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SORPTION PROPERTIES OF PEAT'S ORGANIC MATTER FOR U AND ²²⁶Ra, IN MINING AREAS

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KEYWORDS

uranium, radium, peat, sorption, modeling, ion-exchange, uranium mines

ABSTRACT

The environmental footprint of former uranium mining activities is a major concern for AREVA who is in charge of monitoring these ancient mining sites. In order to limit the radiological impact on the biosphere we must have a good knowledge of the chemical properties controlling the migration of uranium U(VI) and its decay products, in particular radium (²²⁶Ra).

In the environment, among solid phases which can retain U(VI) and ²²⁶Ra, organic matter is known to have a relevant affinity for these radioelements. This is why, wetlands are studied and deployed as mining-water passive treatment solutions. Naturally organic matter is often found as peat. This complex material combines many components in various proportion such as organic compounds (humic and fulvic acids, organic acids, bacteria, fungi) and mineral phases (iron oxy-hydroxides, clay minerals), each having their own specific reactivity and influence on U(VI) and ²²⁶Ra behaviour.

This study aims to acquire the sorption properties of U(VI) and ²²⁶Ra on natural organic matter from peat according to a predictive and thermodynamic model. Studies about metal sorption on organic matter are usually carried out on humic substances in presence or not of mineral phases (Zeh et al., 1997; Krepelova et al., 2006; Zalina et al., 2010). In our case, we will treat the peat material like other mineral phases, considering that peat reactivity towards metals and other contaminants can be described as an ion-exchange (Tertre et al., 2009).

MATERIAL AND METHOD

Geological setting and sampling

The studied peat (Les Sagnes peat) is located in the vicinity of the former mining site of Fanay (Limousin, France). This peat is of fluviogene and topogene type deposit. Situated in the Les Sagnes watershed, this peat is under the influence of waste rock piles located just upstream. Implanted on a granitic bedrock, this peat is acidic and is mainly composed of sphagnum. Three cores were extracted from the peat land. The drill cores designated HS1 and HS2 (hot spots 1 and 2) are both characterized by a relatively significant radiation dose rate (1.0-1.7 µSv/h), approximately eight times higher than the natural background. The peat samples (designated IRS) used for retention experiment correspond to the lowest radiation dose rate area (*i.e.* 0.1-0.2 µSv/h) measured in that peat land. Radiation survey was completed by gamma ray spectrometry along the different profiles (see figure 1).

Natural peat can be subdivided in three main levels, the first one, namely the acrothelm, is located 0-20 cm deep and is generally representative of a relatively immature organic matter. The deepest level (below 40-50 cm), namely the catotelm, corresponds to the most evolved organic matter. Two levels were chosen to carry out sorption experiments reported in this study: an intermediate level (35-45 cm) and a deeper level (75-85 cm). The intermediate level, also called mesotelm, corresponds to the zone of the groundwater table oscillation. This level and a more deeply one (150 cm of depth) are also marked by the presence of grey clayey material. Between the surface and 30 cm of depth, nodules of ochre colour are also observed.

These samples were extracted either with a trowel by slices of 10 cm thick or with a Russian corer for the deepest samples. Samples were stored immediately after the coring, in zippered bags at 5°C.

Physical and chemical characteristics of peat like carbonate content, element percentages of C, H, S, N, water content, ashes percentage and mineralogy were investigated at Poitiers ERM laboratory.

Sorption experiments

Before carrying out the sorption experiments, it is necessary to eliminate the most labile compounds retained in the peat in order to obtain a material which would stay as stable as possible all over the duration of the experiments. Alternate acidic/basic washings would eliminate the most labile organic products and metal

impurities (metal oxides, pyrite ...). 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 washing, peat is conditioned under Na^+ form with 0.3M NaCl at pH 10. CEC is then measured by Na^+ displacement by Cs^+ with 10^{-2} M CsCl.

