. The lead (II) concentration measured was in the linear range 1-10 ppm.

RESULTS AND DISCUSSION

Adsorption of Pb(II) Ions.

Figure 1 shows the adsorption of Pb(II) ions on Al_2O_3 (0.8 g/L) at Ph 6 as a function of the total Pb(II) concentration (4-44 ppm). The saturation of Al_2O_3 surface with Pb(II) ions is achieved when the $\text{Pb}^{2+}/\text{Al}_2\text{O}_3$ (w/w) ratio approaches 0.05, i.e. the mg Al_2O_3 is 20 times the mg Pb^{2+} ions in the solution.

In order to enhance the Pb(II) uptake, the $\text{Al}_2\text{O}_3/\text{Pb}^{2+}$ weight ratio should be 200 in the aqueous system. Under these conditions the adsorption attains 99% (Figure 1). On the other hand, the Pb(II) uptake is little affected by the ionic strength. The observed small decrease in Pb(II) uptake (from $\mu=0.001$ to 0.02 M NaNO_3) may be attributed to a lowered mobilization of Pb(II) ions to the Al_2O_3 surface by the action of the NO_3^- ions as a weak ligand.

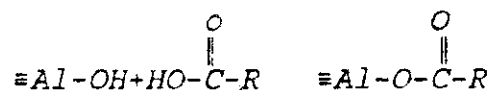
Adsorption System with Inorganic Ligands

Figure 2 shows the effect of chloride and sulphate ions on the Pb(II) uptake by Al_2O_3 . Lead uptake is enhanced above Ph 5 in the presence of SO_4^{2-} ions indicating a higher adsorbability of the complex species. Such species are believed to bond to the surface via sulphate ion. The mechanism of Pb(II) removal from solution may involve

complexation by the adsorbed SO_4^{2-} ions, which is indistinguishable from adsorption of Pb(II) complex formed in solution. At Ph less than 4, the SO_4^{2-} ions have no effect on the Pb(II) uptake since the former is immobilized and not free in solution as previously described ⁽¹³⁾. In presence of chloride ions, the Pb(II) uptake is small below Ph 5 due to a competition between Pb^{2+} and Cl^- ions for adsorption on Al_2O_3 ⁽¹⁸⁾. Above Ph 5, the Cl^- ions have a little effect on the Pb(II) uptake though the Cl^- ions have a lower tendency for adsorption. Higher concentration of Cl^- ions decreases the Pb(II) uptake (Figure 2) owing to adsorption of more Cl^- ions on Al_2O_3 . This finding is in agreement with the results of MacNaughton and James ⁽¹⁴⁾ who found that some other metals are weakly adsorbed in the presence of high chloride concentrations.

Adsorption Systems with Organic Ligands

The effects of some organic ligands (with chemical structures similar to naturally occurring organic compounds) on the Pb(II) uptake are studied in the present work to offer a direct application to natural waters. The adsorption behaviours of such organic ligands over a large Ph range was previously reported ⁽¹³⁾. Such adsorption was interpreted on the basis that the anions of the organic acids replace the surface OH groups of hydrous Al_2O_3 ⁽¹⁹⁾.



In general, the adsorption of most organic ligands on hydrous oxide is decreased on going from acidic Ph~4 to Ph~7

acid molecules in solution results in a decrease of Pb(II) uptake. Such Pb(II) complexes formed in solution have low adsorptive affinities which decrease (at Ph₂ 6) in the order: free Pb(II) > Pb(II) succinate > Pb(II) ascorbate > Pb(II) citrate. This finding indicates that the presence of citric acid can effectively prevent the Pb (II) removal from water by adsorption on AL₂ O₃ .

The presence of tartaric acid (10⁻⁴ mole/L) enhances the Pb(II) uptake above pH 4 where the adsorbed tartrate ions become able to complex Pb(II) ions at the surface. The presence of tartaric acid in higher concentration (10⁻² mole/L) inhibits the Pb(II) uptake. Nevertheless, this uptake was found to increase slowly with the increase of Ph of solution. This finding may be attributed to a slow desorption of tartaric acid with the increase of pH of solution. Consequently, the Pb(II) ions can slowly replace such desorbed molecules at the AL₂ O₃ surface.

The decrease of Pb(II) uptake by AL₂ O₃ caused by addition of EDTA and NTA is in conformity with that predicted by the surface complexation model⁽¹⁶⁾ . The Pb(II) uptake remains relatively high up to pH 3.5-4.0 as a result of Pb(II) complexation with the adsorbed ligand in acid medium. With further increase of pH, these ligands become weakly adsorbed and form stable Pb(II) complexes in solution which inhibit the Pb(II) up take. This finding implies that the presence of EDTA even in trace amount (5x10⁻⁵ mole/ L) can effectively prevent the Pb(II) up- take by AL₂ O₃ above pH 4.

