

Hydroxyl Radicals produced from Oxygenation of Fe(II)-bearing Clay Minerals and the Resultant Oxidizing Impact

SONGHU YUAN^{*1}, XIXIANG LIU¹

¹China Univ Geosci, State Key Laboratory Biogeol & Environm Geol, Wuhan 430074, Peoples R China
(*correspondence: yuansonghu622@cug.edu.cn)

Dark production of reactive oxygen species (ROS) has attracted great interests in recent years. Oxygenation of reduced component such as Fe(II) is an important source of ROS in nature. We recently reported the production of hydroxyl radicals ($\bullet\text{OH}$) from oxygenation of sediment Fe(II) in subsurface when the redox condition was disturbed by O_2 [1]. Herein we show that Fe(II)-bearing clay minerals, i.e., reduced nontronite (NAu-2), can efficiently activate O_2 to produce $\bullet\text{OH}$ under neutral conditions. A stepwise one-electron transfer process with the involvement of superoxide ($\text{O}_2^{\bullet-}$) and hydrogen peroxide (H_2O_2) was identified for O_2 reduction to $\bullet\text{OH}$ by the reduced NAu-2 (54.5% of Fe as Fe(II)). The electron transfer from structural Fe(II) in NAu-2 to O_2 was explored through characterizing the reduced NAu-2 upon oxidation for different time by fourier transform infrared spectroscopy (FT-IR), Mössbauer spectra, X-ray photoelectron spectroscopy (XPS) and ultraviolet-visible spectrum (UV). Different coordination of structural Fe(II) showed different reactivities upon oxygenation, and both structural Fe(II) and Fe(III) rearranged during the course of oxygenation. We finally found that the $\bullet\text{OH}$ produced from oxygenation of chemically and biologically reduced NAu-2 led to the oxidative transformation of environmental contaminants like trichloroethylene, and from oxygenation of field sediment induced benzoic acid oxidation. Thus, we suggest that $\bullet\text{OH}$ produced from oxygenating Fe(II)-bearing clay minerals could be an important mechanism for contaminant attenuation in redox-dynamic conditions.

[1] Tong et al. (2016) Environ. Sci. Technol. 50, 214-221.