EFFECTS OF A FULVIC ACID ON THE SPECIATION AND MOBILITY OF MERCURY IN AQUEOUS SOLUTIONS

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ABSTRACT. The presence of humic substances in aqueous systems generally has a large impact on speciation as well as on mobility of metal ions at trace levels. At $pH<pH_{ZPC}$, the humic substances tend to adsorb and enhance the uptake of trace metals from the solution phase. At $pH>pH_{ZPC}$, the reverse effect is expected. Experimental data on the adsorption of Hg on an oxide (alumina) in the presence of a fulvic acid (FA; 0 to 25 mg L^{-1}) is reported in the present work. Generally the presence of the FA enhances the Hg adsorption in the whole pH-range studied (2.5 to 9.5). A Hg-FA complex is the dominant species already in the presence of 1 mg L^{-1} FA in the solution phase. Chloride increases the adsorption at $pH<pH_{ZPC}$ possibly related to the formation of the negatively charged $HgCl_3^-$ species. The Hg adsorption is compared with Zn and Cd in the corresponding systems. The mobility of these bivalent metals in the aqueous environment is discussed.

1. Introduction

The speciation and mobility of heavy metals in the aquatic environment are governed by a number of processes. Formation of sparingly soluble inorganic compounds (precipitation or coprecipitation) and adsorption of heavy metals onto geologic media will generally decrease the mobility. On the other hand, complexation of heavy metals with organic and inorganic ligands in solution will change their physical-chemical properties and may thereby increase their mobility.

The adsorption onto geologic materials is a primary mechanism that affects the mobility of Hg in aquatic systems. Numerous studies have shown that the adsorption of Hg is dependent on pH of the water phase (e.g. Macnaughton and James, 1974; Forbes *et al.*, 1974), as well as on the ionic strength (Lockwood and Chen, 1973; Dalland *et al.*, 1986), the presence of complexing ligands such as chloride (Lockwood and Chen, 1974; Newton *et al.*, 1976; Farrah and Pickering, 1978; Wang *et al.*, 1985;) and the nature of the solid sorbent (Lockwood and Chen, 1974; Sen and De, 1987). In natural water/soil systems, organic substances are of great importance for the Hg speciation and consequently also for the adsorption. Li and Liu (1982) reported that humic acid could adsorb more Hg(II) than oxides and clay minerals. A maximum adsorption of Hg(II) on sediment humic substances was observed around pH 4.7 to 6.5 (Zvonarev, 1982; Zvonarev and Zyrin, 1982). The sorption efficiency on humic acid from

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soil increased with increasing pH (from 2.4 to 5.8) and the amount of humic acid in the solution (Kerndorff and Schnitzer, 1980). However, all these studies used humic substances from soils and sediments. Furthermore, the concentrations of humic acids were very high so as to supply enough surface adsorption sites. No information is available on the effects of dissolved humic substances which may act only as ligands, not as adsorbents.

The objectives of the present work are to determine the effects of a fulvic acid from a surface water, as well as pH and chloride, on the adsorption of Hg(II) on an oxide (alumina) at low total Hg concentration representative of natural levels. Results are compared with data for the two other bivalent group IIb elements (Zn and Cd).

2. Methods and materials

2.1. ADSORPTION SYSTEMS

Alumina (α-Al_2O_3; Aldrich-Chemie) was selected as adsorbent. It was crushed and sieved. The 0.063 to 0.125 mm particle fraction was collected, washed with Milli-Q water (Millipore Corp., Bedford, Mass) several times and then gently dried at 105 °C.

A solution of 0.1 M $NaClO_4$ was used as aqueous phase. The initial pH was adjusted to a preselected level with $HClO_4$ or NaOH. A stock solution of Hg(II) was prepared containing the isotope ^{203}Hg (as $Hg(NO_3)_2$; Amersham) plus inactive carrier (4.9×10^{-6} M $Hg(NO_3)_2$) in 0.1 M HNO_3. The radiochemical purity of the ^{203}Hg-stock solution was checked by gamma spectroscopy.

