



Reduction of Np(V) by leonardite humic acids and their quinonoid-enriched derivatives

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Humic substances (HS) are natural polyelectrolytes ubiquitous in the environment. Having acidic character, they have high affinity for binding heavy metals and actinides. The presence of phenolic and quinonoid moieties in the structure of HS provide for their ability to take part in redox interactions. In the context of the remediation technologies, of particular importance is that HS are known to display reductive properties in relation to most mobile oxoforms of heavy metals and actinides, e.g. Cr(VI) and Pu(VI, V). This offers their use as reducing agents for in situ remediation technologies such as permeable reactive barriers. However, natural HS are known to possess high structural heterogeneity, which translates into reactive properties that are highly variable between humic fractions and sources of humic materials. This could explain the contradicting results published in the literature on the ability of natural HS to reduce Np(V). The goal of this research was to demonstrate a novel approach of designing reactive humic materials with predictable properties based on directed chemical modification of parent materials. To reach this goal, the following two objectives were formulated: 1) to obtain humic derivatives of the enhanced redox properties using chemical modification; and 2) to assess their reductive performance with respect to Np(V).

For the synthesis of the humic derivatives of enhanced redox properties, formaldehyde copolycondensation was used. It allows enrichment of the existing humic backbone with quinonoid-moieties of the known structure. The corresponding reaction was conducted between parent humic material and two model dihydroxybenzenes: catechol (PC) and hydroquinone (HQ). Leonardite humic acids isolated from the commercially

available potassium humate Powhumus (Humintech Ltd, Duesseldorf) were used as the parent humic material (CHP). The condensation was conducted at the monomer to humics ratio of 100 mg per 1 g of CHP.

The reduction of Np(V) by the CHP and PC- and HQ-copolymers was studied at concentration of 10^{-4} M and concentration of humic materials of 100 mg/L. High concentration of Np(V) was chosen to allow its direct NIR-spectrophotometric determination in the aquatic solution in the presence of HS. The Np(V)-HS solutions were prepared in bidistilled water at pH 4.5. The experiments were conducted under anoxic conditions in the dark to prevent carbonate complexation of Np(V) and photolysis of HS. The reduction kinetics of Np(V) was followed by measurements of absorbance at the bands corresponding to NpO_2^+ and Np-humate complexes: at 981.3 and 987.4 nm, respectively. It was found that the parent humic material used in this study (CHP) was able to partially reduce Np(V). However, the reduction kinetics were very slow: a loss of Np(V) of only 12% after 100 hours. The quinonoid-enriched humics were characterized with faster reduction kinetics: the loss of Np(V) approaching 20 and 25 % in the presence of hydroquinone and catechol enriched copolymers, respectively. Thus, the ranking of Np(V) reduction by the humic copolymers is of the following order: PC100 > HQ100 > CHP.

The obtained results demonstrate a viability of the undertaken approach to producing humic materials of the enhanced redox properties. This opens a way for broad application of the reactive humic materials in the practice of remediation technologies.

Acknowledgements: This research was supported by the grants of NATO-CLG (980508) and DOE (RUC2-20006 MO-04).