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Investigation of complexation of thorium by humic acid using chemically immobilized humic acid on silica gel

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*Humic acid / Thorium /
Conditional interaction constant (β)*

Summary. To model the influence of humic substances on the migration of tetravalent actinides (Pu, Np, U) in and around nuclear waste repositories we have immobilized humic acid on silica gel and investigated its complexation of Th(IV). It is anticipated that this material might serve as a geochemical model of the humate-coated minerals that are likely to be present in the vicinity of the repositories. The binding of Th(IV) by the immobilized humic acid was examined at pH 4, 5 and 6 in 0.1 mol L⁻¹ NaClO₄ by the batch method. Th(IV)-humate conditional interaction constants have been evaluated from data obtained from these experiments by using non-linear regression of binding isotherms.

Introduction

The determination of the speciation of radionuclides in natural waters is important for the safety assessment of radioactive waste disposal in geological formation. As pointed out in the literature [1, 2], formation of complexes with humic substances might play an important role in the migration behaviour of radionuclides. This supposition has been confirmed by many *in vitro* studies as well as by environment-based investigations, which have primarily studied the potential of humic substances to influence the migration of transuranic radionuclides. As expected, both sets of literature are extensive. Reports by Choppin and his co-workers [3, 4], Moulin and Ouzounian [5] Moulin and Moulin [6] and Zhang *et al.* [7] give accounts of the relevant literature for both research topics.

The chemistry of interaction of actinides with humic substances needs to be understood so that humate-mediated migration of actinides in the environment can be predicted. The complexation behaviour of mono- [Np(V)], di- [U(VI)] or trivalent [Am(III), Cm(III)] actinides with humic acid is well documented in the literature [8–13]. However, satisfactory data on tetravalent actinides are scarce due to experimental difficulties, namely, the low solubility of their

oxide-hydroxide [14, 15] and their high affinity for vessel walls [16]. In order to study the interaction between humic acid, especially when adsorbed on to the surface of minerals, and as dissolved tetravalent actinides, it is advantageous to reduce the number of uncertain experimental parameters. This can be achieved by using chemical analogues (eg Th(IV)) of transuranic tetravalent actinides [17, 18]. As humic acid becomes a gelatinous precipitate on acidification of strongly alkaline solutions of humic acid, Bulman and Szabó and their co-workers simplified the reaction procedures for evaluating reactions between cations of the transuranic elements and humic acid by using a composite (SiO₂-HA) formed by the chemical immobilization of humic acid on silica gel [19, 20]. This material was also used to study the interaction of other pollutants with humic acid [21, 22]. Subsequently, other groups [23–26] also prepared composite materials of humates and silica gel by using similar chemical reactions.

In this paper, we seek to advance the understanding of the modeling of the complexation of tetravalent actinides by humic substances by investigating the reactions of Th⁴⁺, a chemical analogue of Pu⁴⁺, with SiO₂-HA.

Experimental

Materials and methods

Silica gel (Polygoprep Si-NO₂-300, 20 μ m, BET surface area 100 m² g⁻¹) was obtained from Macherey-Nagel. Humic acid, sodium nitrite and thorium(IV) nitrate pentahydrate were purchased from Aldrich Chemical Co. Ltd. Humic acid was purified by the method of Kim *et al.* [27]. The composite material SiO₂-HA was prepared by using the previously described procedure [21, 22]. The specific surface area of the prepared solid phase was determined by Brunauer-Emmett-Teller (BET) method as given in Table 1. C, H and N analyses of SiO₂-HA were conducted on an automatic CHNS-O (EA1108, Fisons Instruments) analyzer. The IR spectra (Fig. 1) of SiO₂-HA was recorded using a NICOLET 5PC FT-IR Spectrometer. The KBr pellet technique was applied. Th(IV) concentrations were determined by ICP-MS (HP-4500, Hewlett-Packard, USA). The

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Table 1. Characteristics of SiO₂-HA.