The natural organic material used was a fulvic acid (FA) extracted from a surface water, with molecular weight around 1750 and total acid capacity of 4.65 meq g^{-1} (Ephraim *et al.*, 1989).

All chemicals used were analytic grade and all solutions were prepared with Milli-Q water.

2.2. DISTRIBUTION MEASUREMENTS

The distribution of Hg(II) between the solid and aqueous phase as a function of pH and presence of FA and chloride was studied in batch experiments. Samples were prepared by adding 19.0 mL of the aqueous phase into 50-mL polycarbonate centrifuge tubes containing 0.200 g of alumina (0.063 to 0.125 mm size fraction). After pH-adjustment the samples were pre-equilibrated for 3 d. Appropriate amounts of stock solution (with ^{203}Hg) were added to give the desired total Hg concentration (in most cases 2.77×10^{-8} M). Additions of FA and NaCl solutions were made to some of the samples. After readjustment of pH the volume was adjusted to 20.0 mL with 0.1 M $NaClO_4$. After 3 d (up to 18 d in a few cases) of contact time, with gently shaking, the aqueous phase was separated from the solid by centrifugation (3700 g; 15 min). An aliquot of the supernatant was taken for analysis of ^{203}Hg using a scintillation counter, and pH was measured in each tube. The amount of Hg adsorbed by alumina was calculated from the fraction of the activity of the tracer remaining in solution. Adsorption on the tube walls was negligible in the presence of alumina, representing a total surface area much larger than that of the tube itself.

3. Results and Discussion

3.1. EFFECTS OF FA

The adsorption of Hg on alumina as a function of pH (2.5 to 9.5) at various concentrations of FA (0, 1, 10 and 25 mg L^{-1}) and low chloride concentration (estimated as 10^{-7} M, set by impurities in the chemicals) is shown in Figure 1. The presence of FA generally increased the adsorption of Hg(II) in the whole pH range studied. This was significant already at a concentration of 1 mg L^{-1} of FA. An increase from 10 to 25 mg L^{-1} of FA did not markedly change the adsorption. However, unexpected brown precipitates were observed at pH below 5 in the systems with 10 and 25 mg L^{-1} FA . In the case where alumina was pre-equilibrated with the FA, the precipitates also appeared after the addition of Hg under acidic conditions. Evidently, the precipitation of Hg-FA is one of the processes removing a large fraction of the Hg at pH below 5 in the presence of 10 and 25 mg L^{-1} of FA.

