

Impacts of Graphene on Microbial Reduction of Ferrihydrite and Settling Behavior of Biomineralization Products

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With the rapid increase in global production and application, graphene materials will unavoidably be released into the environment and form heteroaggregates with iron-containing minerals and microbial cells. While great attention has been paid to the physicochemical interaction between graphene and mineral particles, the role of biological activity like Fe(III) bioreduction in relevant process has long been neglected.

We found that lower concentration of graphene materials physically entrapped by ferrihydrite (Fh) or located between cell and Fh particles could facilitate the transfer of biogenic electrons and stimulate Fe(III) reduction like solid-phase humics, whereas higher concentration of graphene materials suppressed Fe(III) reduction by wrapping certain cells or Fh particles and restricting the accessibility of Fh surface sites for bacteria. While coexisting rGO further increased the inhibition effects of soil humic acid on Fh reduction, it showed synergistic stimulation effects on Fh reduction with aqueous humic acid. Based on results of HRTEM, XRD and Mössbauer spectroscopy, magnetite was identified as the sole mineralization product in the absence or presence of lower concentration of rGO, whereas a mixture of goethite and magnetite was formed in the presence of higher concentrations of rGO. Moreover, the settling behavior of the bioreduction suspensions can be described with an exponential model. It was found that faster reductive transformation of Fh improved the settling behavior and could limit the diffusion of rGO. However, bioreduction at slower rate might cause re-suspension of the originally stabilized rGO. Therefore, biotransformation of iron-containing minerals could change the environmental behavior, exposure risk and biotoxicity of graphene material. And the interaction of graphene with biogeochemical cycle of iron may also affect the fate of other associated nutrients and contaminants in the environment.

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