

# Synthesis and Use of Humic Derivatives Covalently Bound to Silica Gel for Np(V) Sequestration

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## INTRODUCTION

The most commonly applied technology for treatment of groundwater contaminated with metals and/or radionuclides is “pump and treat”, followed by disposal or re-injection of treated water. This process can be costly and inefficient due to difficulties arising from the ineffective capture of contaminated groundwaters and the sorption of contaminants on mineral surfaces<sup>1</sup>. A permeable reactive barrier (PRB) is an alternative technology to “pump & treat” systems. A PRB is a subsurface wall of reactive permeable medium emplaced across the flow path of a contaminant plume<sup>2</sup>. The most commonly used reactive materials are zero valent iron (ZVI), activated carbon, zeolites, and cellulose solids. Most PRBs use ZVI to treat chlorinated hydrocarbons, while a limited number remove nitrate, hexavalent chromium, and radionuclides<sup>3</sup>. A typical PRB is costly to install but economical to maintain. Much of the installation cost is related to excavation of aquifer material that is then replaced with reactive porous medium<sup>2</sup>.

The goal of this study was a proof of the concept that the reactive agents of a new technology can be designed that can be used for creating broad spectrum sorptive PRBs without excavation. As those agents, the proposed innovative technology uses soluble Humic Substances (HS) that have been specifically modified to adhere to the surfaces of the mineral support and to mediate redox-transformations of actinides. These customized humic materials are immobilized onto silica gel to imitate reactive media of in situ created PRB and to assess their sequestering performance with respect to highly mobile actinide species – NpO<sub>2</sub><sup>+</sup>.

## EXPERIMENTAL PART

A sample of leonardite humic material of enhanced redox activity with incorporated hydroquinone moieties (HQ100) was synthesized as described by Perminova et al.<sup>4</sup> and kindly provided by A.N. Kovalenko. Parent and modified leonardite materials (CHP and HQ100, respectively) were used for preparing alkoxysilyl-derivatives as described in our PCT-application<sup>5</sup>. 3-amino-propyltrimethoxy-silane (APTS) was used to incorporate alkoxysilyl-groups into both humic materials. To prepare solid-phase humic scavengers, aqueous solutions of either HA-APTS or HQ-APTS at concentrations of 5 g/L (10 mL) were added with 0.1 g of silica gel and mixed for 24 hours. The silica gel with immobilized APTS-derivatives was centrifuged

and washed with distilled water. The carbon content in HA-APTS, immobilized on silica gel, was 9.2% mass, and in HQ-APTS, immobilized on silica gel, – 3.3% mass.

The experiments on Np(V) sequestration were conducted under anoxic conditions in the dark in the glovebox. Solutions of Np(V) at concentration of  $3.5 \cdot 10^{-5}$  M (20 mL) were added with 40 or 70 mg of solid HA-APTS-SiO<sub>2</sub> or HQ-APTS-SiO<sub>2</sub>, respectively, and adjusted to pH 4.5. The prepared solutions were sampled over 9 days exposure. The content of Np(V) in the solution was determined using extraction with HDEHP followed by liquid scintillation counting<sup>5</sup>.

## RESULTS AND DISCUSSION

Figure 1 shows the sequestration kinetics of Np(V) in the presence of pure SiO<sub>2</sub>, HA-APTS-SiO<sub>2</sub> containing not enriched leonardite HA and of HQ-APTS-SiO<sub>2</sub> containing hydroquinone enriched leonardite HA at pH 4.5. As it can be seen from the shown kinetic curves, both humic containing scavengers efficiently sequester Np(V) from solution with efficiency of hydroquinone-enriched scavenger being higher, as compared to that of the non-enriched scavenger.

The obtained results demonstrate a viability of the undertaken approach to producing reactive humic materials applicable for in situ installation of sorptive PRBs in actinide-contaminated aquifers. This opens a way for broad application of the humic materials in the practice of remediation technologies.

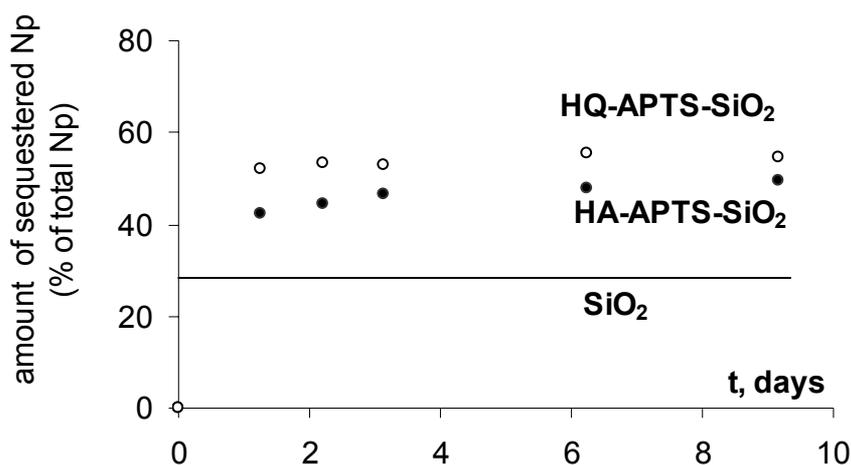


Fig. 1. Sequestration kinetics of Np(V) in the presence of pure SiO<sub>2</sub> and of SiO<sub>2</sub> with covalently bound leonardite HA (HA-APTS-SiO<sub>2</sub>) and of their hydroquinone enriched derivative (HQ-APTS-SiO<sub>2</sub>) at pH 4.5.

*This research was supported by US DOE (project RUC2-20006) and NATO-CLG (grant 980508).*

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