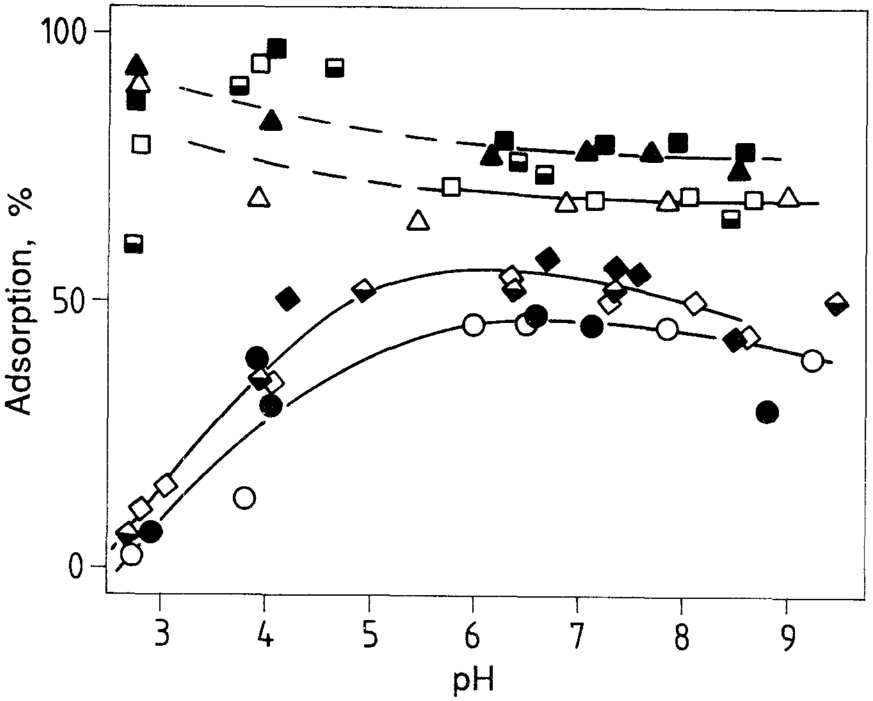

Fig. 1 Adsorption of Hg(II) on alumina as a function of pH, FA and time ([Hg] = 2.77×10^{-8} M; solid/liquid = 10 g L^{-1}): ○ FA = 0 mg L^{-1}, ◇ FA = 1 mg L^{-1}, □ FA = 10 mg L^{-1}, △ FA = 25 mg L^{-1}, 3 d of contact time; ● FA = 0 mg L^{-1}, ◆ FA = 1 mg L^{-1}, ■ FA = 10 mg L^{-1}, ▲ FA = 25 mg L^{-1}, 18 d of contact time; ⬙ FA = 1 mg L^{-1}, ⬓ FA = 10 mg L^{-1}, 3 d of contact time (the solid was pre-equilibrated with FA for 1 week).

Figure 1 also shows time effects on the adsorption of Hg(II). Apparent equilibrium was reached within 3 days in the systems without and with 1 mg L^{-1} FA. However, in the presence of 10 and 25 mg L^{-1} FA , an increase in the adsorption could still be observed after 3 days, which implies that not only physical adsorption is involved.

The calculated Hg speciation in the presence of FA (0, 1, 10 and 25 mg L^{-1}) and at 10^{-7} M Cl^- is shown in Figure 2, assuming the following formation constants (log β): $Hg(OH)^+$, 10.35; $Hg(OH)_2$, 21.71; $Hg(OH)_3^-$, 21.01; $HgCl^+$, 5.99; $HgCl_2$, 12.51; $HgCl_3^-$, 14.50; $HgCl_4^{2-}$, 15.10; HgClOH, 3.67 (Högfeldt, 1983); HgFA, 4.86, 5.08, 5.2 and 10.1 at pH 3, 4, 5, and 8, respectively (based on data by Strohal and Huljev, 1971; Cheam and Gamble, 1974; Millward and Burton, 1975). In the absence of FA, Hg^{2+} is the dominating species only at pH below 3.2. Above this pH $Hg(OH)_2$ would prevail. Since the alumina has a pH_{zpc} (the point of zero charge) of 7.8, the surfaces are positively charged at pH < pH_{zpc}, and therefore the adsorption of Hg^{2+} is suppressed. As the proportion of $Hg(OH)_2$ in the solution increases, the adsorption is increasing. This is in qualitative agreement with previous studies on hydrous manganese oxide (Lockwood and Chen, 1973), quartz (Macnaughton and James, 1974) and hydrous oxide gels (Kinniburgh and Jackson, 1978).

