Fe(II) oxidation by nitrite under anoxic conditions: pH effect and secondary minerals

CHEN DANDAN, LIU TONGXU*, LI FANGBAI*

Guangdong Institute of Eco-Environmental and Soil Sciences, Guangzhou 510650, China, txliu@soil.gd.cn; cefbli@soil.gd.cn

While both the biological and chemical processes are involved in the microbially mediated NO_3^--reducing Fe(II) oxidation, the importance of the chemical reaction between NO_2^- and Fe(II) was overlooked previously. To clearly understand the reaction between NO_2^- and Fe(II) under anoxic conditions, the kinetics and mineralization at various pH from 5.5 to 8.0 were systematically investigated. The reaction kinetics of Fe(II) oxidation and nitrite reduction clearly showed that the reaction rates were greatly enhanced with the increase of pH, except for pH 7.5. At pH 5.5-7.0, strong correlations were observed for the Fe(II) oxidation rates vs pH (R^2=0.847) and the rates of NO_2^- reduction vs pH (R^2=0.926), however, weak correlations were observed at pH 7.0-8.0, which might be attributed to the formation of secondary minerals. Powder XRD, FE-SEM and HR-TEM were used to characterize mineral phases. Only goethite was observed under acidic and neutral conditions (pH 5.5-7.0). However, an obvious mineral transformation was observed under alkaline condition (pH 7.0-8.0). In the first 12 hours, only green rust was formed; after 24 hours, green rust decreased while goethite and lepidocrocite increased; after 48 hours, all green rust disappeared, which might be transformed into goethite and lepidocrocite, and magnetite was only observed at pH 8.0. During these processes, OH^- was considered as a key factor for the reaction kinetics and secondary mineral transformation. The redox potentials under different pH were measured and the Pourbaix diagram was drawn based on the thermodynamic calculation of all the iron species and minerals observed in this study. The calculated and measured redox potentials were well matched with the results of kinetics and secondary mineral formation. These observations in this study provide a comprehensive understanding of the chemodenitrification process, which may be very helpful to disclose the underlying mechanisms of microbially mediated NO_3^--reducing Fe(II) oxidation and quantitatively evaluate the contributions of the biological and chemical processes.

This work was funded by the National Natural Science Foundations of China (41571130052 and 41522105).