



Assessing Contaminant Reduction by Fe(II) associated with iron-bearing Clay Minerals using Nitroaromatic Probe Compounds and Infrared Spectroscopy

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Ferrous iron species are of great relevance for the reductive transformation of organic soil and groundwater contaminants under anoxic conditions. To date, many field and laboratory studies have shown that Fe(II) associated with various iron containing minerals such as iron oxides and green rusts can efficiently reduce compounds such as nitroaromatic pesticides and explosives and chlorinated solvents. In contrast, ferrous iron species in clay minerals, which are ubiquitously present in the environment, have rarely been assessed with regard to their potential to reduce organic contaminants. Using nitroaromatic compounds (NACs) as probe molecules to evaluate Fe(II) reactivity and infrared spectroscopy to monitor changes of Fe redox state in selected clay minerals, we investigated the reactivity and availability of different Fe(II) species for contaminant transformation.

Clay minerals can contain three types of potentially reactive Fe(II) species, that is, structural Fe(II), Fe(II) complexed by edge surface hydroxyl groups, and Fe(II) bound by ion exchange to basal surfaces. The analysis of the reduction kinetics of two substituted NACs in suspensions of chemically reduced smectites (nontronite (ferruginous smectite, SWa-1), and montmorillonite (Wyoming montmorillonite, SWy-2)) showed that structural Fe(II) in the octahedral layer of the minerals was the predominant reductant, whereas Fe(II) bound to surface hydroxyl groups and Fe(II) bound to the basal surfaces by ion exchange did not contribute significantly to the overall reactivity [1].

The reactivity of Fe(II) species, which was quantified as rate constant of NAC reduction normalized to the Fe(II) content in the mineral, was up to 3 orders of magnitude

higher in iron-rich nontronite (12 wt % total Fe) compared to montmorillonite (1.5 wt % total Fe). We hypothesize that this observation is due to the presence of Fe(II) species exhibiting different reactivity in the octahedral sheet of the two smectites. Whereas in nontronite highly reactive Fe(II)-O-Fe(II) and Fe(II)-O-Fe(III) clusters can form [2], octahedral Fe(II) in montmorillonite has no neighboring Fe atoms due to the lower iron content leading to slower NAC reduction. This assumption is further corroborated by the fact that NAC reduction kinetics were biphasic in suspension of nontronite but strictly followed pseudo-first order behavior in the presence of montmorillonite.

Additional evidence for redox changes of octahedral Fe was obtained from the analysis of M-O-H and Si-O vibrations in nontronite by infrared (IR) spectroscopy. In particular, using a custom-made attenuated total reflection (ATR) unit, we examined both, the oxidation of structural Fe(II) and the concomitant NAC reduction, by IR spectroscopy. Spectra of oxidized and reduced nontronite were taken as references and their decomposition yielded characteristic bands which, in turn, were used to decompose the spectra measured during Fe(II) oxidation by NACs. The bands corresponding to reduced nontronite decreased whereas the bands taken from the spectrum of the oxidized mineral increased during the course of the reaction. Spectroscopic results were verified by NAC concentration measurements in the above mentioned assays and support our findings of octahedral Fe(II) being the predominant reductant in reduced smectites.

[1] T. B. Hofstetter, A. Neumann, R. P. Schwarzenbach, *Environ. Sci. Technol.*, 40 (2006), 235

[2] P. Komadel, P. R. Lear, J. W. Stucki, *Clays Clay Mineral.*, 38 (1990), 203