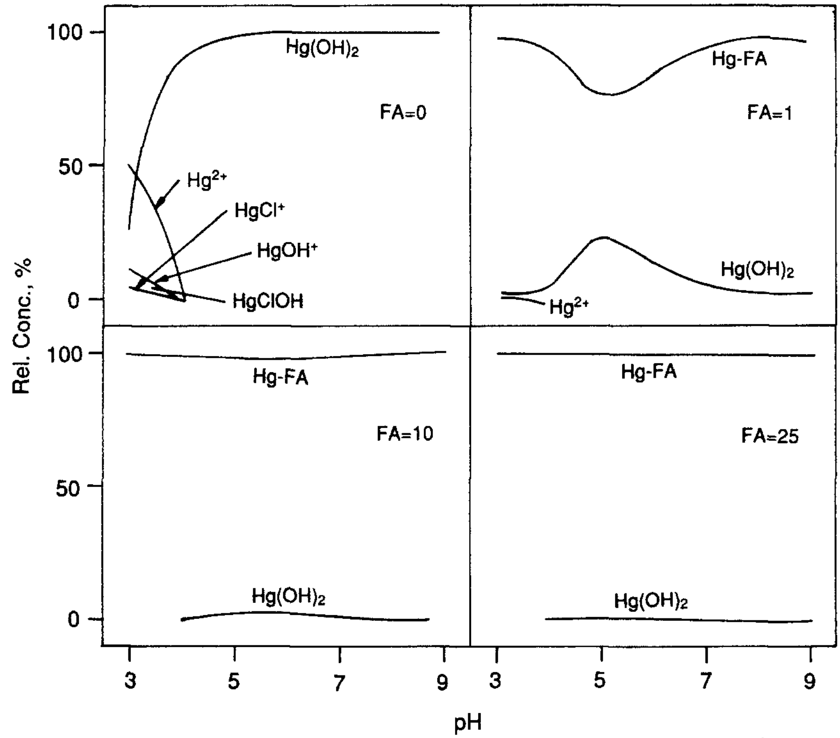

Fig. 2 Calculated distribution of Hg-species in the presence of 0, 1, 10 and 25 mg L^{-1} of FA ([Cl] = 10^{-7} M).

In the presence of 1 mg L^{-1} of FA, Hg exists mainly as a Hg-FA complex, and a significant enhanced adsorption is observed. An enhanced uptake at pH<pH_{zpc} would be expected, since the FA itself would be adsorbed and have a bridging function. When FA levels are increased to 10 mg L^{-1}, almost all the Hg is in the form of HgFA and the adsorption is further increased even at $pH>pH_{ZPC}$. A significant surface loading of FA is evidently obtained. Thus, a further increase of the FA concentration (to 25 mg L^{-1}) did not significantly enhance the adsorption of Hg. Possibly, the removal of Hg from the solution phase at 10 and 25 mg L^{-1} FA should be denoted as a surface precipitation process rather than adsorption, not only at $pH<5$ but also in the higher pH-region.

3.2. EFFECTS OF CHLORIDE

The effects of chloride on the adsorption of Hg(II) on alumina are shown in Figure 3. In contrast to some previous studies (e.g. Macnaughton and James, 1974; Lockwood and Chen, 1973), the presence of a chloride concentration of 10^{-4} M led to a significant increase of the Hg adsorption in the present experiments and this effect was even stronger when the concentration was increased to 10^{-2} M. Similar effects were also observed in the systems with 1 mg L^{-1} FA. To confirm the effects of chloride, a series of experiments were conducted with different initial Hg(II) concentrations (10^{-8} M and 10^{-6} M) and different sources of chloride (NaCl and KCl). No effects related to the Hg-concentration or the chloride source were observed.

Calculations on Hg-speciation in the presence of chloride and FA are given in Figure 4, using the same constants quoted above. In the presence of 10^{-2} M chloride, both $HgCl_3^-$ and $HgCl_2$ are dominating species at pH below 6.5. As mentioned above, the alumina surfaces are positively charged at pH below 7.8. Therefore, the adsorption of negatively charged $HgCl_3^-$ is favorable due to the electrostatic attraction. At a chloride concentration of 10^{-4} M, only $HgCl_2$ is the dominant species at pH below 5 leading to a lower adsorption of Hg than in the 10^{-2} M chloride system. Some oxides, e.g. quartz as well as most clay minerals, have a low pH_{ZPC}. Their surfaces are already negatively charged under neutral or weakly acidic conditions. This may explain the difference in the results from the present studies in comparison with some previously published data in the literature. However, the higher adsorption of $HgCl_2$ (at 10^{-4} M chloride) than that of $Hg(OH)_2$ (at 10^{-7} M chloride) could not solely be explained by differences in electrostatic interactions. Further studies are needed to clarify the adsorption mechanisms.

