

Heterogeneous Reduction of 2-Chloronitrobenzene by Co-substituted Magnetite Coupled with Aqueous Fe²⁺

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Reductive transformation is a predominant degradation pathway for nitrobenzene (NB) derivatives in natural matrices. Magnetite coupled with aqueous Fe²⁺ (Fe²⁺_{aq}) displays reducing capability towards NB derivatives, but it is still unclear whether the substitution of redox-active metals in magnetite has significant influence on the reducing capability of the coupled system. This study investigated the potential of the heterogeneous reduction of 2-chloronitrobenzene (2-Cl-NB) by Co-substituted magnetite (Fe_{3-x}Co_xO₄, 0.00 ≤ x ≤ 1.00) coupled with Fe²⁺_{aq}. Both the reaction kinetics and extent of electron transfer illustrated that appropriate Co substitution (x < 0.85) significantly promoted the reduction activity of Fe_{3-x}Co_xO₄/Fe²⁺_{aq} systems, while excess Co (x ≥ 0.85) retarded the process. A good linear correlation (R² ≥ 0.94) was established between the electrical conductivity of Fe_{3-x}Co_xO₄ and the rate constant (k_{obs}), calculated from a three-parameter single exponential decay model. The improvement of reduction activity was ascribed to the redox pairs Co(II)/Co(III) and Fe(II)/Fe(III) on the octahedral sites, which accelerated the electron transfer in magnetite. During the redox reaction, the adsorbed Fe²⁺_{aq} and structural Fe(II) were oxidized gradually while the spinel structure of Fe_{3-x}Co_xO₄ was maintained. These results shed light on the role of magnetite-group minerals and their impact on the fate of contaminants in anoxic environments.