Immobilization of Hexavalent Chromium by Utilizing Fe³⁺-bearing Clay Mineral as an Electron shuttle

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Cr(VI) usually exists in form of oxyanions (i.e., CrO₄²⁻, $Cr_2O_7^{2-}$) in natural environment, which are not easily adsorbed on soil, leading to leaching into groundwater. Promoting a reduced environment in aquifer by using a reductant (i.e., dithionite) results in reduction of Cr(VI) to Cr(III), which can be an effective remediation technology. Structural iron (Fe³⁺) in clay minerals is a key reaction medium, mediating electron transfer between dithionite and Cr(VI) through Fe3+/ Fe2+ coupling reaction. This study deals with the feasibility of utilizing Fe-bearing clay minerals as an electron shuttle for the immobilization of Cr(VI). The redox behavior of structural Fe³⁺ in three types of clay minerals including kaolinite (total Fe³⁺, 0.01 wt%), montmorillonite (total Fe³⁺, 2.3 wt%), and nontronite (total Fe³⁺, 22.3 wt%) was investigated in the presence of dithionite at various pH. Results showed that the reduction ratio (Fe²⁺/Total Fe) was highest in kaolinite reaching up to 100%, following montmorillonite and nontronite, increased up to pH 9 and decreased at pH 11. Calculated standard redox potential (Eh_0) of structural iron showed that it differs depending on the types of clay minerals and surrounding pH, and reduction of structural iron prefers when the environmental redox potential is lower than Eh₀. However, the mass of structural iron reduced was the highest in nontronite (i.e., ca. 112 mg/g of clay mineral, whereas 16.78 mg/g in montmorillonite and 0.03 mg/g in kaolinite), attributed to its high Fe content. An experiment, to reduce Cr(VI) with the reduced structural Fe²⁺ in clay minerals was also conducted. The results showed that the structural Fe^{2+} in clay minerals was able to convert Cr(VI) into Cr(III), with a more rapid reduction rate observed at lower pH. The reduced Cr(III) is thought to exist as Cr(III)-clay mineral complex at pH 3 and 5, and as Cr(OH)₃ at pH above 7.