3.3. COMPARISON WITH Zn AND Cd

A comparison of effects of pH on the adsorption of Hg(II), Zn(II) and Cd(II) is given in Figure 5. In the absence of FA and chloride the adsorption increases with increasing pH and reaches a maximum around pH 5.5 for Hg, and around 8.8 and 9.4, or above, for Zn and Cd, respectively. This appears to be related primarily to the hydrolysis properties of the elements. The amount adsorbed at adsorption maximum is, however, much less for Hg than for Zn and Cd. A similar low Hg-adsorption has been obtained in goethite at the initial Hg concentration of 2.9×10^{-5} M, as reported by Forbes *et al.* (1974). Only about 50% of the Hg was adsorbed by quartz at the initial Hg concentration of 1.8×10^{-7} M (Macnaughton and James, 1974) and by bentonite at 10^{-6} M (Newton *et al.*, 1976). Evidently, the low adsorption of Hg in comparison with Zn and Cd can not simply be attributed to the difference in the initial metal concentrations in the present study (10^{-8} M for Hg and 10^{-6} M for Zn and Cd).

The formation of metal-FA complexes at $pH<pH_{ZPC}$ enhances the adsorption since FA could act as a bridge. At $pH>pH_{ZPC}$, however, soluble metal-FA complexes are less adsorbed than hydrated metals so that the adsorption is decreased for Zn and Cd, but not

