

## **The improvement of zinc substitution on the reactivity of magnetite coupled with aqueous Fe(II) towards nitrobenzene reduction**

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Biogeochemical iron cycling is ubiquitous in anoxic environment. The iron oxides coupled with Fe(II) display reductive activity towards environmental pollutants, e.g., organics, heavy metals and radionuclides, considered as an important way for the abiotic transformation of pollutants in anaerobic environment. Among the iron oxides, the study of magnetite is compelling, due to its interesting structural features. Magnetite is the only iron oxide mineral containing Fe<sup>2+</sup>, where structural Fe<sup>2+</sup> is a potential electron donor. The Fe<sup>2+</sup> and Fe<sup>3+</sup> on octahedral sites facilitate the electron transfer from bulk phase to environmental contaminants, while keeping the structure stable. In most natural cases, iron is isomorphously substituted by transition metals. Several substitutions significantly change the microstructure and physicochemical properties of magnetite, and probably affect the surface reactivity with aqueous Fe(II).

In anoxic environment, Zn(II) can be introduced into magnetite structure through the reduction of Fe(III) compounds by iron reducing bacteria. In this study, effect of Zn substitution (Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub>) on the activity of magnetite coupled with Fe(II) was investigated toward nitrobenzene (NB) reduction. Zn<sup>2+</sup> mainly occupied tetrahedral sites in spinel structure, but partially moved to the octahedral sites at high Zn level. NB reduction was mainly through the heterogeneous reaction by Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub> and adsorbed Fe(II), where aqueous NB was reduced by structural Fe<sup>2+</sup> in magnetite recharged by adsorbed Fe(II). Various factors, i.e., aqueous Fe(II) concentration, magnetite stoichiometry and Zn level were investigated to illustrate their effects on the reduction process. Both the rate constant  $k_{obs}$  and electron transfer amount illustrated that Zn substitution generally improved the reduction activity of Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub>/Fe(II) system, while overdose of Zn retarded the process. Such variation of reduction activity by Zn substitution was discussed in terms of reaction mechanism and the cationic microstructure and physic-chemistry properties of Fe<sub>3-x</sub>Zn<sub>x</sub>O<sub>4</sub>.