

Bioreduction of Cr(VI) over the composites of birnessite and *Shewanella oneidensis* MR-1

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The interaction between soil mineral and microorganisms will inevitably affect the process of bioreduction of Cr(VI). In this study, the reduction process and mechanism of Cr(VI) over the composites of birnessite and *Shewanella oneidensis* MR-1 was studied through the reduction kinetic experiment, and the analysis of surface sites, surface charge, functional groups and chromium speciation. Birnessite increased the negative charge on the surface of *Shewanella oneidensis* MR-1 but decreased the concentration of surface sites. High concentration of birnessite inhibited the metabolism of microorganisms, but it has little effect when the concentration is less than 5g/L. Birnessite promoted the reduction of Cr(VI) because of its enhanced capacity of adsorption. In addition, the introduction of electron shuttle (AQDS and AQS) enhanced the reduction of adsorbed Cr(VI) to soluble Cr(III). The reduction rate increased with the increase of pH in the range of 5-8 and decreased with the increase of initial Cr(VI) concentration due to the toxicity of Cr(VI). As indicated by the XPS results, Cr₂O₃ and Cr(OH)₃ is the main form of chromium at the surface of *Shewanella oneidensis* MR-1–birnessite composites after the reduction of Cr(VI). During the process of Cr(VI) reduction, Mn(IV) in birnessite was reduced to Mn(II) and Mn(III) by *Shewanella*, and the generated Mn(III) participated in the reduction of Cr(VI). Through the ATR-FTIR/2D-CoS analysis, the order of function groups reacted with Cr(VI) is: O-Mn-O → amide II → amide I → MR-1 PO₂⁻ → octahedral MnO₆ → PO₂⁻ of monodentate complex → CH₂/CH₃. These results also indicate the contact of Cr(VI) with birnessite is prior to that with *Shewanella oneidensis* MR-1.