SEQUESTRATION ABILITY OF HUMIC COATINGS DIFFERING IN CARBOXYL CONTENT WITH RESPECT TO ACTINIDES

Shcherbina N.S.[ab], Perminova I.V.[a], Karpiouk L.A.[a], Kalmykov S.N.[a], Ponomarenko S.A.[c]

[a]*Lomonosov Moscow State University, Chemistry Department, Moscow 119992, Russia*
[b]*Vernadsky Institute of Geochemistry and Analytical Chemistry, RAS, Moscow 119991, Russia*
[c]*Institute of Synthetic Polymer Materials, RAS, Moscow 117393, Russia*

Humic Substances (HS) are ubiquitous in the environment. They possess a broad spectrum of functional groups and can take part in different interactions with metal ions like redox transformation or complexation. Due to these interactions, HS could strongly affect actinides migration in the environment[1,2]. This work proposes new technology that uses soluble HS which are further immobilized onto surface of silica gel to produce a reactive phase or sorbent for metal sequestration. The proof of principle of this technology was demonstrated in our previous publication[3] that has shown an increase in sequestration ability of humic coatings covalently bound to silica gel with respect to highly mobile $Pu(V)O_2^+$ and $Np(V)O_2^+$ as compared to SiO_2. The goal of this work was to test sequestering abilities of humic coatings obtained by immobilization of alkoxysilylated derivatives with different modification degree, that is, with varying amount of remaining carboxyl group which are being derivatized during incorporation of alkoxysilyl-groups into humic backbone.

Parent leonardite material (CHP) was used to prepare alkoxysilyl-derivatives (HA-APTS) with modification degree 20, 50, and 100%,[4] and then, HA-APTS derivative was immobilized into silica gel (HA-APTS-SiO_2). A number of derivatives with different content of carboxylic groups were prepared in order to estimate role of carboxylic sites in actinide-HS interaction process.

It was demonstrated that the ratio of Pu(V) bound to humic derivatives immobilized onto silica gel increased with the time until the quantitative Pu(V) sorption occurred. This was much higher as compared to that for Np(V). Equilibration in the system with Np(V) was established during 1-1.5 days, while for Pu(V) it took almost 5 days. We suppose that this was caused by Pu(V) reduction upon sorption, while Np(V) remained in the pentavalent form during the whole exposure time. Kinetics of Pu(V) sorption was pH-dependent. It was shown that the rate of Pu(V) sorption onto samples with different content of carboxyl groups increased with an increase in the carboxyl content or a decrease in modification degree of the immobilized derivative. This demonstrates a key role of carboxyl groups in actinide complexation. The optimum modification degree providing for both high mineral-affinity and sequestration ability was around 20%.

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References

1. Takahashi, Yo, et al. Formation of actinide (III)-humate and its influence on adsorption on kaolinite. Mat. Res. Soc. Proc., Vol. 353, pp. 205-212 (1995).
2. Moulin V. Impact of humic substances on speciation of heavy metals and organic xenobiotics: implicatios for bioromodiation technologies. In: Use of humic substances to remediate polluted environments: from theory to practice, Ch. 7, P. 155-173 (2003)
3. Perminova, I.V., Karpiouk, L.A., Shcherbina, N.S., Ponomarenko, S.A., Kalmykov, St.N., Hatfield, K. Preparation and use of humic coatings covalently bound to silica gel for Np(V) and Pu(V) sequestration J. All. Com. In press http://dx.doi.org/10.1016/j.jallcom.2007.01.089 (2007).
4. Perminova I.V. et al.,Humic derivatives, methods of preparation and use. PCT application RU2006/000102.filed on March 7 (2006).