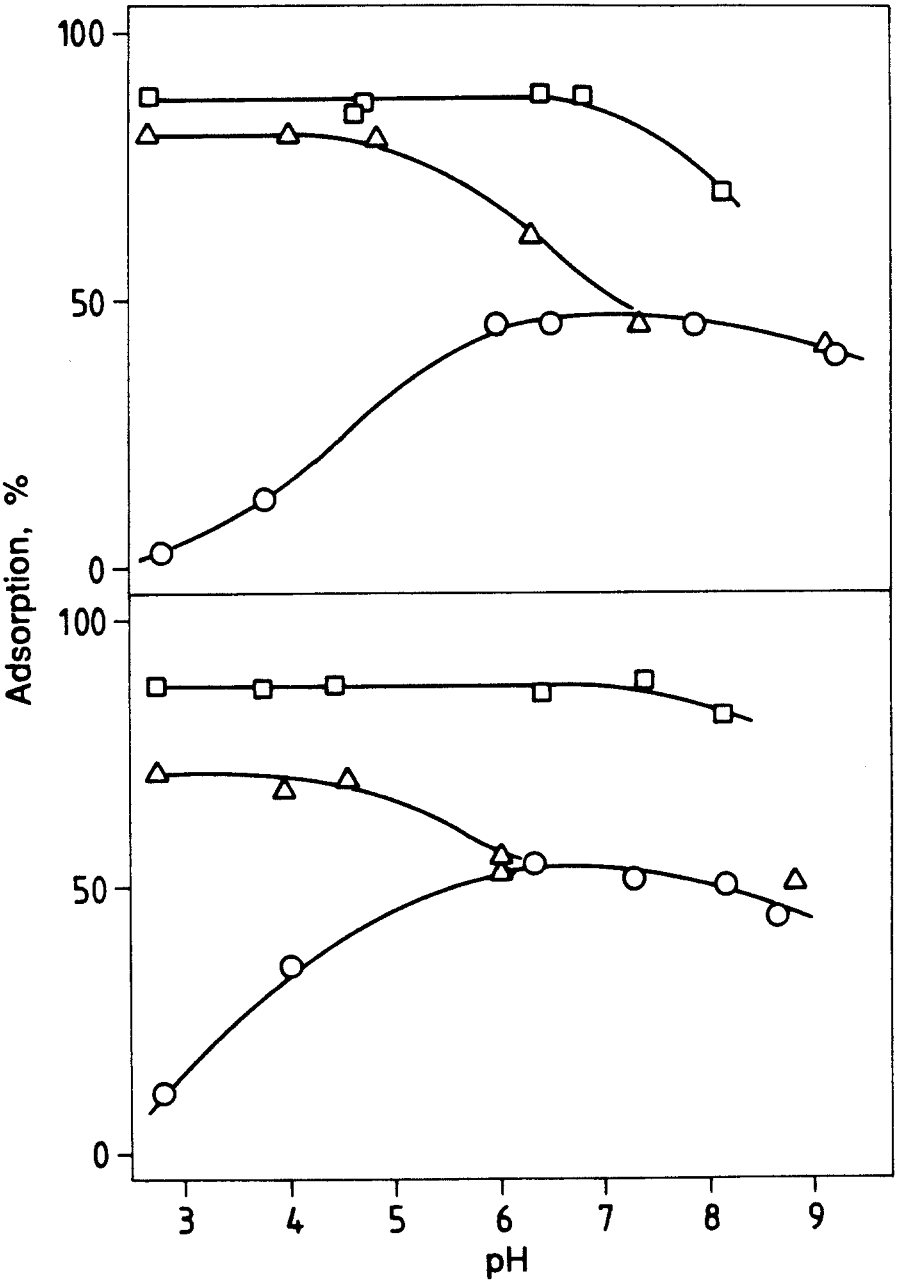

Fig. 3 Adsorption of Hg on alumina as a function of pH and chloride without FA (top) and with 1 mg L^{-1} FA (bottom) ([Hg] = 2.77×10^{-8} M; solid/liquid = 10 g L^{-1}; 3 d of contact time): ○ [Cl^-] = 10^{-7} M, △ [Cl^-] = 10^{-4} M, □ [Cl^-] = 10^{-2} M.

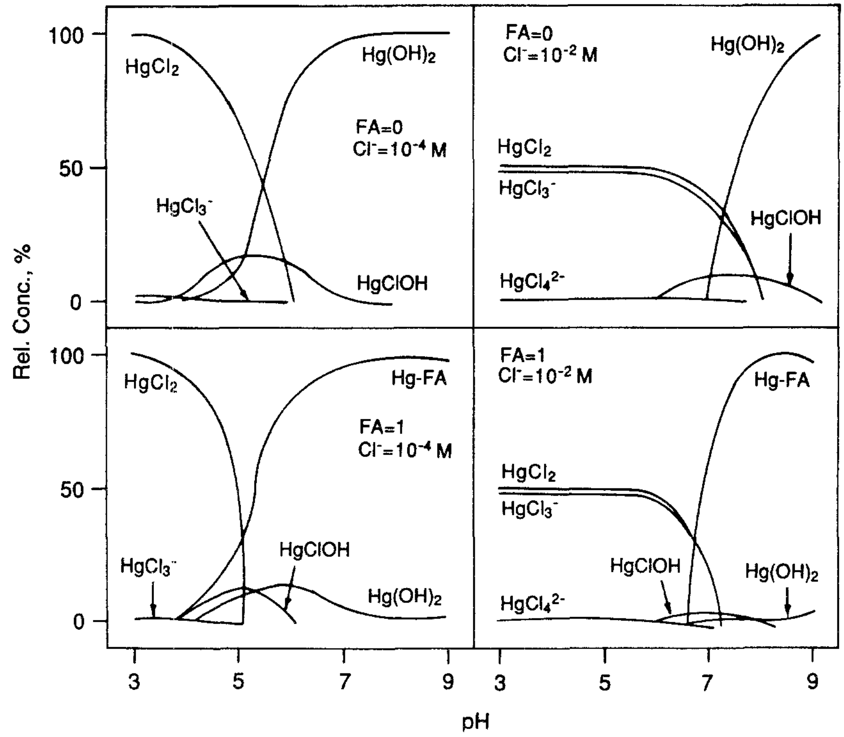

Fig. 4 Calculated distribution of Hg-species in the presence of chloride (10^{-4} M and 10^{-2} M) and FA (0 and 1 mg L^{-1}).

