

the relative toxicity of the platinum metals. The anomaly is Pt^{4+} , which is classified as soft, but which is relatively non-toxic; however, some softness is lost when Pt^{2+} is oxidized to Pt^{4+} .

The most prominent toxic symptom at low levels was the appearance of reddish-brown streaks in the leaves of *Eichhornia crassipes*. Such phytotoxic symptoms have been observed in beans (*Phaseolus vulgaris*) and soybeans (*Glycine max*) treated with high quantities of zinc. Cd^{2+} , Co^{2+} and Ni^{2+} are reported to cause similar symptoms. In contrast to the toxic effects of Pt^{2+} , Rh^{3+} appears to exhibit a tonic effect. When treated with 10 ppm Rh^{3+} applied as $\text{Na}_3[\text{RhCl}_6]$, water hyacinth increased its biomass some 6.7% more than control plants, grown under the same conditions. When the South African grass *Setaria verticillata* was treated with 0.5 ppm Pt^{2+} (as $\text{K}_2[\text{PtCl}_4]$), vascular discolouration was absent and the roots were growth stimulated some 65% more than controls. Thus the phytotoxic symptoms of platinum vary according to which species is treated, though with water hyacinth, some stimulation of vegetative reproduction was apparent with platinum complexes, at low levels.

When applied as the antitumour complex *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ at low levels, some 47.9% of the platinum found in the leaves of water hyacinth was associated with α -cellulose and lignin; 16.1% was removed by the proteolytic enzyme pronase and 20.8% found with water soluble pectates. A similar distribution of platinum was found in the floats of water hyacinth. In the roots of treated plants, the values were 35%, 9.5% and 14.2% respectively; in addition to this, a further 23.1% was removed with low molecular weight alcohol soluble materials and 12.0% with polar water soluble materials. Thus in water hyacinth, the cell wall acts as an ion exchange column trapping most of the platinum, though some is found bound to water soluble pectates. Together, this accounts for 49.2% of the platinum found in the roots and this figure rises to 68.7% in the leaves. The platinum released by pronase may represent that which is bound to protein from a number of sources including organelle protein, membrane protein and cell wall glycoprotein.

S17

Energetics of the Adsorption of Cu(II) on Activated Sludge

CORRADO SARZANINI

Istituto di Chimica Fisica, C.so M. d'Azeglio 48, Turin, Italy
and LUIGI STRADELLA

Istituto di Chimica Generale Inorganica, Via P. Giuria 9,
Turin, Italy

Dried activated sludge (DS) and thermally modified samples (MDS) [1] were used as adsorbents

of Cu(II) from water at zero and 0.1 ionic strength. Three mechanisms are essentially implied at the solid-liquid interface:

(i) ion exchange of free metals and hydroxo-complexes with surface protons,

(ii) adsorption and hydrolysis at the surface,

(iii) hydrolysis followed by an adsorption reaction.

The use of activated sludge as adsorbent is also justified by its bacterial nature [2].

Experimental

Two kinds of adsorbent were prepared: the samples obtained from a pilot plant were thickened and dried at 100 °C in air, powdered and sieved in the 42–200 mesh range (DS), and heated at 110 °C in air for 24 h (MDS). The BET surface evaluation resulted in $2 \pm 0.1 \text{ m}^2/\text{g}$ for DS and $0.5 \pm 0.1 \text{ m}^2/\text{g}$ for MDS; this may be interpreted assuming that grain agglomeration takes place.

The calorimetric experiments were carried out using a SETARAM rotating C.R.M.T. calorimeter [3], with a cell we constructed because of the impossibility of any handling from outside after introduction of the sample. The method has already been described in detail [4].

Results and Discussion

In Fig. 1 we have reported the enthalpies of displacement, $-\Delta H_{12}$ (J/g), as a function of the specific quantities of Cu(II) adsorbed, n_{2s} (mg/g).

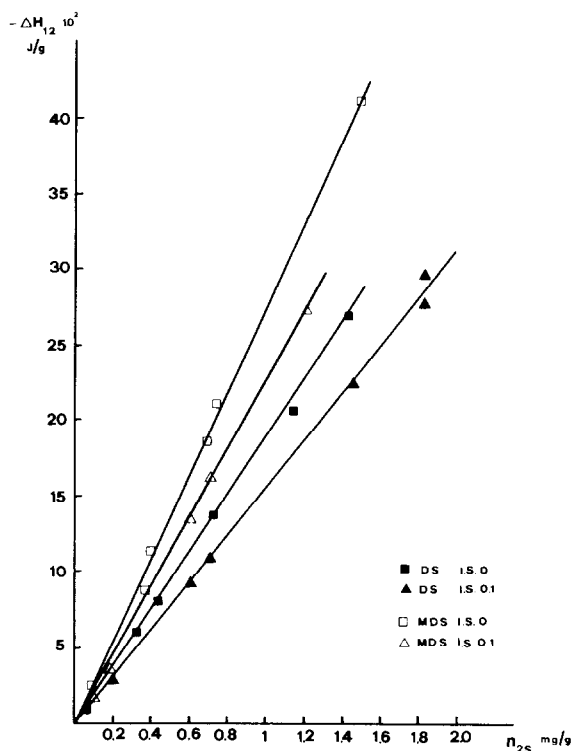


Fig. 1. Enthalpies of displacement vs. Cu(II) adsorbed.