Adsorption experiments were performed in batches with a solid/solution ratio of 10 g/L in a 10^{-2} M NaCl electrolyte. Experiments were carried out in the 3-10 pH range, pH were adjusted using suprapur HNO_3 , after having added the radiotracers. Samples were spiked with 1.10^{-6} M of U(VI). After shaking (96h), samples were centrifuged (15000 rpm during one hour) and supernatants were analysed by ICP-MS (the detection limit is estimated at 10^{-11} M with an uncertainty of 5%). In order to test reversibility of the ion-exchange reactions, uranium free electrolyte was added to the remaining solid, shaken for a few days and centrifuged. Desorbed U in the supernatant was then analysed by ICP-MS. Similarly prepared samples were spiked with ^{226}Ra solutions from 8.10^{-8} to 10^{-7} M. The adsorption and desorption experiments were carried out in the same way, except that the supernatant ^{226}Ra activity was counted by γ spectrometry (the detection limit is estimated at 10 ± 5 Bq or $1.2 \cdot 10^{-12}$ moles).

Ion-exchanger model

An ion-exchanger model was used to describe the chemical reactivity of the peat. This approach has already been described in details in the literature (see for instance Tertre et al., 2009; Reinoso-Maset and Ly, 2014). Considering an ion-exchanger characterized by different negative charged ion-exchange sites (X_i^-), these sites are able to sorb cations, including protons, present in the solutions in contact with the solid. The global charge of the solution and the exchanger with the adsorbed cations is neutral. Each ion-exchange reaction can be written in function of protons according to the following reaction:



This reaction is associated with the corrected selectivity coefficients as follows:

$$K_{\text{M}^{m+}/\text{H}^+}^{*i} = \frac{[> \text{M}(\text{X}_i)_m] \cdot [\text{H}^+]^m}{[> \text{HX}_i]^m \cdot [\text{M}^{m+}]} \cdot \frac{\gamma_{\text{H}^+}^m}{\gamma_{\text{M}^{m+}}} \quad (2)$$

where $[> \text{HX}_i]$ and $[> \text{M}(\text{X}_i)_m]$ are the concentrations of H^+ and M^{m+} (mol.kg^{-1} of dry solid) sorbed on the i ion-exchange site, and $[\text{H}^+]$ and $[\text{M}^{m+}]$ are their respective aqueous concentrations (mol.L^{-1}). γ_{H^+} and $\gamma_{\text{M}^{m+}}$ are the activity coefficients of the aqueous species calculated with the Davies equation. The activity coefficients of the adsorbed species are unknown, but their ratio is expected to be constant.

RESULTS

Elementary analysis

In the studied profile (reference sample), results of elemental analysis indicate a C percentage ranging from 31.1 to 46.6% (of dry peat weight), $\text{H} \approx 5\%$, $\text{N} \approx 2\%$ and S from 0.2 to 2.1% (maximum reached at level -30-35 cm depth). The ashes percentage is above 10% with a peak of 40% for level -35-45 cm, which is also the level with the lowest water content (80%). Contrary to usual values observed in peat (Gobat et Portal, 1985), ashes percentages are particularly high and are indicative of a relatively high amount of detrital material, which is respectively of 40 and 20% for the 35-45 cm and 75-85 cm level samples, as it can be seen on figure 1. Major and trace elements were also checked after digestion of dry peat samples by hydrogen peroxide. Elementary analysis confirmed the high proportion of detrital minerals, with 56.8% of SiO_2 in the 35-45 cm level and 36.9% in the 75-85 cm level, 13.6% of Al_2O_3 and 6.2% of $\text{Fe}_2\text{O}_{3\text{total}}$. Consequently, the loss on ignition is around 17.6% for the upper level while it is around 40% for the deeper one. XRD spectrum on the same digested sample is interpreted as a set of quartz, plagioclase, feldspar, kaolinite and mica typical of granitic context.

γ spectrometry

γ spectrometry measurements were carried out along the different profiles of peat. In the two hot spots HS1 and HS2, total activity of radionuclides ($^{234}\text{Th} = ^{238}\text{U}$, ^{226}Ra , ^{210}Pb) is relatively constant along the profile (around 50

Bq/g) between the surface and 30 cm of depth, except for some uranium anomalies (^{234}Th peaks) located at the surface and at 30 cm of depth in a zone enriched in nodules of ochre colour. In depth activity is negligible. In the drill hole of reference, the activity of each radionuclide is inferior to 7 Bq/g except at 20-30 cm of depth where ^{234}Th and ^{226}Ra reach 20 Bq/g.