Figure 4 shows the effect of reaction time on Pb (II) remobilization by NTA. At low concentration of NTA (i.e., Pb:

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NTA is 2:1), the Pb(II) uptake slowly increases with the time up to 70% after 24 hours. Higher concentration of NTA can remobilize Pb(II) ions so that a complete remobilization is attained after 24 hours. This indicates that the presence of NTA in a concentration double that of Pb(II) ions can completely prevent the Pb(II) uptake by Al_2O_3 .

conclusion

Aluminium oxide is an effective reagent for removal of Pb(II) ions from aqueous solutions especially above pH 5 in the presence of sulphate, glutamate, salicylate or tartrate ions. The Pb(II) complexes with these anions are formed at the Al_2O_3 surface, whereas Pb(II) - citrate remains in solution and prevents Pb(II) uptake by Al_2O_3 . The adsorptive affinities of the investigated Pb(II) complex species increase in the order: Pb(II) < Pb(II) Glutamate < Pb(II) Salicylate < Pb(II) Tartrate. It can be suggested that the efficiency of a treatment plant can be optimized by adding some additives at the right place.

Ligands which form stable Pb(II) complexes, e.g. EDTA and NTA decrease the efficiency of Pb(II) removal and can remobilize Pb(II) ions above pH 5. Therefore, in water treatment the main reactions have to be controlled carefully. If NTA is used as substitute for phosphate in detergents, the Pb(II) uptake by Al_2O_3 will be distinctly decreased.

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REFERENCES

1. Turekian, k.k.; Scott, M.R., Environ. Sci. Technol., 1, 940 (1967).
2. Harding, S.C.; Brown, H.S., Environ. Geol., 1, 181 (1975).
3. Pita, F.W.; Hyne, N.J., Water Res., 9, 701 (1975).
4. Catanzaro, E.J., Environ. Sci. Technol., 10, 386 (1976).
5. Ramamoorthy, S.; Rust, B.R. Can. J. Earth Sci., 13, 530 (1976).
6. Lewis, D.M., Geochim. Cosmochim. Acta, 41, 1557 (1977).
7. Taylor, D., Estuarine Coastal Mar. Sci., 2, 417 (1974).
8. Bloom, H.; Ayling, G.M., Environ. Geol., 2, 3 (1977).
9. Leckie, J.O.; James, R.O., in Aqueous- Environmental Chemistry of Metals, Rubin, A.J., Ed.; Ann. Arbor Science, Ann Arbor; Mich., Chapter 1 (1975).
10. Parks, G.A., in Chemical Oceanography, 2nd ed.; Riley and Skirrow, Eds.; Academic press: New York, Vol. 1, 241 (1975).
11. Jenne, E.A., in Symposium on Molybdenum in the Environment, Chappel, W. and Petersen, K., Eds.; Marcel Dekker: New York, Vol. 2, Chapter 5 (1977).
12. Luoma, S.N.; Jenne, E.A., Proceedings, Trace Substances in Environmental Health-x, Hemphill, D.D. Ed., Univ. of Missouri, Columbia, Mo., P. 343 (1976).
13. Davis, J.A.; Leckie, J.O., Environ. Sci. Technol., 12, 1309 (1978).
14. MacNaughton, M.G.; James, R.O., J. Colloid Int. Sci., 47, 431 (1974).
15. Vuceta, J.; Morgan, J.J., Environ. Sci. Technol. 12 (12), 1302 (1978).

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- 16, Osaki, S.; Kuroki, Y.; Sugihara, S.; Takashima, Y., Sci. Total Environ. 99(1-2), 93 (1990).
- 17, Neuwinger, H.D., Ph.D. Thesis, University of Heidelberg, (1970)
- 18, Rohmann, U.; Sontheimer, H., Vom Wasser 50, 301 (1978).
- 19, Kummert, R.; Stumm, W., J. Colloid Int. Sci. 75 (2), 373 (1980).

Caption of Figures

1. Percent Pb(II) ions adsorbed as a function of Pb: Al_2O_3 ratio.
2. Percent Pb(II) ions adsorbed by 0.8 g/L Al_2O_3 as a function of pH in presence of NaCl and Na_2SO_4 .
3. Percent Pb(II) ions adsorbed by 0.8 g/L Al_2O_3 as a function of pH in presence of salicylic acid and Glutamic acid.
4. Percent Pb(II) ions adsorbed by 0.8 g/L Al_2O_3 as a function of Pb: NTA ratio.

