Humic acid promoted goethite bioreduction, hydroxyl radical production and sulfanilamide degradation during anaerobic-aerobic transition

GUANGFEI LIU [1]*AND HUALI YU[1]

[1]School of Environmental Science and Technology, Dalian University of Technology, Dalian 116024, China (*correspondence: guangfeiliu@dlut.edu.cn)

The biogeochemical cycles of Fe and C are always intimately associated in natural environments. It has been found that abundant hydroxyl radical (•OH) was produced during the oxygenation of reduced Fe-bearing minerals at anaerobic-aerobic interface. However, little was known about the impacts of coexisting natural organic carbon on this process. Here, it was found that 10-100 mg/L humic acid (HA) could significantly promote the reduction of both abiogenic and biogenic goethite (Gt_{chem} and Gt_{bio}) by *Shewanella oneidensis* MR-1 under anaerobic condition. When trasferred to aerobic environment, systems containing higher Fe(II) concentrations generated higher concentrations of •OH, whereas the production of •OH by oxidation of reduced HA in these systems was negligible. Adsorbed Fe(II) played a significant role in •OH generation, and contributed to at least 72.8% and 90.1% of •OH generation in the systems of Gt_{chem}+HA and Gt_{bio}+HA. HA-complexed Fe(II) contributed to the rest •OH generation. Sulfanilamide (SA), a widespread antibiotics was selected as typical pollutants to assay the degradation performance of different systems. The trend of SA degradation was consistent with that of •OH generation. About 15.2%-72.5% of SA was degraded in different systems. Four redox fluctuation cycles with different regimes were condcuted to evaluate the sustainability of •OH production in subsurface environments with different redox conditions. Stable production of •OH were obtained in repeated cycles with “fluctuation 3:1” (3-day anaerobic and 1-day aerobic), while •OH production decreased with the increasing cycles of “fluctuation 6:1” (6-day anaerobic and 1-day aerobic), suggesting that higher fluctuation frequency might facilitate the stable •OH production. While the crystallinity of both Gt_{chem} and Gt_{bio} decreased with increasing anaerobic-aerobic transitions, the repeated redox fluctuation did not cause the formation of new crystalline mineral phase. In conclusion, our findings indicated that the presence of HA promoted •OH generation and oxidative contaminant degradation by enhancing the production of adsorbed and complexed Fe(II) under redox fluctuation conditions.