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Sorption properties of peat for U(VI) and ^{226}Ra in U mining areas

Gabrielle Bordelet[a]*, Catherine Beaucaire[a], Vannapha Phrommavanh[b], Michaël Descostes[b]

[a] *CEA, DEN, DANS, DPC, SECR, L3MR, F-91191 Gif-sur-Yvette, FRANCE*
[b] *AREVA – BG Mines, 1, Place Jean Millier – F-92084 Paris La Défense, FRANCE*

Abstract

Understanding the environmental behavior of U and ^{226}Ra is important for remediation of former mining sites and assessment of their durability. The aim of this study is to determine the sorption properties of an acidic peat for U and ^{226}Ra, located near a former U mine. A 90% retention of U over a pH range of 3 to 10 was observed in Na-conditioned peat samples issued from the mesotelm, with a R_d between 1000 and 12000 mL/g. It seems that U sorption in peat is not only governed by organic matter. The K_d for ^{226}Ra adsorption increases with pH from zero to 4849 mL/g. However in this mining environment, the peat bog proved to be significantly impacted by anthropogenic activities, with the presence of detrital components in the peat material that can also contribute to U and Ra sorption.

Keywords: sorption; uranium; radium; organic matter; peat; mine; activity; batch

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1. Introduction

In order to guarantee the protection of ecosystems and thus minimize the radiological impact in the vicinity of the former uranium mines on the biosphere, it is important to understand the phenomena controlling the migration of uranium and its decay products, in particular ^{226}Ra.

In the environment, among solid phases which can retain U(VI) and ^{226}Ra, organic matter is known to have a high affinity for U. Studies of metal sorption on organic matter are usually carried out on humic substances in the presence or absence of mineral phases [1-3]. Peat is a complex material which combines many components such as organic compounds (humic acids, organic acids, bacteria, fungi) and mineral phases, each having their own specific reactivity and influence on U(VI) and ^{226}Ra behavior.

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* Corresponding author. Tel.: +033-(0)169-083-393; fax: +33-(0)169-087-503.
E-mail address: gabrielle.bordelet@cea.fr

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The objectives of this study are to assess the sorption properties of U(VI) and ^{226}Ra on natural organic matter from peat, considered as a sole sorbent phase.

2. Materials and methods

2.1. Geological setting and sampling

The Sagnes peatbog is an acidic peat land, close to the former mining site of Fanay (Limousin, France). A 60 cm-deep trench was carefully dug with a shovel around a 50 x 50 cm square area. Samples were taken from that intact square area with a trowel in 10 cm-thick slices, except at the depth of 30-35 cm that was only 5 cm thick. Soil layers from 55 to 95 cm and 140-150 cm depths were extracted with an Eikelkamp© peat corer and then cut into 10 cm-thick slices.

Natural peat can be subdivided in three main layers, the first one 0-20 cm is generally representative of a relatively immature organic matter while the deeper layer (below 40-50 cm) corresponds to the most evolved organic matter. An intermediate layer (35-45 cm) was chosen to carry out sorption experiments reported in this study.

2.2. Elementary analysis and mineralogy

Physical and chemical characteristics of peat such as carbonate content, elemental percentages of C, H, S, N, water content, ash percentage and mineralogy (XRD) were investigated at Poitiers ERM laboratory.

2.3. Sorption experiments

Before carrying out the sorption experiments, it is necessary to obtain the most stable substrate representative of organic component and also the most stable substrate. Alternate acidic/basic washings would eliminate the most labile products. Several protocols with acidic, basic and water washings of different durations were tested through TIC-TOC (Total Inorganic Carbon - Total Organic Carbon) analysis and CEC (Cationic Exchange Capacity) measurement. After NaCl (0.3 M) conditioning (at pH 10), CEC is measured by Na^+ displacement with Cs^+ using 10^{-2} M CsCl solution.

Adsorption experiments were performed in a solid/solution ratio of 10 g/L in a 10^{-2} M NaCl electrolyte. Samples were spiked with 10^{-6} M of U(VI). After shaking (96 h), supernatants were analysed by ICP-MS. Uranium-free electrolyte was added again to the remaining precipitates, shaken (for a few days), centrifuged and the desorbed U was analysed by ICP-MS. Other samples prepared in the same conditions were spiked with ^{226}Ra from 8×10^{-8} to 1×10^{-7} M. ^{226}Ra adsorption and desorption experiments were carried out in the same way and ^{226}Ra activity was counted by γ-spectrometry (186.21 keV peak).

3. Results

3.1. Elementary analysis and mineralogy

In the studied profile, results of elemental analysis indicate a C percentage ranging from 31.1 to 46.6% (of dry peat weight), H $\approx$ 5%, N $\approx$ 2% and S from 0.2 to 2.1% (maximum reached at level 30-35 cm depth). The ash percentage was above 10 % with a peak of 40% for 35-45 cm depth, which is also the level with the lowest fire loss (60 % instead of $\approx$ 90 %) and the lowest water content (80 %). Major and trace elements were also checked on the remaining solid after digestion of dry peat samples by hydrogen peroxide. Such preparation allows dissolution of all the organic matter but also soluble minerals in acidic and oxidizing conditions (e.g. sulphides, oxides, carbonates). The results showed that the 35-45 cm soil layer contained almost 40% inorganic matter which is composed of 56.8 % SiO_2, 13.6 % Al_2O_3 and 6.2% Fe_2O_{3total}. XRD spectrum on the same digested sample is interpreted as a mixture of quartz, plagioclase, feldspar, expanding clays, kaolinite and mica. At depths greater than 30 cm, the ash percentage seems to be too high for a natural peat land [5] (ash % > $20\%_w$ instead of ash % < $10\%_w$). This high mineral content might come from the alteration of some granitic mine tailings lying on the river bank, upstream from the peat land, or from other anthropogenic activities.

