

# Interaction of Modified Humic Substances with Np(V): Influence of Monomer Nature on Redox Properties of Humic Substances

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## 1. INTRODUCTION

The complexation of radionuclides with humic substances (HS), which are ubiquitous in the environment, is recognized as an important factor for the safety assessment of geological disposal of radioactive wastes. HS possess a whole variety of functional groups with prevailing contribution of carboxyls and hydroxyls. This provides for their redox and complexation properties. As a result, HS impact substantially speciation of heavy metals and radionuclides in the contaminated environments. Interactions of HS with neptunium (Np) are of particular concern due to high radiotoxicity and long half-life of this actinide. The most stable oxidation state of neptunium is (V) presented by dioxocation  $\text{NpO}_2^+$ . The latter has a low ion charge which results in high migration ability of these species. Interactions with mineral phases, complexation with different ligands and redox transformation can strongly affect transport of Np(V). Besides inorganic ligands such as carbonate, sulfate and phosphate, HS play an important role in speciation of Np in the environment. Most of the models of HS–metal ion interaction assume that carboxylic groups act as major complexing sites for metal ions (1, 2). At the same time, phenolic and quinonoid groups are considered to be responsible for redox properties of HS (3). In our previous publication (4) we have demonstrated that incorporation of additional hydroquinone groups into backbone of leonardite humic acids (HA) resulted to a substantial increase in reducing ability of the humic materials with respect to  $\text{NpO}_2^+$ .

The goal of this research was to find out if the kinetics of this reaction can be improved by changing structure of the quinonoid center, nominally, by using methyl-substituted hydroquinone.

The idea behind using the substituted hydroquinone for improving kinetics was the known fact that the presence of methyl-substituent in the hydroquinone ring hinders formation of quinhydrone (5). The stability of quinhydrone slows down substantially reactions with participation of non-substituted hydroquinones.

## 2. MATERIALS AND METHODS

All experiments were performed in Milli-Q-water (Milli-RO/Milli-QSystem, Millipore, France) and in a glove box filled with nitrogen (99,9%). All reagents were of analytical grade. The methods of HS modification and further characterisation have been previously described in details by Perminova et al. (6). Oxidative polymerization with hydroquinone and 2-methyl-hydroquinone was used to prepare hydroquinone- and 2-methyl-hydroquinone derivatives of HS. Leonardite HA was used as parent humic material.

Study of Np(V) reduction under anoxic conditions was performed according to method published elsewhere (4). Np(V) stock solution was prepared by dilution of the  $\text{NpO}_2\text{NO}_3$  solution (RIAR, Dimitrovgrad, Russia). Absorption spectra were collected using UV/Vis-NIR spectrophotometer (Cary-50, Varian) outside the glove box in the wavelength range between 950÷1030 nm. Absorption maxima for free neptunoyl and complexed form were detected at  $980,9 \pm 0.2$  nm and 987 nm, respectively (7).

The experimental concentrations of Np(V) and HS were maintained constant  $6,62 \cdot 10^{-5}$  M and 0,5 g/L, respectively; pH values was kept constant to  $4.4 \pm 0.1$ .

## 3. RESULTS AND DISCUSSION

For the derivative characterization the methods of elemental analyses (C, H, N), acidic group analyses, capillary zone electrophoresis, IR- and NMR-spectroscopy were used. To quantify redox properties of HS redox capacities of HS were determined using ferricyanide as a oxidizing agent (8). Results of HS redox capacity determination are shown in Table 1. Among modified HS sample CHP – HQMe was of maximal redox capacity that decreases in the following order: CHP-HQMe > CHP-HQ > CHP. From this point of view we expected sample CHP-HQMe to be the most effective towards Np(V) reduction.

Table 1. Redox properties of HS

Humic Substances	Redox capacity, mmol/g	Residual of Np(V), %
CHP	0.20	70
CHP-HQ	1.32	35
CHP-HQMe	1.55	45

Figure 1 represents kinetic curves for Np(V) reduction by humic derivatives. Np(V) content reduces in time for all HS, even for parent HA. We tried to estimate the reaction order of Np(V) reduction. The best approximation has been got for the kinetics of first order reaction with respect to neptunoyl-cation. In frames of this approximation, concentration of

Np(V) should decrease in time according to logarithmic law. Correlation coefficient ( $r^2$ ) for all cases of linearization ranged from 0.96 till 0.84.

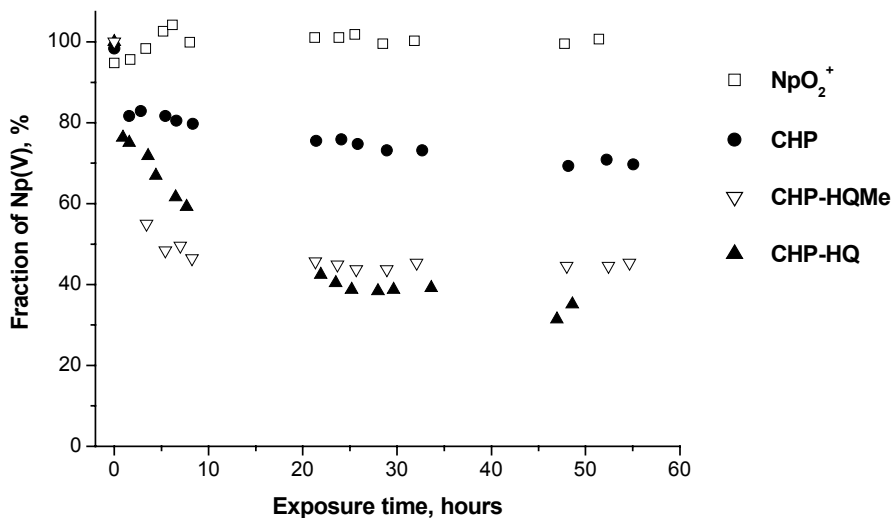


Figure 1. Np(V) reduction by modified HS;  $C(\text{Np}) = 6,62 \cdot 10^{-5} \text{ M}$ ,  $C(\text{HS}) = 0,5 \text{ g/L}$ ,  $\text{pH } 4,4 \pm 0,1$ ,  $I = 0 \text{ M}$  (no background electrolyte was used).

One of the important factor in quantification of Np(V) reduction process is the residual of Np(V) in the system after equilibration. For all derivatives equilibration time was considered to be 25-30 hours. Table 1 summarizes final content of Np(V) fraction: sample CHP-HQ showed the most complete reduction of neptunium. It probably can be because the stability of hydroquinone gomopolymer is higher than that of substituted derivatives. Therefore kinetics of Np(V) reduction by CHP-HQMe is higher, but after equilibration residual of Np(V) in the system with CHP-HQ is lower.

#### 4. CONCLUSIONS

Incorporation of 2-methyl-hydroquinone into humic backbone has improved substantially kinetics of Np(V) reduction as compare to hydroquinone-modified HS. Distinctive relationship between a value of the rate constant and structure of the quinonoid reaction center demonstrates that chemical modification is an excellent tool for preparing humic materials with the tailored properties. These results also show the important

application of specifically customized HS as a redox-agents in remediation technologies concerning redox sensitive metal ions and organic contaminants.

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