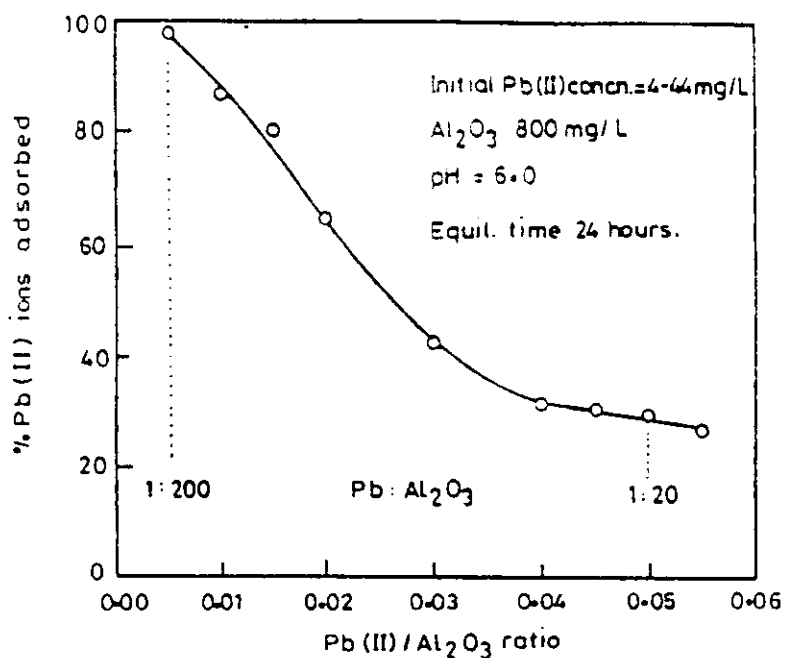


Fig.(1): Percent (II) ions adsorbed as a function of Pb: Al_2O_3 ratio.

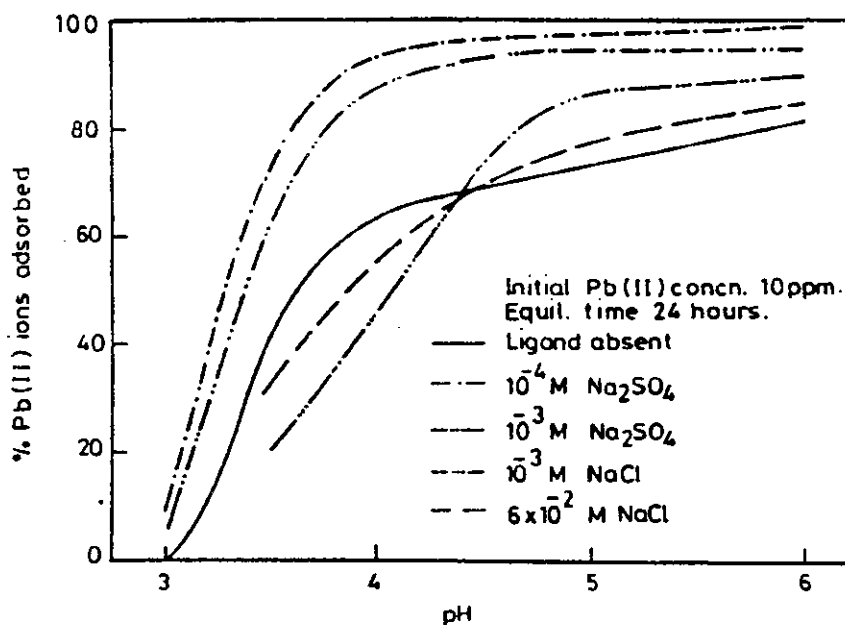


Fig.(2): Percent Pb(II) ions adsorbed by 0.8 g/L Al_2O_3 as a function of pH in presence of NaCl and Na_2SO_4 .

