Which phase drives adsorption of organic acids on sedimentary rocks?

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This study focuses on adsorption of soluble organic acids on a sedimentary rock (Callovo-Oxfordian), which is investigated by the French radioactive waste management agency (Andra, Cigéo project). The objective is to improve our understanding on adsorption mechanisms on a material displaying various phases (clayey minerals, tectosilicates, carbonates, natural organic matter). Indeed, adsorption might occur simultaneously on clayey minerals (by cation bridging), on oxides (by electrostatic interaction), on organic matter (by hydrophobic interaction) and on all these phases by ligand exchange or van der waals interactions.

In order to determine which solid phase drives adsorption, different experiments were prepared. The first series used the raw and sound clay rock. The second series was obtained after carbonates dissolution. The third series was the smallest granulometric fraction (<2μm). The chosen separation method of mineral phases minimized chemical perturbation, avoiding solvent extraction, oxygen, or temperature. Adsorption-desorption experiments were carried out on the three materials with radioactive tracers of selected organic acids. Results showed unexpected differences between similar carboxylic acids. Acetate and adipate which are representative of the sole carboxylic function displayed a low adsorption, specifically on clays. Phthalate displayed an increased adsorption on clay phase despite its anionic nature. A different behaviour was found for oxalate and citrate with a much higher adsorption on minor phases and desorption hysteresis.

Therefore, adsorption data of several anthropogenic organic acids on specific phases of a heterogeneous sedimentary rock were gathered. This work demonstrated the interest to perform measurements on various molecules in order to evidence useful links between physicochemical properties and adsorption. It also highlighted differences between a reducing deep-geological media and oxidized sub-surface rocks. The results will be discussed with emphasis on classifying soluble organic acids fate in geological disposals, landfill leachates or water treatment processes.