	SiO ₂ -HA
Substrate content (mg g ⁻¹)	19.9 ± 1.2
Proton exchange capacity (μeq g ⁻¹ solid matter)	67.3
BET surface area ^a (m ² g ⁻¹)	74 ± 8

a: The surface area of the parent silica gel is 100 m² g⁻¹.

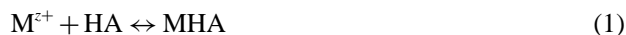
proton exchange capacity (PEC) of the immobilized HA was determined by potentiometric titration (see Table 1) under an argon atmosphere using an automatic titration device (Mettler-Toledo, Germany). Stock solutions of Th(IV) were prepared by dissolving thorium nitrate pentahydrate in 0.1 mol L⁻¹ NaClO₄ at different pHs to obtain the concentrations 10⁻⁷ mol L⁻¹.

Determination of maximal complexing capacity (B_{\max}) and conditional interaction constants (β) for Th_{total} of the prepared solid phase

The complexing capacity (B_{\max}) of SiO₂-HA was determined for Th(IV). Accurately weighed quantities of the gels, typically about 1 mg, were added to 10 ml of 0.1 mol L⁻¹ NaClO₄ solutions (pH 4–6) containing different concentrations (10⁻⁸–10⁻⁷ mol L⁻¹) of Th(IV). The resulting suspensions were shaken at room temperature for 48 h. Total concentrations of Th(IV) in aliquots, after centrifugation, were measured by ICP-MS. After sorption, the Th(IV) sorption on to vial walls was investigated. The vials were washed with distilled water and dried, then 10 ml of 2 mol L⁻¹ HClO₄ were added and shaken for 48 h. The Th(IV) concentration in the washing solutions was determined by ICP-MS. The amount of Th(IV) bound by SiO₂-HA was calculated as a difference between the initial Th(IV) concentration (10⁻⁸–10⁻⁷ mol L⁻¹) and the sum of Th(IV) remaining in solution and Th(IV) sorbed onto vial walls.

Calculation of maximal binding capacity (B_{\max}) and conditional interaction constants (β) of Th_{total} from binding isotherm

The conditional interaction constant (β) is relative to the following equilibrium:



with

$$\beta = \frac{[MHA]}{[M^{z+}]_f [HA]_f} \quad (2)$$

where M^{z+}: the metal cation; HA: the total concentration of humic acid; [MHA]: the concentration of the metal humate complex; [M^{z+}]_f: the concentration of the free thorium ion; [HA]_f: the concentration of the free humic acid.

The assumption is made that the macromolecule is the central group and the complexation can be described in terms of a Langmuir-type adsorption. The free ligand concentration in Eq. (2) can be calculated by introducing B_{\max}

$$[HA]_f = [B_{\max}] - [MHA] \quad (3)$$

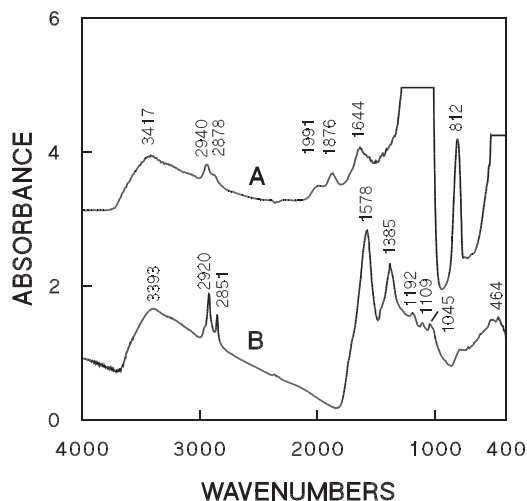


Fig. 1. IR spectra of HA-SiO₂ (A) and the parent humic acid (B).

where B_{\max} : maximal complexing capacity of humic acid.

A combination of Eq. (2) and 3 gives the relationship that could be used for calculation of conditional interaction constants:

$$\beta = \frac{[MHA]}{[M^{z+}]_f ([B_{\max}] - [HA]_f)} \quad (4)$$

or after alteration

$$[MHA] = \frac{\beta [M^{z+}]_f B_{\max}}{1 + \beta [M^{z+}]_f} \quad (5)$$

After plotting the bound Th(IV) [MHA] versus (Th_{total})_{free} [M^{z+}]_f and using the binding isotherms, the maximal binding capacity and the conditional interaction constants (β) of Th_{total} could be determined.