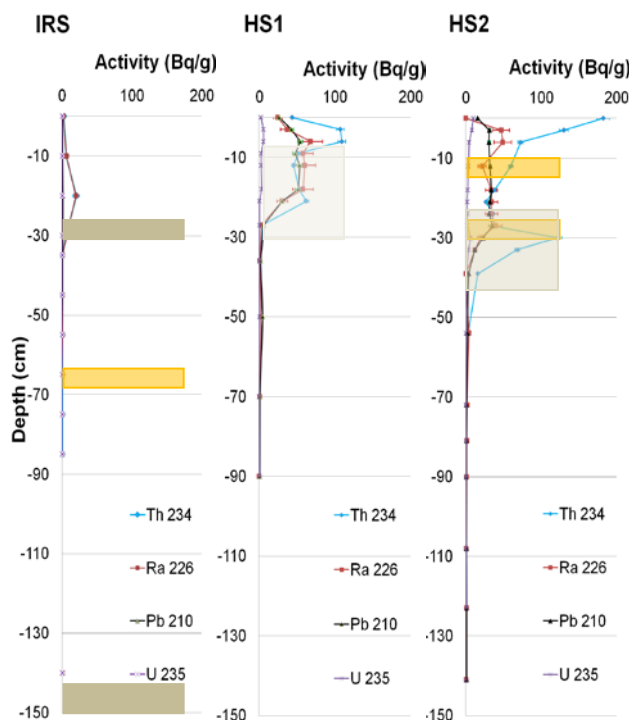


Figure 1: Profiles of gamma activity of ^{234}Th , ^{226}Ra , ^{210}Pb and ^{235}U in hot spots HS1, HS2 and the reference (IRS). The zones rich in nodules of ochre colour (yellow) and clay layers (brown) are indicated.

U and Ra sorption experiments

Whatever the sample treatment (acid/base washing or water alone), conditioning of the peat material requires *a minima* three weeks of interaction between peat and NaCl electrolyte at pH 10. After conditioning, CEC are comprised between 0.58 ± 0.12 eq/kg of dry peat (35-45 level) and 1.0 ± 0.1 eq/kg (75-85 level). The total organic carbon loss during the treatment of samples is estimated at 30% for the water washing and 40% for the acid/base washing. U background concentration in batches is evaluated at 10^{-8} M and is taken into account in the mathematical treatment of sorption experiments. ^{226}Ra natural activity is under the limit of detection.

Radioelements adsorption and desorption experimental data are illustrated by the K_d values over pH in figure 2. K_d is the ratio of the adsorbed metal concentration (mol.kg^{-1}) on the aqueous concentration of metal in solution at equilibrium (mol.L^{-1}). Adsorbed U(VI) amount is close to 90% of total U whatever the pH, with K_d values varying from 1000 at pH 3.0 to a maximal value of 10000 mL/g at pH 4.0 (Fig. 2-A). Then the K_d values decrease and stabilize at around 1000 mL/g. The desorption K_d values are slightly higher than the adsorption K_d values attesting that the retention is not completely reversible.

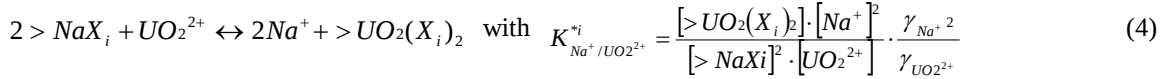
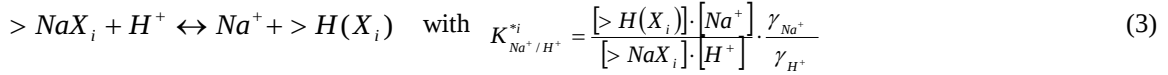
In the case of radium, the percentage of Ra uptake increases from zero at pH 2.5 to 98% at pH 9.6 and above. The associated adsorption K_d values (Fig. 2-B), over the same pH scale, are ranged from zero to 4800 mL/g $\pm$ 1200 mL/g and seem to remain stable for $\text{pH} \geq 7$. However, in the sample enriched with detrital material (35-45 cm, with blue symbols on Fig. 2-B), the trend of K_d values at acidic pH is slightly shifted towards more alkaline pH.

