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# Redox interactions of Pu(V) in solutions containing different humic substances

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## Abstract

Humic substances play an important role in the speciation of actinides in the environment due to complexing, redox and sorptive interactions. This work is devoted to plutonium(V) reduction studies in solutions containing different humic substances, eluted from Mollisol and Sod-podzolic soil samples, as compared to real Pu distribution is contaminated soils. On the basis of kinetic curve slopes, the reducing ability is increased in the order: HA < FA ~ low molecular weight fraction. The data obtained show that the different humic compounds play different roles in Pu(V) migration ability due to differing reducing and complexing properties.

*Keywords:* Humic substances; Plutonium speciations; Actinide migration

## 1. Introduction

The migration ability of Pu in the environment depends on its speciation. Pu in the environment is mostly present as Pu(V) and Pu (IV). Pu(V) shows high migration ability and, on the contrary, Pu (IV) appears more immobile due to its high affinity to mineral surfaces, although, it can be very mobile when bounded with colloidal particles, that can be particularly presented by colloidal humic substances (HS). HS are complex mixtures of natural macromolecules and smaller molecules and ions which occur throughout the environment, including deep anoxic underground systems. They can be generally separated into humic acids, fulvic acids and humie.

In fact, the formation of actual Pu species depends on the complex of actual geochemical conditions, particularly the presence of reducing agents that can be metal ions and organic chemicals. Humic substances comprise from 50 to 80% of the organic carbon pool content in soils and waters and are the most widely distributed natural organic matter [1–4]. Furthermore, HS have high reducing ability towards Pu [5]. Therefore, redox interactions of humic substances are important for estimation of Pu mobility in aqueous systems.

The aim of the current study is to define the role of different humic substances in Pu(V) reduction in aqueous system. For this purpose kinetics of Pu(V) reduction by natural occurring HS was studied and comparison of the results obtained with real Pu distribution among humic fractions in contaminated soils is presented.

## 2. Experimental

The humic acid sample was purchased from Aldrich (AHA) and purified by several precipitations and ion exchange according to the procedure described in reference [6].

Contaminated and non-contaminated soil samples were collected. Contaminated Mollisol and Sod-podzolic soil samples were collected under birch wood and coniferous-birch wood in the territory of the East Ural Radioactive Trace. Non-contaminated Mollisol samples were collected in Kursk District and non-contaminated Sod-podzolic soil was sampled in the Moscow region from the well-characterized location of the Moscow State University biological station.

Both soils can be classified as loamy soil according to their particle-size composition and are characterized with a similar content of organic carbon, exchangeable $Ca^{2+}$, $Mg^{2+}$ as well as with similar pH values. The properties of the soil samples were determined and summarized in Table 1.

From non-contaminated soil samples humic and fulvic acids were isolated and purified using the procedures described below (Section 2.1). Contaminated

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Table 1
The chemical and physical characteristics of the collected soil samples

| Soil | C (%) | pH | Exchangeable cations ($cmol_c\ kg^{-1}$) | | | | Particle-size composition (%) | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | $Ca^{2+}$ | $Mg^{2+}$ | $K^+$ | $Na^+$ | >0.01 mm | 0.01–0.001 mm | <0.001 mm |
| Non-contaminated soil | | | | | | | | | |
| Sod-podzolic | 3.8 | 4.7 | 3.1 | 1.2 | 0.3 | – | 71 | 15 | 14 |
| Mollisol | 5.8 | 6.6 | 30.8 | 6.9 | 0.5 | 0.4 | 59 | 19 | 22 |
| Contaminarted soil | | | | | | | | | |
| Sod-podzolic | 2.0 | 5.7 | – | 8.0 | – | – | 50 | 25 | 25 |
| Mollisol | 4.1 | 6.2 | 20.0 | 9.0 | – | – | 53 | 14 | 33 |

soils were treated for fractionation of organic matter (OM) depending on their nature (HA or FA), solubility and affinity to mineral part of soil (Section 2.1). The Pu content was determined in the OM fractions obtained. The soil properties given in Table 1 suggests, that the humic materials isolated from the pairs of non-contaminated and contaminated soils possess the similar properties.

The kinetics of Pu(V) by the obtained HS was studied.

## *2.1. Isolation and purification of organic matter from non-contaminated soil*

### *2.1.1. Isolation of HA from soil*

The isolation was carried out in accordance with the IHSS-procedure [7] and was as follows. After removing the plant roots, the dry soil samples were sieved through a 2.0 mm sieve. The pH value was adjusted to 1–2 using 1 M HCl at room temperature. The solution volume was adjusted with 0.1 M HCl to a final *V/m* ratio of 10 mL of liquid per 1 g of dry sample. The suspension was shaken for 1 h and then the supernatant was separated from the residue by decantation. The supernatant (FA 1) was stored for the isolation of FA.

