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Interaction of uranium(VI) with peptidoglycan

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Bacteria have a great influence on the migration behaviour of heavy metals in the environment. Peptidoglycan (PGN) forms the main part of the outer membrane of Gram-positive bacteria. We investigated the interaction of the uranyl cation (UO_2^{2+}) with PGN from Bacillus subtilis by using potentiometric titration and time-resolved laser-induced fluorescence spectroscopy (TRLFS) over a wide pH range (2.4 – 9) and at environmentally relevant low uranium concentrations (10^{-4} – 10^{-5} M). The PGN polymer contains a high density of functional groups for metal ion binding, like carboxyl, amino and hydroxyl groups.
With potentiometric titration the dissociation constants of the functional groups and the corresponding site densities could be detected. We found four functional groups, which can be dedicated to two different carboxyl functionalities, amino and hydroxyl groups. Using the same technique, two different uranyl PGN complexes could be identified, one complex with a carboxyl ligand (R-COO-UO_2^+) and a second complex with additional hydroxyl coordination (R-COO-UO_2^+-HO-R). The complex stability constants were determined to be $\log \beta = 5.16 \pm 0.13$ for the first, and $\log \beta = 13.00 \pm 0.05$ for the second complex, respectively.

TRLFS measurements show from pH 2.4 to 4.5 a red shift of the peak maxima of about 8 – 10 nm, in comparison to the free uranyl ion, connected with an increase of the luminescence intensity. Over pH 4.5 up to pH 9 the luminescence intensity decreases. The time resolved measurements show beneath the lifetimes of the free uranyl ion (1800 ± 200 ns) and the known uranyl hydroxides only one additional lifetime (224 ± 54 ns) which can be dedicated to a uranyl PGN complex species. From these we conclude that the two uranyl PGN complex species found by potentiometry can also be identified with TRLFS. The first complex (R-COO-UO_2^+) shows luminescence activity, but the second complex (R-COO-UO_2^+-HO-R) not. Complex stability constants for these two complexes were determined using the computer program SPECFIT. They are in good accordance to those calculated from potentiometric titrations.