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Structural aspects of uranyl complexes with lipopolysaccharide

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It is well-known that microorganisms play an important role in bioremediation. Because of the high retention capability of heavy metal ions, they significantly influence mobilization and immobilization of cations in soils. The prediction of the radionuclide transport in the environment and the improvement of technical bioremediation strategies require a detailed understanding of the binding mechanisms on a molecular level. Lipopolysaccharide (LPS), the main part of the outer membrane of Gram-negative bacteria, sticks out of the cell wall and is in direct contact with the (aqueous) environment. With its high content of negatively charged functional groups (mainly carboxyl and phosphoryl groups) it plays a key role in protection of contaminants. We investigated the uranyl LPS interactions to gain detailed information about the coordination sphere in the molecular environment of the uranyl ion. We focused on the identification of the coordinating functional groups over a wide pH range (from 2.5 to 7) and under different stoichiometric conditions. In particular, the discrimination between carboxyl and phosphoryl groups and their binding behaviours was elucidated by extended X-ray absorption fine structure (EXAFS) spectroscopy at the U LIII-edge and attenuated total reflection Fourier-transform infrared (ATR FT-IR) spectroscopy. With respect to environmental conditions, samples with an excess of LPS were investigated by EXAFS. Furthermore, samples with equimolar ratios of uranyl and functional groups of LPS according to a slight deficit of phosphoryl groups were determined with FT-IR. EXAFS spectra show great similarities to the uranyl mineral phase meta-autunite. A four-fold complexation of the uranium was derived from very short U Oeq distances of 2.28 Å and U P distances of 3.58 Å indicating unidentate coordinated phosphoryl groups. Furthermore, U U interactions can be observed at 5.2 Å and 6.9 Å.

FT-IR spectra show spectral evidence for both, carboxyl and phosphoryl coordination. A downshift of the antisymmetric stretching mode of the carboxylate group from 1576 (uncomplexed LPS) to 1530 cm^{-1} and an upshift of the symmetric stretching mode from 1404 (uncomplexed LPS) to 1455 cm^{-1} upon complexation provides evidence for a bidentate complexation to carboxylate groups. The antisymmetric and symmetric stretching modes of the complexing phosphoryl groups are observed at 1105 and 1060 cm^{-1} .

In summary, we determined at high LPS excess preferential phosphoryl coordination, whereas with an increasing relative amount of uranyl ions, corresponding to a decreasing number of functional groups of LPS, additional carboxylate coordination becomes important. This complexation behaviour remains within a broad pH range from slight acidic to neutral values. Under the investigated experimental conditions, the coordination of uranyl ions to the LPS molecule is obviously controlled by the U/LPS concentration ratio irrespective from prevailing pH.

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