The soil residue was neutralized with 1 M NaOH to pH 7.0 and then 0.1 M NaOH was added to get a final extractant to soil ratio of 10:1. The alkaline suspension was settled overnight. Afterwards, the supernatant was collected by means of decantation. The supernatant was acidified with 6 M HCl with constant stirring to pH 1.0 and then the suspension was left for 12–16 h. The suspension was centrifuged to separate the HA (precipitate) and FA (supernatant—FA 2) fractions. The HA fraction was redissolved by adding a minimum volume of 0.1 M KOH and solid KCl was added to attain a concentration of 0.3 M [$K^+$] and then centrifuged at 6000 rpm to remove the suspended solids. The HA were reprecipitated by adding 6 M HCl with constant stirring to pH 1, centrifuged and the supernatant was discarded. The HA precipitate was suspended in 0.1 M HCl/0.3 M HF solution, shaken overnight and centrifuged. This procedure was repeated four times. Then, HA was purified by dialysis (membrane MEMBRA-CEL-MD-44-4, 14 kD) and freeze dried.

### *2.1.2. Isolation of soil FA*

FA 1 and FA 2 were concentrated using XAD-8 resin. Then, XAD-8 column was back eluted with 1 column volume of 0.1 M NaOH, followed by 3 column volumes of distilled $H_2O$. FA was purified by passing through $H^+$-saturated cation exchange resin (KU-2-8) and freeze dried.

## *2.2. Isolation and partitioning of organic matter from contaminated soil*

### *2.2.1. Isolation of Fraction 1*

For this purpose, 0.1 M NaOH was added to the corresponding samples to obtain a *V/m* ratio of 20:1 The slurry obtained was shaken vigorously and left over night and then centrifuged at 3000 rpm; the supernatant obtained was filtered through a 1 μm lavsan Wattman filter and acidified to pH 1–2 using 6 M HCl for coagulation of HA.

The acidified solution was heated at 70–80 °C for 30 min and centrifuged at 3000 rpm. The supernatant was filtered through a Wattman filter. The HA precipitate was dissolved in hot 0.1 M NaOH. Fraction 1 was presented by free humic and fulvic acids, and those bound to Fe, Mn, Al, etc. hydroxides.

### *2.2.2. Isolation of Fraction 1a (decalcinate)*

To another part of the contaminated samples 0.1 M HCl was added to get a *V/m* value of 10:1. The slurry obtained was left for 12–16 h under continued stirring and then centrifuged at 3000 rpm.

The supernatant obtained was filtered through a 1 μm Wattman filter. The solid phase was repeatedly treated with 0.1 M HCl until a negative calcium test of the filtrate (indicator reaction with murexide). This fraction was presented by free fulvic acids and low molecular weight organic acids and those bound to Fe, Mn, Al, etc. hydroxides.

### *2.2.3. Isolation of Fractions 1 + 2*

To the residual solid after decalcination 0.1 M NaOH was added to get a *V/m* ratio of 10:1. The obtained slurry was vigorously mixed and left for 12–18 h. Then $Na_2SO_4 \cdot 10H_2O$ was added and mixed until complete dissolution of sulfate to provide a coagulation of mineral colloids. The dark brown solution obtained was centrifuged at 3000 rpm and filtered. The extraction of humic acids was repeated until a slightly colored solution was obtained. For separation of humic and fulvic acids, 6 M HCl was added to the basic filtrate until pH 1 as described above for Fraction 1. The acidic solution containing fulvic acids was collected into a separate vessel. The precipitate of humic acids was dissolved in hot 0.1 M KOH, and then KCl was added. The solution was left until precipitation of mineral colloids which were separated by centrifugation. Humic acids were then precipitated again by addition of 6 M HCl until the pH is 1. The suspension was left for 12–16 h and humic acids were centrifuged and washed sequentially with 0.1 M HCl and distilled water. The precipitate was washed with water until the solution started turning brown. The washings were collected into a separate vessel. Fractions 1 + 2 was free humic and fulvic acids and those bound to Fe, Mn, Al, etc. hydroxides and calcium.

### *2.2.4. Isolation of Fraction 3*

After isolation of Fractions 1 + 2 the residual solid was treated with 0.02 M NaOH (the *V/m* ratio was 10:1) by heating in a water bath (80 °C) for 6 h. After the suspension settled, it was centrifuged and filtered through lavsan Wattman filter (1 μm pore size). Humic and fulvic acids were separated as described above. Fraction 3 was humic and fulvic acids strongly bound to hydroxides and mineral components of the sample. The residue of the subsample after separation was ashed at 500 °C and then was dissolved in 7.5 M $HNO_3$. The non-soluble residue was filtered and the Pu concentration was determined in the filtrate.

## *2.3. Preparation of the $^{239,240}$Pu(V) stock solution*

Two ml of 0.074 M solution of $^{239,240}$Pu in 1–3 M $HNO_3$ was combined with 350 μg $KBrO_3$, and heated in a water bath (80 °C) for 3 h. Twenty microliters of the solution obtained was added to 20 ml of distilled water to obtain a Pu concentration of $7.4 \times 10^{-5}$ M. To the solution obtained, 0.22 mL of 0.1 M $H_2O_2$ was added and kept at room temperature for 1 h.

Then $^{239,240}$Pu(V) was extracted from 2 mL of Pu solution using 1 mL of 0.01 M HDEHP in octane. The aqueous phase, after phases separation and containing Pu(V), was used for kinetic experiments. Ten percent of Pu reduction was observed during 3 months of keeping the stock solution in a plastic vial at room temperature and in sunlight.