MODELING AND DISCUSSION

Only a few studies exist about U sorption on organic matter issued from peat bogs (Omar et al., 2007). In this former study, U behaviour is characterized by a maximum U removal from the solution for pH comprised between 4 and 6, which can be related to U speciation over pH. In presence of humic acids (10 mg.L^{-1}), below pH 3.5, U principally remains in solution as UO_2^{2+} but between pH 3.5 and 7.5, formation of uranyl complexes with humic acids seems to be responsible for the highest values of U sorption on peat. At equilibrium with

atmospheric p_{CO_2} , decrease of U sorption for pH above 7.5 is assigned to the uranyl-carbonate complexes formation.

Assuming that retention is mainly due to the organic fraction closely bond to the solid material, the observed uranium evolution trend has been relatively well reproduced with the model of ion-exchange (see Fig.2-A) considering the sorption of Na^+ and the uranium species on a single site X_i representative of organic compounds such as:



In the case of trace elements sorption, their concentration in the exchanger being neglected with regards to other species present as major elements, the concentration of X_i (mol/kg) is equal to the sum of the concentration of $[\text{Na}(\text{X}_i)]$ and $[\text{H}(\text{X}_i)]$. Therefore, we can deduce from the mass conservation relation and the equations 3 and 4, an expression of the K_d values as a function of the total concentration of site X_i and the constants of selectivity of the different species adsorbed as follows:

$$K_{\text{UO}_2^{2+}}[\text{Na}^+]^2 = \frac{K_{\text{Na}^+/\text{UO}_2^{2+}}^{*i} \cdot [\text{X}_i]^2}{\alpha \cdot (1 + K_{\text{Na}^+/\text{H}^+}^{*i} \cdot [\text{Na}^+]^{-1} \cdot \gamma_{\text{Na}^+} 10^{-\text{pH}})^2} \quad (5)$$

α is the Ringbom coefficient (Ringbom and Still, 1972) which relates the total concentration of uranium with the sum of the concentration of the different uranium species, with $\text{U}_{\text{total}} = \alpha \cdot [\text{UO}_2^{2+}]$.

Considering that UO_2^{2+} is the main uranium species present between pH 2 and 5.0, best fitting is obtained with the following selectivity constants: $\log K_{\text{Na}^+/\text{H}^+} = 2.09$; $\log K_{\text{Na}^+/\text{UO}_2^{2+}} = 1.8$. These values confirm that at acidic pH, carboxylic groups contribute mainly to the natural organic matter reactivity (pKa of carboxylic acids are generally comprised between 3.0 and 4.5). According to the titration curve of peat, the concentration of binding site (X_i) is estimated between 0.2 mol.kg⁻¹ of dry peat for the upper sample (35-45) and 0.6 mol.kg⁻¹ for the deeper one (75-85).

However, contrary to the former study (Omar et al., 2007) we observe that around 90% of U is still removed from the solution for pH > 8. That phenomenon has already been observed in experimental studies where humic acids are associated to mineral (Krepelova et al., 2006) but is not explained yet.

Therefore, it seems that U behaviour in peat is not only governed by sorption on organic matter. U can also be adsorbed on mineral particles of the detrital fraction (oxy-hydroxide, clay-minerals) and/or controlled by solubility of secondary uranyl-silicate mineral phases. If we cannot exclude precipitation of any silicate phases (such as soddyite or Na-boltwoodite) at medium and alkaline pH, it seems that such a precipitation cannot explain this trend in any case. Simulation with PhreeqC® software (Parkhurst et al., 1999) showed that the contribution of 2% of smectite and less of 1% of iron oxy-hydroxide can explain 90% of U retention in the 7-9 pH range.

Up to pH 8.0, radium is essentially present in solution under the Ra^{2+} form. The curve of retention of Ra in function of pH can be easily reproduced by ion-exchange reaction on carboxylic type site identified for uranium (see Fig. 2B). $\log K_{\text{Na}^+/\text{Ra}^{2+}}$ is estimated at 0.9. In the case of radium, if we cannot exclude any contribution of clay-minerals and oxy-hydroxide on the radium retention in peat (principally in the more enriched with detrital minerals zone, *e.g.* 35-45 cm level), we can assume that radium is essentially retained by organic component.

