Adsorption of Cs⁺ and IO₃⁻ Ions by PseudoBoehmite Before and After the Decomposition of Citrate Adsorbed on Its Surface

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Abstract—Citrate is distributed widely in the Earth’s surface environments as a biological product released by microbes and plants. Citrate is also often used as a chelating agent for the selective dissolution of iron coatings and free iron oxides in soils. Adsorption experiments of Cs⁺ and IO₃⁻ before and after the decomposition of citrate with the pseudoBoehmite surface were conducted to evaluate the effects of citrate on the adsorption of these ions on the surface of pseudoBoehmite. Additional adsorption experiments of Cs⁺ and IO₃⁻ after the decomposition of citrate adsorbed on the pseudoBoehmite surface were also performed to confirm the recovery of the original surface properties. Citrate decomposition was carried out by means of 10% H₂O₂ treatments at 75°C and pH 5, 7, and 9. The results indicated that citrate complexation decreased remarkably the adsorption of both Cs⁺ and IO₃⁻ in the pH range 3–10, which was due to a decrease in the number of active charged sites available for adsorption of these ions. Decomposition of citrate adsorbed on the pseudoBoehmite surface was found to be complete after three rounds of treatment with 10% H₂O₂ at 75°C and pH > 7. After the decomposition of citrate adsorbed on the pseudoBoehmite surface, the adsorption of both Cs⁺ and IO₃⁻ was restored completely to the initial amounts before citrate complexation, and the inhibition effect of citrate on the adsorption of these ions disappeared under all pH conditions.

Key Words—Adsorption, Citrate, Complexation, Cs⁺, Decomposition, IO₃⁻, PseudoBoehmite, Surface Properties.

INTRODUCTION

The surface properties of clay minerals including various oxide and hydroxide minerals are important factors which affect the chemical processes occurring at mineral—water interfaces in the Earth’s surface environments. Surface chemical processes involve various elementary reactions such as the transport of chemical species, adsorption, and precipitation, which control the rate and extent of elemental transport, the dissolution and crystal growth of minerals, weathering, and other geochemical processes in soils and aquifers (Hochella and White, 1990; Stumm and Morgan, 1996). In general, surface properties including surface charge and affinity for dissolved chemical species in solutions depend primarily on the dissociation of surface functional groups such as silanol and aluminol groups. At pH < pHₚ₂zc, the surface will be positively charged because of the protonation of functional groups, resulting in enhanced adsorption affinity for anionic species. Conversely, functional groups are deprotonated at pH > pHₚ₂zc, which results in a negative surface charge and increases the adsorption affinity for cationic species. However, organic molecules interact widely with mineral surfaces and influence the surface properties of minerals by adsorbing to specific functional groups in natural soil environments (Lowenstam and Weiner, 1989; Barker et al., 1997; Ullman and Welch, 2002; Dove et al., 2003; amongst others).

Citrate is a common, low-molecular-weight organic acid exuded by plant roots and produced by microbes in soils (Jones, 1998; Adeleke et al., 2017; Violante et al., 2002). It forms stable chelate complexes with dissolved metal ions, and also adsorbs strongly on the mineral surfaces via inner-sphere complexation with specific functional groups such as aluminol groups (Boily and Fein, 1996; Hidber et al., 1996; Sparks, 2003). In addition, surface complexation between citrate and mineral surfaces occurs during chemical treatments using citrate, such as in the selective dissolution of amorphous iron contaminants using the dithionite-citrate-bicarbonate (DCB) method (Mehra and Jackson, 1960). The surface properties of minerals are influenced heavily by these surface complexes because they decrease the surface charge, which in turn causes pHₚ₂zc to become more acidic and alters the surface affinity for dissolved chemical species (Huang and Violante, 1986). For example, the surface speciation of Al-citrate (Al-cit) complexes based on the adsorption data of citrate on the surface of corundum was determined by Boily and Fein (1996); those authors found that the surface complexes of Al-HCit groups formed at pH < 4, and Al-Cit²⁻ groups formed at pH between 4 and 9. This implies that citrate adsorption decreases the surface charge of corundum by forming negatively charged surface complexes, which also

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