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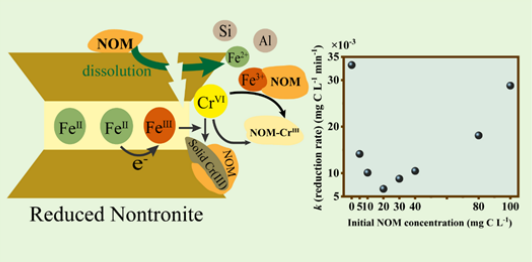

Effect of Natural Organic Matter on Cr(VI) Reduction by Fe(II)-bearing clay mineral

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The environmental behaviors of hexavalent chromium (Cr(VI)) are of great concern due to its high toxicity and mobility. Despite the common co-occurrence of natural organic matter (NOM), Fe(II)-bearing clay minerals, and Cr(VI) in contaminated environments, how their mutual interactions affect the fate of Cr has rarely been studied. In this manuscript, we investigated the kinetics and possible mechanisms of Cr(VI) reduction by reduced nontronite (rNAu-2), a typical Fe(II)-bearing clay mineral, in the presence of Suwannee River NOM under circumneutral pH. The aqueous-phase and solid-phase at different time intervals were characterized with wet chemical methods, X-ray diffraction, transmission electron microscopy, and X-ray photoelectron spectroscopy analyses. Our results demonstrated that besides the predominant solid Cr(III) species, soluble NOM-Cr(III) complexes were formed during reduction. Overall, NOM inhibited the reduction rate of Cr(VI), possibly because the solid Cr(III) products formed during Cr(VI) reduction co-precipitated and/or sorbed NOM, which impeded the sorption of Cr(VI) onto rNAu-2 reactive sites. Interestingly, the reduction rate decreased with the increase of NOM from 0 to 20 mg C/L, but kept increasing when NOM increased from 30 to 100 mg C/L. The opposing trend was likely attributed to the increase of promotion effects with increasing NOM concentrations, which offset the inhibitory effect. The main promotion effects may include: (1) NOM offered electrons to Cr(VI) through NOM-Fe(II/III) complexes and/or NOM-Cr(V) complexes; (2) NOM caused NAu-2 dissolution and resulted in the release of Fe(II) and Fe(III), which enabled better contact between Fe(II) and Cr(VI) and/or offered additional electron transfer pathways from NOM-Fe(II/III) complexes to Cr(VI), respectively; (3) NOM weakened the passivation of rNAu-2 by forming stable and aqueous NOM-Cr(III) complexes, which stimulated the sorption of Cr(VI) on rNAu-2. This study points out that NOM is a factor that cannot be neglected in understanding the fate of Cr(VI) in the geochemical cycling of Fe in NOM-rich environments given the reduction rate of Cr(VI) and the mobility and potential re-oxidation of reduction products.

Reference: Liyan Deng, Fu Liu, Zecong Ding, Yuzhen Liang, Zhenqing Shi, Effect of natural organic matter on Cr(VI) reduction by reduced nontronite, Chemical Geology, 615, 2023, 121198.