This first approach to represent the sorption of radionuclides on a complex natural material with an important organic component showed that it is possible to characterize the chemical reactivity of such a material and to deduce coefficients of selectivity. An operational model has been elaborated to predict the sorption of radium and uranium on peat. It is intended to apply it applied in different environmental situation in order to evaluate its robustness.

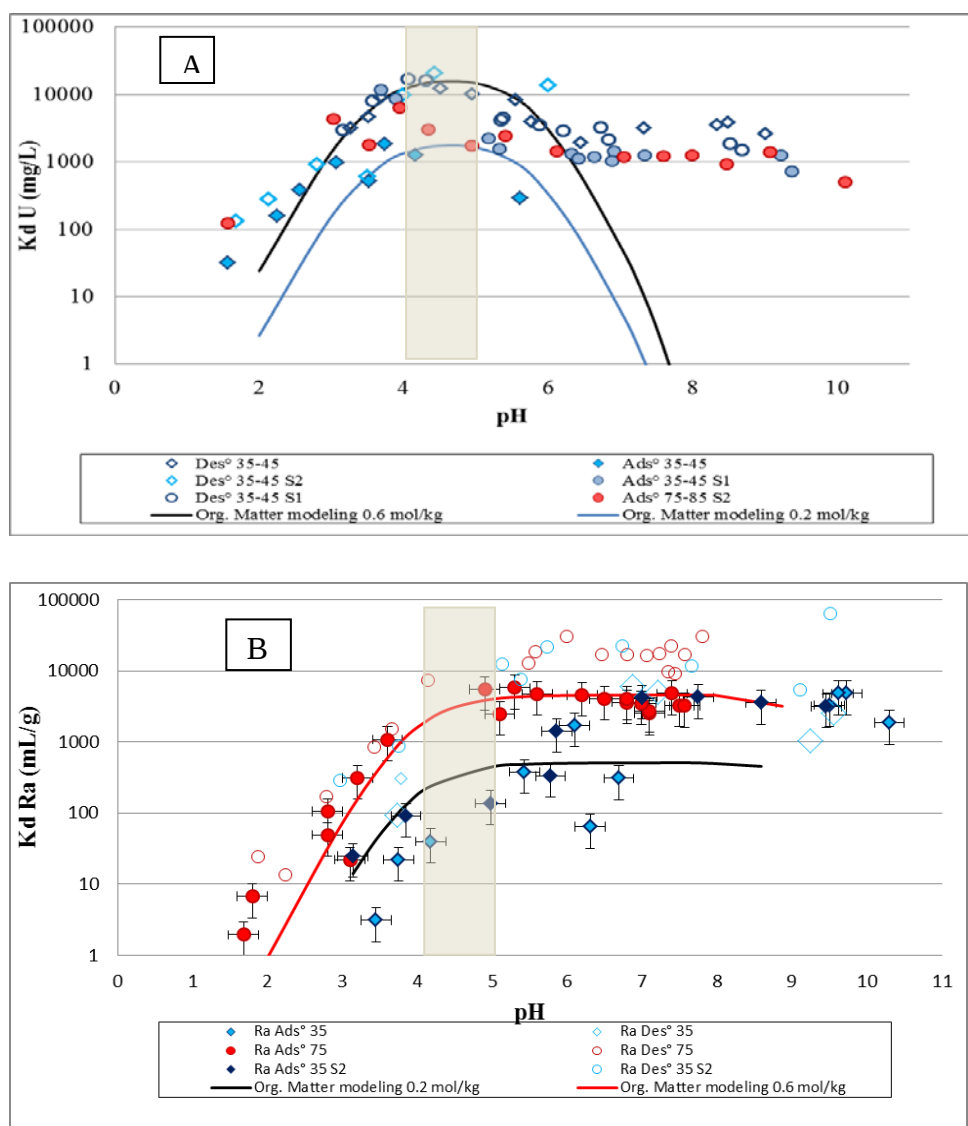


Figure 2: A- K_d of adsorbed and desorbed U on Les Sagnes peat over pH compared to modeling of retention on the organic component and B- K_d of adsorbed and desorbed ^{226}Ra on Les Sagnes peat over pH compared to modeling of retention on the organic component. Band of grey color is indicative of the *in situ* pH conditions at les Sagnes.

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