

Interaction of Np(V) with hybrid clay based material

V. Vicente Vilas, J.V. Kratz

Institut für Kernchemie, Universität Mainz, D-55099 Mainz, Germany

Humic substances may be found in the interlayers of swelling clays [1]. There are many laboratory evidences of defined organic compounds absorbed into the interlayers of clay minerals, but little is known about the existence of those complexes in natural soils. In order to simulate natural conditions, a different approach like the preparation of hybrid clay-based materials (HCM) [2] may throw new light on the problem as humic-clay-complexes are likely to be formed in statu nascendi of the humic substances [3]. Neptunium will become a major contributor to the radiation inventory in nuclear waste due to the long half-life of its isotope ^{237}Np ($2.14 \cdot 10^6$ years). It can exist in the oxidation states III – VII, but the cation NpO^+ dominates the aqueous speciation under a wide range of environmental conditions.

The samples tyrosine hybrid material solid (THS) and glutamic acid hybrid material solid (GHS) were pre-equilibrated at least 3 days; the equilibrium with CO_2 was accelerated by adding NaHCO_3 and Na_2CO_3 (Merck). The pH was daily controlled and if necessary readjusted with HClO_4 , or NaOH (Merck). The contact time with Np was 3 days, after that, phases were separated using a Beckmann Coulter Avanti J-301 High Performance Centrifuge (108800g, 1 hour). For the determination of the organic substances in the supernatant of the samples, UV/Vis-spectroscopy was used. The $^{239}\text{Np(V)}$ stock solution was produced by irradiation of ^{238}U ($\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$) at the TRIGA Mainz research reactor at 100 kW for 6 h, followed by separation from uranium and other fission products via anion-exchange chromatography [4].

We can conclude from the scanning transmission x-ray microscopy (STXM) data [2], that the organic matter bound to montmorillonite is similar to the free melanoidin synthesized (Figure 1). Therefore, the quantification of the melanoidin content in the HCM was possible (Table 1).

Sorption of neptunium on the hybrid materials was studied for the pH-range from 6 to 8.5 under ambient conditions (presence of CO_2), and at Np concentrations of 10^{-12} M (Figure 2). With increasing the pH, dissolution of organics was observed, which was confirmed by UV/Vis absorption spectroscopy. Neptunium was also determined in the organic

fraction $>1\text{kDa}$, which was separated by using ultrafiltration [4].

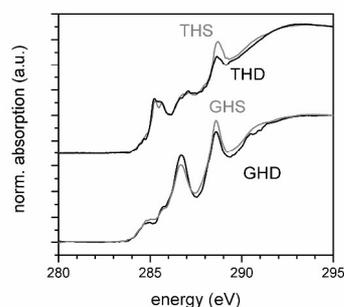


Fig. 1: STXM spectra of THS and its associated melanoidin (THD) as well as of GHS and its associated melanoidin (GHD).

Sample	%C in HCM	%C in related melanoidin	Calculated melanoidin content (mg)
GHS	1.7	51.64	5.27
THS	1.3	53.32	3.9

Table 1: Calculated melanoidin content for the two HCM.

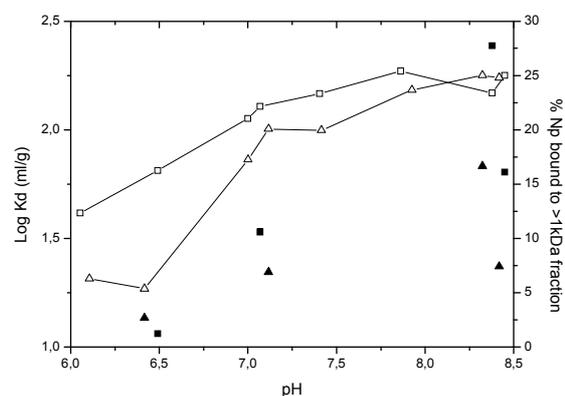


Fig. 2: Log Kd (open signs) and Np bound to organic (filled signs) as a function of pH for GHS (triangles) and THS (quadrangles).

References

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