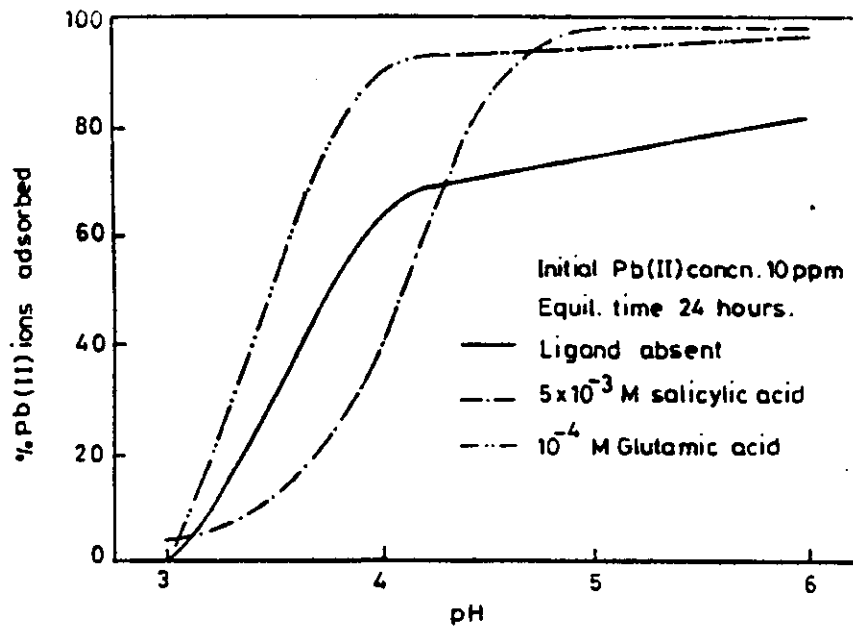


Fig.(3): Percent Pb(II) ions adsorbed by 0.8 g/L Al_2O_3 as a function of pH in presence of salicylic acid and Glutamic acid.

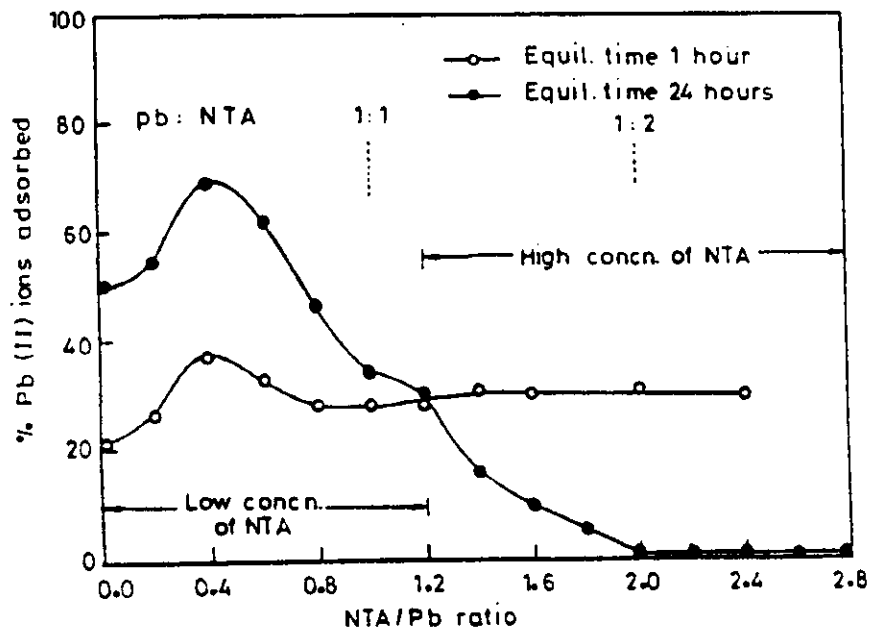


Fig.(4): Percent Pb(II) ions adsorbed by 0.8 g/L Al_2O_3 as a function of Pb:NTA ratio.

**طريقة مبسطة لتثقية المياه من العناصر الثقيلة
تأثير الليجانينات على ازالة ايونات الرصاص من الماء
بامتزازها على
اكسيد الألومنيوم
حسين محمد عبد الفتاح
قسم الكيمياء - كلية العلوم - جامعة القاهرة - الجيزة
جمهورية مصر العربية**

تم دراسة عملية امتزاز ايونات الرصاص على سطح اكسيد الالومنيوم وتأثيرها بوجود الليجانينات العضوية وغير العضوية وتغير الاس الهيدروجيني وقد وجد ان بعض الليجانينات مثل حمض الستريك يكون مع الرصاص متراكبات غير متمزة وبذلك يحول دون امتزاز الرصاص على سطح اكسيد الالومنيوم كما لوحظ ان بعض الليجانينات الاخرى مثل حمض الجلوتاميك يمتاز على السطح وبالتالي يزيد من امتزاز الرصاص وحيث ان امتزاز الرصاص يصل الى 99% عند اس هيدروجيني اكبر من 5 فان معالجة المياه الطبيعية بهذه الطريقة سوف لاتحتاج الى تغير اسها الهيدروجيني وعلى هذا فان هذا البحث يقدم طريقة للتحكم فى تركيز الرصاص فى المياه الطبيعية عن طريق ارتباط الرصاص بسطح اكسيد الالومنيوم .

