1 Parameters and evidences for heavy metals adsorption mechanisms from batch adsorption studies with variable charge soils

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In a complex system with amphoteric behavior, the comprehension of the mobility, availability and fate of pollutants in the soil system is crucial for the prediction of the environmental consequences and for development of prevention/remediation strategies. A comparative study of cadmium (Cd), copper (Cu), nickel (Ni) and zinc (Zn) adsorption by highly weathered soils was conduct using quantitative adsorption parameters: (i) parameter D=%ads/(100-%ads), calculated and considered as $\log\{[M]_{ads}/[M]_{sol}\}$ in order to transform the S-shaped curves obtained from %ads vs pH (Kurbatov plots); (ii) pH_{50}, defined as the pH value at which 50% of the initial metal concentration is adsorbed, and; (iii) $\Delta pH_{50-100\%}$, the difference between the pH of 100 and 50 percent metal adsorption. Surface (0-0.2m) and subsoil (B horizon) samples were taken from a Rhodic Kandiudalf (RH), an Anionic "Xanthic" Acrudox (XA) and an Anionic "Rhodic" Acrudox (RA), located in brazilian humid tropical area. As the pH and the ionic strength are important environmental factors influencing the solution chemistry of heavy metals in variable charge systems, adsorption envelopes, in a batch adsorption experiment, were elaborated by reacting, for 24 h, soil samples with individual 0.01, 0.1 and 1.0 mol L^{-1} Ca(NO$_3$)$_2$ aqueous solutions containing nitrate salts of the adsorptive heavy metal (Cd, Cu, Ni and Zn) at the initial concentration of 5 mg L^{-1}, with an increasing pH value from 3.0 to 8.0. In the simple correlation analysis, pH explained the majority of the variation in adsorption parameters for Cd, Ni and Zn. A sharp increase of adsorption density (adsorption edge) was

observed within a very narrow pH range, usually less than two pH units. Kurbatov plots for Cd, Ni and Zn adsorption could be distinguished into two linear parts, correspond to regions I and II. The line slope was comparatively flat within both the low pH range (3.0 to 5.0), while region II was relatively steep region within the high pH range (>6.0). Probably, in region I, because of the increase in negative surface charge, electrostatic adsorption contributes to a certain extent. In region II, 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 pH range. Cadmium and Cu exhibited the highest and the smallest pH_{50} values, respectively, while Ni and Zn presented intermediate pH_{50} values. pH_{50} values for Cd, Ni and Zn increased as the ionic strength increased, but not for Cu. This behavior indicated the weak electrostatic bonding mechanisms involved in the formation of outer-sphere complex between these metal ions and the soil adsorbents. The smallest pH_{50} values for Cu, indicated that Cu retention can preferentially occurs. Additionaly, as the smaller the pH_{50}, the more selective the adsorbent for the metal, and then, the follow affinity sequence was suggested: Cu>Zn>Ni=Cd. $\Delta pH_{50-100\%}$ indicated that Cu was preferentially adsorbed, as the adsorption increase from 50 to 100% of the initial concentration added occurred in very narrow pH interval, never upper 2.3 units.