Calculation of conditional interaction constants (β) of ThHA

The reaction between Th⁴⁺ and HA can be written



with

$$\beta = \frac{[ThHA]}{[Th^{4+}]_f [HA]_f} \quad (7)$$

Th⁴⁺ is readily hydrolysed and it is not expected that only Th⁴⁺ ion exist in solution at pH 4–6. From the Th(IV)_{total} the [Th⁴⁺]_f can be calculated by using the stability constants of the hydroxo complexes Th(OH)³⁺, Th(OH)₂²⁺, Th(OH)₃⁺ and Th(OH)₄ [14, 18]:

$$[Th(IV)]_{\text{total}} = [Th^{4+}] + [Th(OH)^{3+}] + [Th(OH)_2^{2+}] + [Th(OH)_3^+] + [Th(OH)_4] \quad (8)$$

$$[Th(IV)]_{\text{total}} = [Th^{4+}] \alpha_{Th} \quad (9)$$

where α is the species (Ringböm) coefficient [28] related to hydrolysis:

$$\alpha = 1 + \sum_i \frac{* \beta_i}{[H^+]^i}$$

If we measure the total Th(IV) concentration in the liquid phase and calculate the Th^{4+} concentration using Eq. (9), it becomes possible to calculate the conditional interaction constants ($\log \beta$) of ThHA using the following equation:

$$\log \beta_{\text{total}} + \log \alpha_{\text{Th}} = \log \beta_{\text{ThHA}} \quad (10)$$

Results and discussion

The characteristics of the prepared silica gel are shown in Table 1. From C, H, and N analyses of SiO_2 -HA it has been established that the gels have average humic substances contents of 19.9 mg g^{-1} solid matter. The surface area of the silica gel was reduced from $100 \text{ m}^2 \text{ g}^{-1}$ to $74 \text{ m}^2 \text{ g}^{-1}$ for SiO_2 -HA. The potentiometric properties of SiO_2 -HA are shown in Table 1. From a total of seven determinations an average value for the PEC of $3.38 \pm 0.14 \text{ meq g}^{-1}$ was obtained for the bound humic acid (assuming a content of $19.9 \text{ mg HA g}^{-1}$ composite). From a comparison with the purified Aldrich HA [PEC value of $5.43 \pm 0.16 \text{ meq g}^{-1}$ [29]], it can be concluded that a fraction of the carboxylate groups are lost during the synthesis procedure or become inaccessible for complexation.

The FT-IR spectra of the humic acid and its derivative (SiO_2 -HA) are shown in Fig. 1. Both humic acid and SiO_2 -HA show two peaks at $2940\text{--}2850 \text{ cm}^{-1}$, which are characteristic of the asymmetric and symmetric stretch vibrations of CH_2 and CH_3 . More specific are the peaks at 1644 cm^{-1} and 1578 cm^{-1} that can be assigned to the $\text{C}=\text{O}$ stretch vibration of carboxyl groups. The FT-IR spectra confirm that immobilisation of humic acid was successful.

Determination of maximal binding capacity (B_{max}) of SiO_2 -HA and conditional interaction constants (β) of Th_{total} from binding isotherm

Typical binding isotherms (solid phase concentration vs. liquid phase concentration in equilibrium) of Th(IV) on SiO_2 -HA at different pH values in $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ are presented in Fig. 2. As seen from the Fig. 2, a high reproducibility in the isotherms is obtained. From these binding isotherms it has been possible to calculate, see Table 2, the complexing capacity B_{max} (expressed in mol g^{-1} solid