Heat changes measured are actually heats of displacement, the water being gradually replaced by the solute [3]. The trend of the enthalpies of displacement in Fig. 1 considering the influence of the thermal treatment shows that the MDS exhibit at every surface coverage a higher enthalpy of displacement; this fact is interpreted by supposing that the thermal treatment favours the exhibition at the surface of chemical and polar groups capable of strong interaction with the Cu(II) ions. This fact could be interpreted as due to an increase in the electrical potential of the Stern Gouy diffuse layer [5] with a consequent more difficult diffusion of Cu(II) ions toward the polar surface: analogous results have been obtained on an oxide surface [6]. From the analysis of calorimetric peaks, relative to DS and MDS samples, we can deduce that the thermokinetic trend is somewhat different, the MDS showing an apparently smaller reaction rate.

Starting from the hypothesis that the rate determining step is the diffusion of the solute, we have tried to apply a semiempirical treatment assuming a time dependence of the diffusion equation [8].

In Fig. 2 we have reported the function:

$$F(t) = \log P + 3/2 \log t$$

where $P \cong KW$ is the instantaneous deviation of the calorimeter vs. the reciprocal of time. The linearity of the curves in Fig. 2 is satisfactory enough both for DS and MDS samples.

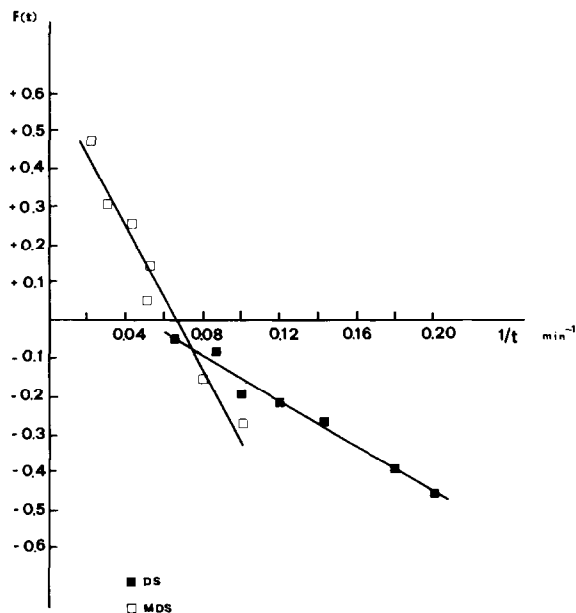


Fig. 2. The function: $F(t) = \log P + 3/2 \log t$.

The MDS samples show a greater slope, that means a smaller diffusion coefficient; that would correspond to a more dense Gouy layer; in other words, the MDS sample that exhibits a greater number of polar and

ionic groups would have a higher repulsive potential field in the diffuse layer. We may conclude that kinetic [1] and thermokinetic studies are in agreement and show that the initial uptake rate is smaller on MDS than DS; but the limiting adsorption quantities are higher for the former. This situation could be interpreted by assuming that the determining step is the diffusion of the ions through the double layer which should be characterized by a higher electrical potential in the case of MDS.

- 1 C. Sarzanini, *Sep. Sci. and Technol.*, 18, 1 (1982).
- 2 J. F. Wilkinson, *Bacteriol. Rev.*, 22, 46 (1958).
- 3 G. Della Gatta, L. Stradella and G. Venturolo, *Zeit. für Phys. Chemie, Neue Folge*, 106, 95 (1977).
- 4 G. Della Gatta, L. Stradella and P. Venturolo, *J. Solution Chem.*, 10, 209 (1981).
- 5 H. B. Abramson, M. J. Jaycock and R. H. Ottewill, *J. Chem. Soc.*, 5041, 5034 (1964).
- 6 M. H. Kubatov, G. B. Wood and J. D. Kubatov, *J. Phys. Chem.*, 55, 1170 (1951).
- 7 C. Sarzanini and L. Stradella, *Entropie*, to be published.
- 8 R. E. Weston, Jr. and H. A. Szwarcz, *Chemical Kinetics, N. J.*, 162 (1972).

S18

New Approach for the Determination of Stability Constants of Metal Ions—Soil Organic Matter

Y. BIZRI, M. CROMER and J. P. SCHARFF*

Laboratoire de Chimie Minérale, Université Claude Bernard Lyon I, 69622 Villeurbanne, France

The binding of metal ions to organic materials in soil and water is an area of considerable interest. A better understanding of the equilibria that determine the behaviour of the chemical elements in the superficial environment is clearly essential for effective geochemical research. Naturally occurring organic compounds are an integral part of soils and aquatic systems. These substances play a major role in the retention and deactivation of anthropogenic organic and mineral chemicals and are involved in the geo-transport of metals.

Humic substances make up the bulk of organic matter and they probably control the abundance and distribution of trace metals in the environment by complexation or chelation processes through functional groups including carboxylic, phenolic, alcoholic and enolic OH, carbonyl and NH_2 sites at which binding may occur [1].

The determination of stability constants of metal-humic and fulvic acid complexes permits the prediction of the chemical speciation of many metals and the elucidation of their dispersion cycles.

The present work deals with the interactions of lead(II), cadmium(II) and copper(II) ions with water