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Cadmium, copper, nickel and zinc adsorption as a function of pH and ionic strength in variable charge soils

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There is little information on the fate and mobility of heavy metals in highly weathered soils. In variable charge systems, the metal ion adsorption may occur by both electrostatic attraction and specific adsorption. The adsorption of metal cations was studied in surface and subsurface samples from an alfisol [Rhodic Kandiudalf (RK)] and from an highly weathered oxisols [Anionic “Rhodic” Acrudox (AR) and Anionic “Xanthic” Acrudox (AX)] of the State of São Paulo, Brazil. Adsorption envelopes were elaborated by reacting the soil samples with individual aqueous solutions containing nitrate salts of the adsorptive heavy metal (Cd, Cu, Ni and Zn) at the initial concentration of 5 mg L^{-1}, and having an increasing pH value from 4.0 to 7.0. In order to study adsorption mechanisms, the experiments were carried out under variation of the ionic strength, $Ca(NO_3)_2$electrolyte solution 0.01, 0.1 and 1.0 mol L^{-1}. The parameter D = % ads / (100 - % ads) was calculated and considered as $\log\{[M]_{ads}/[M]_{sol}\}$ in order to transform the S-shaped curves obtained from %ads x pH. Thus, the log D x pH relationship was employed to obtain a simple two-parameter linear equations and to identify different adsorption mechanisms. Under specified condition, using $Ca(NO_3)_2$ 0.01 mol L^{-1}, the relative contribution of specific and electrostatic adsorption would be different. Curves for Cd, Ni and Zn adsorption on surface samples could be distinguished into three linear parts, correspond to regions I, II and III. The line slope was comparatively steep within both the low (4.0 to 5.0) and the high (6.0 to 7.0) pH range, while region II was relatively flat region within the middle pH range (5.0 to 6.0). For subsurface samples, two regions for Cd, Ni and Zn adsorption were identified from

4.0 to 6.0 and 6.0 to 7.0 pH range. Probably, in region I, specific adsorption was the major mechanism. In region II, because of the increase in negative surface charge, electrostatic adsorption contributes to a certain extent. In region III, where probably the degree of hydrolysis of metal ions increases, specific adsorption of metal species in the form of MOH^+ becomes the dominant mechanism. Relevant curves for Cu adsorption exhibited only one region along the 4.0 to 7.0 pH range. This may be caused by differences in extent of hydrolysis of Cu ions and in affinity of adsorption sites for Cu. High affinity for Cu was confirmed when the log D x pH was no affected by the ionic strength, indicating that the inner-sphere complex formation was the dominant process. log D values for Cd, Ni and Zn where high in diluted 0.01 $Ca(NO_3)_2$ electrolyte solution and were considered an indicative of the prevalent electrostatic bounding mechanism.