3.2. U and Ra sorption experiments

After conditioning, CEC were close to 70 meq/100 g. Uranium background content (26 ppm) was taken into account in calculations and Ra natural activity was less than the detection limit. For U, adsorption and desorption experimental data are illustrated by the K_d values over pH in Fig 1 (a). K_d is the ratio of the adsorbed metal concentration (mol/kg) over the aqueous concentration of metal in solution at equilibrium (mol/L). Adsorbed U(VI) amount is close to 90% of total U whatever the pH, with K_d values varying from 1000 to 12000 mL/g. It appears that the desorption K_d values are slightly higher than the adsorption K_d values attesting that the retention is not completely reversible.

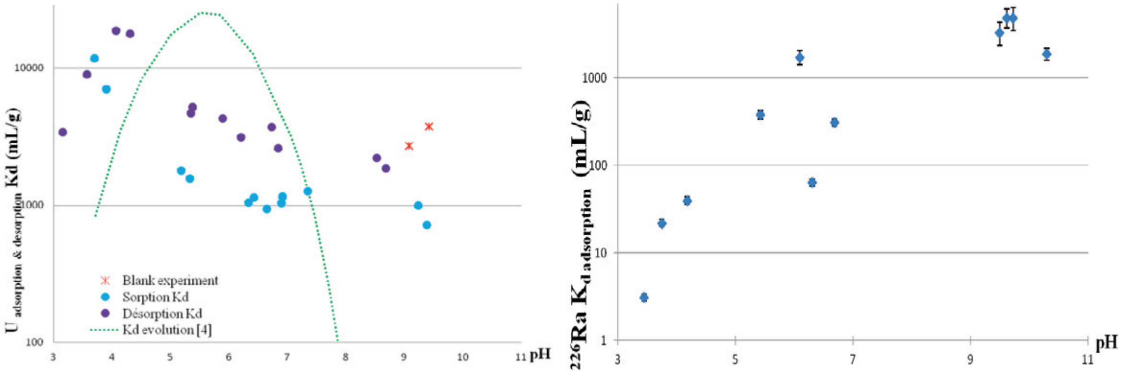

Fig. 1. (a) K_d of adsorbed and desorbed U on Les Sagnes peat (Limousin region, France) over pH compared to K_d values modeled in an alkaline peat [4] and (b) Ra adsorption K_d onto Les Sagnes peat.

Concerning ^{226}Ra adsorption on peat, the percentage of ^{226}Ra uptake increases from zero at pH 2.5 to 98 % at pH 9.6 and above. The associated ^{226}Ra adsorption K_d values, over the same pH scale, range from zero to 4849 mL/g ± 1,183 and seem to remain stable for pH ≥ 7. A slight decrease in ^{226}Ra uptake at pH 10.5 is not concluded taking into account the high uncertainties due to the concentration of radium remaining in solution, which is close to the γ-spectrometer detection limit.

4. Discussion

There are only a few studies of U sorption on organic matter in peat bogs [2, 4]. In these studies, U behavior is characterized by a maximum U removal from the solution for pH between 4 and 6, which can be related to U speciation changes with pH. In the presence of humic acids (10 mg/L), below pH 3.5, U principally remains in solution as UO_2^{2+} but between pH 3.5 and 7.5, $UO_2HA(II)$ and $UO_2(OH)HA(I)$ forms seem to be responsible for the highest values of U sorption on peat. At equilibrium with atmospheric p_{CO2}, decrease of U sorption for pH above 7.5 is assigned to the uranyl-carbonate complexes formation. On the contrary, this study shows that around 90% of U can still be taken up from the solution for pH > 8. That phenomenon has already been observed [3, 6] but is not yet explained.

Therefore, it seems that U behavior in peat is not only governed by sorption onto organic matter. Uranium could be also adsorbed on mineral particles of the detrital fraction (oxy-hydroxide; clay minerals) and/or controlled by solubility of secondary uranyl-silicate mineral phases. The measured silica concentrations in U batches rose from 0.2×10^{-3} to 4.2×10^{-3} M when pH increased from 3.5 to 10. PhreeqC® modeling showed that in 10^{-2} M NaCl aqueous solution, at equilibrium with both the atmospheric p_{CO2} and the amorphous SiO_2, it is possible in a 6.5-8.5 pH range to precipitate uranyl-silicate minerals such as soddyite, Na-boltwoodite and other U-silicate more or less amorphous phases.

Radium is essentially present in solution as the Ra^{2+} species. The maximum uptake is obtained at pH > 7 and can be compared with the results obtained on coir pitch with humic acids [1]. The authors reported adsorption K_d for radium from approximately zero at pH 3 to 5544.44 mL/g at pH 11. However, the possibility that some radium is also adsorbed on mineral components mixed with peat has to be considered. Indeed, Ra sorption onto minerals such as kaolinite ($0 < K_d < 4000$ mL/g, [6]) and Fe oxy-hydroxide ($K_d > 20000$ mL/g [7]) is not negligible.

5. Conclusion

Retention of U is about 90% of total U under our conditions, from pH 3.5 to 9.5. These results could be partially explained by the precipitation of some silicate phases between pH 6.5 and 8.5. Moreover, in order to discriminate the mutual role of organic and mineral sorbent, the assessment of sorption properties of the peat for U requires new sorption experiments on another peat sample with a low mineral fraction.

Ra adsorption experiments show that K_d values increase from zero to almost 5000 mL/g from pH 2.5 to 7 and seem to remain constant for pH ≥ 7. The role of the mineral fraction on Ra adsorption onto peat is not yet clear.

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