ADSORPTION OF ZINC AND CADMIUM BY SOILS AND SYNTHETIC HYDROUS METAL OXIDES

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Antony Hugh Coleby Roberts

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ABSTRACT

This study involved an investigation into the adsorption of Zn and Cd by soils and synthetic hydrous metal oxides, and the effect of several factors on the adsorption reactions in controlled laboratory experiments.

Initially, in order to determine low concentrations of Zn and Cd in solution, a concentration procedure involving solvent extraction was developed. The procedure utilised a chelating agent, dithizone, and an organic solvent, carbon tetrachloride. Zinc and Cd were back-extracted from the organic solvent into hydrochloric acid to achieve a ten-fold increase in concentration.

For soils and Fe gel, adsorption of both Zn and Cd was characterised by an initial, rapid removal from solution which was followed by a much slower, continuing decrease in solution concentration.

Isotherms (40 hr) for Zn and Cd adsorption from 3×10^{-2} M NaCl by soils, synthetic hydrous ferric oxide (Fe gel) and allophane, were described using two Langmuir equations. Values for the derived free energies of adsorption, for each region of adsorption, were similar for both Zn and Cd on all soils and on Fe gel. Allophane, however, had higher free energies of adsorption than either the soils or Fe gel. For all adsorbents, Langmuir constants derived from adsorption data indicated that the adsorbing surface contained a relatively small number of sites with a high free energy of adsorption and a much larger number of sites with a lower adsorption energy. Iron gel appeared to provide a satisfactory model for describing Zn and Cd adsorption by soils.

Amounts of Zn and Cd adsorbed by Fe gel increased as pH increased. Adsorption of Zn and Cd by Fe gel in each Langmuir region appeared to be

affected similarly by changes in pH, although the pH_{50} values (the pH at which 50% of the initial amount added was adsorbed) were higher for Cd than for Zn.

Experimental data obtained in the study are consistent with a two-mechanism model for both Zn and Cd adsorption. It is proposed that the first mechanism involves the formation of a bidentate complex. Adsorption of Zn and Cd into this region involves the release of two protons for each Zn or Cd ion adsorbed, resulting in a bond of higher energy than when Zn or Cd is adsorbed by the second mechanism. In this latter case, it is proposed that a monodentate complex is formed with one proton released for each cation adsorbed.

In addition to proton release, data in support of the two-mechanism system was obtained in isotopic exchangeability and desorption studies. For example, the mole ratios (i.e., number of protons released for every Zn or Cd ion adsorbed) for Zn and Cd were non-integer values. For Zn the mole ratios ranged between 1.31 and 1.67, and for Cd from 0.80 to 1.12, at pH 6.4. There was no obvious trend in mole ratios for Zn either with increasing amounts of Zn adsorbed or increasing pH, but for Cd mole ratios increased with increasing amounts of Cd adsorbed or increasing pH. The isotopic exchangeability of Zn was similar at all levels of Zn adsorbed, but decreased with increasing pH (pH 5.85 - 6.65) from 58% exchangeability to 27%, possibly due to an increased proportion of more-tightly bound Zn. Cadmium, by contrast, had a lower exchangeability at low levels of Cd adsorbed (55 - 76%) than at higher levels (80 - 85%) but was more exchangeable (55 - 85%) than Zn at equivalent pH values and lower surface coverages, indicating that a greater proportion of adsorbed Cd was less tightly bound compared to Zn. Sequential desorption of Zn by calcium ions followed by copper ions showed that a

proportion of Zn (12 - 24%) was retained by the surfaces against desorption, further indicating the presence of two adsorption mechanisms of different binding strength. Only at low levels of adsorbed Zn did the amount of desorbed Zn closely approximate the amounts of Zn calculated (from Langmuir constants) to be in region II. These desorption data, together with the exchangeability data for Zn, point to the possible limitations in the use of Langmuir equations for quantifying the amount of Zn adsorbed by each mechanism.

The Langmuir isotherm studies, together with proton release, exchangeability and desorption data, indicated two mechanisms of adsorption for Zn and for Cd. However, the greater exchangeability and fewer protons released per mole adsorbed suggest that more Cd is held by the mechanism involving monodentate bonding than is the case for Zn.

Zinc or Cd was not observed to be absorbed or "occluded" by synthetic ferric oxide gel or goethite. There was evidence to suggest that Zn and Cd might diffuse into cracks or defects in the crystal structure of natural goethite, developed by grinding. Although some fraction of adsorbed Zn or Cd was non-exchangeable and non-desorbable (by copper) for all three adsorbents, this Zn and Cd was not in the absorbed phase.

Long term (up to thirty year) additions of superphosphate fertiliser to three soils did not produce measurable accumulations of Zn or Cd in the soils. The calculated additions agreed well with actual increases measured in total Zn, but not with actual increases in total Cd.

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