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Abstract

Quantification of adsorption processes on clay mineral surfaces is often necessary to predict the extent and the evolution of contaminants migration in surficial and underground environments. Many studies have been dedicated to retention measurement as a function of pH and ionic strength in relation with the two main identified adsorption processes for clay minerals, i.e. cation exchange on their basal surfaces and surface complexation on their edge surfaces. The latest process has been repeatedly assessed as an effective retention mechanism at circumneutral pH conditions, which often prevail in natural environments. This assessment must however be tempered by the lack of information about competitive processes that can take place with the numerous chemical species present in natural settings, compared to simplified systems investigated in laboratory experiments. In this study, we quantified experimentally the competition between Pb^{2+}, Co^{2+}, Zn^{2+} and Mg^{2+} for specific adsorption on montmorillonite edge surfaces. Zn^{2+} was an effective competitor with Pb^{2+} and Co^{2+}, and our

results showed also unambiguously the influence of Mg^{2+} concentration levels on the specific adsorption of Pb^{2+} and Co^{2+}. Because of the high ionic strength used in the experiments, cation exchange with Mg^{2+} was dismissed as a possible reason for such competition process, leaving specific competitive adsorption on edge surfaces as a unique explanation for our observations. Modeling of Pb^{2+} adsorption data with a state-of-art electrostatic complexation model for montmorillonite edge surfaces, supported by state-of-the-art, made it possible to distinguish two types of possible competition driving forces: Zn^{2+} competition for adsorption site occupancy, but also detrimental changes in surface electrostatic potential following Mg^{2+} adsorption on sites neighboring those of Pb^{2+} adsorption. Mg^{2+} competition observed in our experiment should apply in most of clayey environments. Consequently, adsorption data obtained on pure clay mineral phases, and the associated models that have been built based on these data without considering the geochemical background in competitive species, may overestimate the retention properties of clay minerals when applied to natural settings.

Keywords: Adsorption; Competition; Surface complexation modeling; Clay; Montmorillonite.