

### Adsorption of Cd(II), Pb(II), Cu(II) and Zn(II) ions on mineral and model surfaces under seawater conditions

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The adsorption of the trace metals Cd, Pb, Cu and Zn was studied on natural Fe-bentonite and kaolinite. Results are presented in the form of Schindler's adsorption isotherms:  $[Me]_{ads}/[Me]_{tot}$  vs.  $\log X$  ( $kg\ dm^{-3}$ ) where  $X$  is the weighted amount of adsorbent.

Adsorption characteristics for the four metal ions on Fe-bentonite and kaolinite showed similar behaviour for Pb, Cu and Zn while Cd was very slightly adsorbed on both solid phases. In comparison with earlier adsorption results on model particulate matter such as  $\gamma$ - $Al_2O_3$  (surface area  $117\ m^2\ g^{-1}$ , number of sites  $8\ nm^{-2}$ ) and  $SiO_2$  (surface area  $220\ m^2\ g^{-1}$ , number of sites  $4.5\ nm^{-2}$ ) (Bilinski et al., 1976; Plavšić et al., 1980) and on synthesized northupite mineral  $Na_3Mg(CO_3)_2Cl$  (surface area  $6\ m^2\ g^{-1}$ ) (Vančina et al., 1986), the following adsorbability order was observed for seawater conditions with respect to the weight of the adsorbent:

for Pb  $\gamma$ - $Al_2O_3 > SiO_2 > bentonite > kaolinite$   
for Cu  $\gamma$ - $Al_2O_3 > bentonite \approx northupite > SiO_2 > kaolinite$   
for Zn  $\gamma$ - $Al_2O_3 \approx SiO_2 > bentonite > kaolinite$   
for Cd very low adsorption was observed except for northupite.

The effect of major and minor cations ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Sr^{2+}$ ) on cadmium adsorption was studied with decreasing inhibition of Cd adsorption in the following sequence:  $Mg^{2+} > Ca^{2+} > Sr^{2+}$ .

For anionic seawater constituents the following effectiveness order was:  $Cl^- > Br^- > J^- \approx SO_4^{2-} \approx SiO_3^{2-}$ .

Cadmium was observed to adsorb less in natural seawater as compared to artificial or UV-irradiated seawater. Because of the weak interaction of cadmium with organic matter in seawater, it appears that the natural organic matter in seawater adsorbs on the bentonite surface, thus interfering with cadmium adsorption at the bentonite surface.

Selected model organic ligands, which were recently found in natural sediments by Hadžija et al., (1985) and by Steinberg et al., (1987) have been studied. Alanine, glutamic acid, galactose and galactosamine have been established as inhibitors, while oxalic acid was found to be a catalyst of cadmium adsorption.

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### The mobility of some Carboxy and Hydroxy Benzene derivatives on thin layers of Silica gel plain and Fe(III)-impregnated

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The mobility of metals through soil and sediments is predominantly attributed to their complexation with humic substances, mainly via their functional groups such as carboxy and hydroxy. These investigations were performed with naturally occurring humic material<sup>(1,2)</sup> and in this way no informations could be obtained about the activity of the functional groups with respect to their position in the benzene ring.

In our previous work we had examined by the use of thin layer chromatography in water systems as developers, on plain and Fe(III)-impregnated silica gel, the behaviour of some phenolic acids usually found as degradation products of humic material<sup>(3)</sup>.

In this work we have tested the benzene derivatives containing more than one hydroxy and carboxy group in different positions and carboxy groups which are not bonded directly to the benzene ring. All tested compounds are derived from some of the presumed structures of humic acids or their precursors.

The following was found:

- on plain plates the compounds tested behaved more or less consequently to their solubility in water. Phenolic acids which are slightly soluble in water exhibit small mobility. Compounds having greater solubility, as are for example, dihydroxy benzenes and benzene carboxylic acids moved faster.
- on impregnated plates the compounds behaved accordingly to physico-chemical properties of the Fe(III)-complexes formed.

From the behaviour of the compounds on impregnated plates, some conclusions about the activities of the corresponding functional groups may be drawn. The fact that on impregnated plates phenolic acids with free hydroxy group and dihydroxy benzenes moved considerably may indicate that Fe(III) as well as other metals, by complexation with the related functional groups in soil and sediments, become movable. On the other hand benzene carboxylic and dicarboxylic acids as well as phenolic acids with protected hydroxy groups moved slowly or stayed practically on the start position on impregnated plates. This behaviour may imply the retardation of the metals depending on the positions of these groups.

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