significantly for Hg where the presence of FA increases the Hg adsorption in a broader pH-range than for Zn and Cd.

4. Conclusions

Fulvic acids in solution would play an important role in the distribution and mobility of Hg in natural waters. In the presence of 1 mg L^{-1} FA or higher, the Hg-FA complex would be a dominant species and the adsorption of Hg is enhanced at $pH<pH_{ZPC}$ of the exposed mineral phases. The presence of chloride increases the adsorption at low pH.

The mobility of Hg would be lower than that of Zn and Cd at low pH and higher at high pH (in relation to pH_{ZPC}). The presence of FA will generally enhance the adsorption of Zn and Cd at low pH and reduce the adsorption at high pH. In contrast to Zn and Cd, FA will reduce the mobility of Hg under both acidic and basic conditions.

There are substantial differences in adsorption behavior between Hg and Zn-Cd, which can not solely be attributed to different speciation in solution. The mechanisms of the Hg adsorption should be further elaborated.

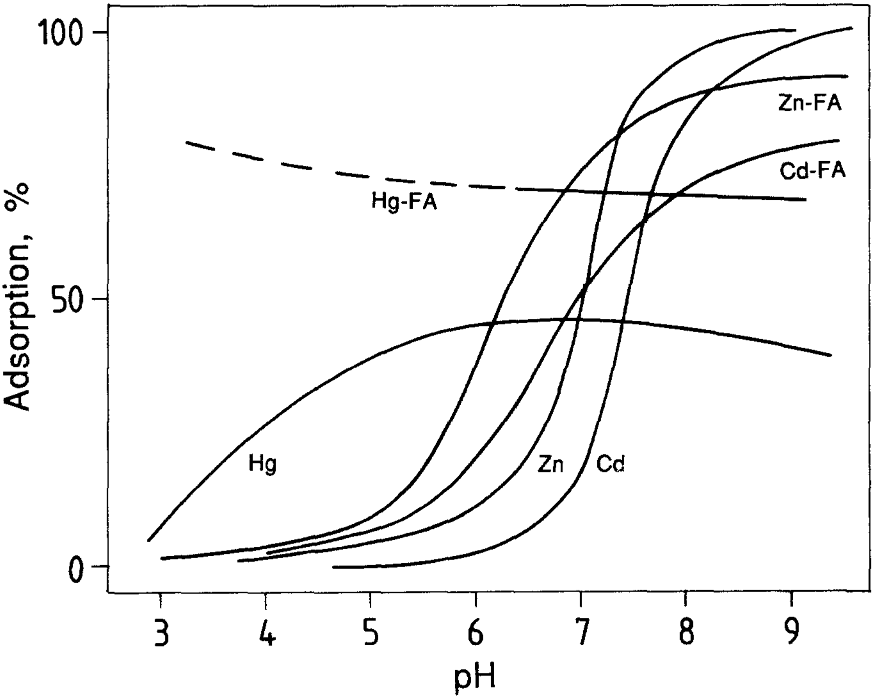

Fig. 5 Adsorption of Hg(II), Zn(II) and Cd(II) on alumina without FA and with 10 mg L^{-1} FA ([Hg] = $2.77x10^{-8}$ M, [Zn], [Cd] = 10^{-6} M; solid/liquid = 10 g L^{-1}; 3 d of contact time).

Acknowledgments

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