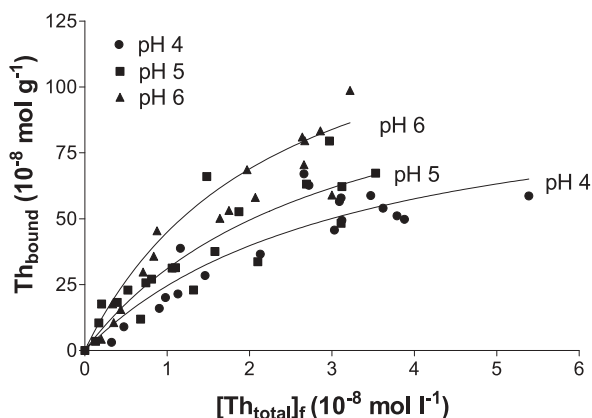


Fig. 2. Binding isotherm of SiO_2 -HA for Th(IV) in $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$ at pHs 4, 5 and 6.

Table 2. Maximal binding capacity (B_{max}) of SiO_2 -HA and conditional interaction constants ($\log \beta$) of Th_{total} with humic acid as a function of pH in $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$.

	pH		
	4.09	5.07	6.19
B_{max} ($\mu\text{mol g}^{-1}$)	1.04 ± 0.24	1.22 ± 0.36	1.48 ± 0.40
$\log \beta$ (l mol^{-1})	7.49 ± 0.33	7.53 ± 0.31	7.64 ± 0.27

phase). As seen from Table 2, the complexing capacity of SiO_2 -HA increases with increasing pH. This increase with pH is likely to have resulted from an increase in the number of ionized carboxylic binding sites. Others [30, 31] have reported a similar phenomenon. By using the nonlinear regression on the binding isotherms (Eq. (5)), the conditional interaction constants (β) of Th_{total} with humic acid can be calculated (see Table 2). From Table 2, it is apparent that the conditional interaction constants appear insensitive to pH.

Calculation of the conditional interaction constants of ThHA ($\log \beta_{\text{ThHA}}$)

The $\log \beta$ values for Th_{total} with humic acid are presented in Table 2. From this table the conditional interaction constants of Th^{4+} with humic acid (β_{ThHA}) can be calculated by using Eq. (10) and hydrolysis constants from Neck and Kim [14]. Fig. 3 shows the pH dependency of $\log \beta_{\text{ThHA}}$. The $\log \beta_{\text{ThHA}}$ varies linearly between 8.87 at pH 4 to 13.51 at pH 6 (see Table 3). The regression line has the following equation:

$$\log \beta_{\text{ThHA}} = 2.12 \text{ pH} + 0.31 \text{ with } r^2 = 0.995.$$

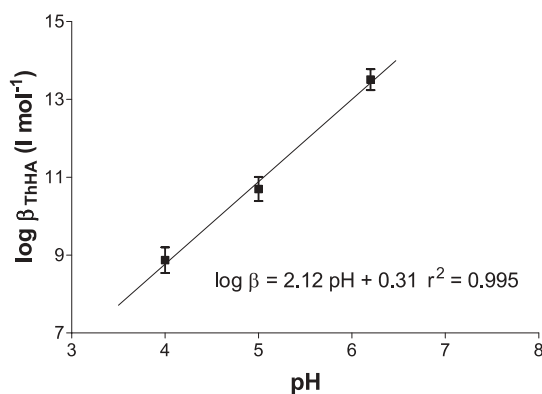


Fig. 3. Variation of the conditional interaction constants $\log \beta_{\text{ThHA}}$ for Th^{4+} humic complexes as a function of pH.

Table 3. Conditional interaction constants ($\log \beta$) of Th_{total} , side reaction coefficient ($\log \alpha_{\text{Th}}$) and $\log \beta_{\text{ThHA}}$, as a function of pH in $0.1 \text{ mol L}^{-1} \text{ NaClO}_4$, according to the hydrolysis constants from Neck and Kim [14].

	pH		
	4.09	5.07	6.19
$\log \beta_{\text{total}}$ (L mol^{-1})	7.49 ± 0.33	7.53 ± 0.31	7.64 ± 0.27
$\log \alpha_{\text{Th}}$	1.38	3.17	5.87
$\log \beta_{\text{ThHA}}$ (L mol^{-1})	8.87 ± 0.33	10.70 ± 0.31	13.51 ± 0.27

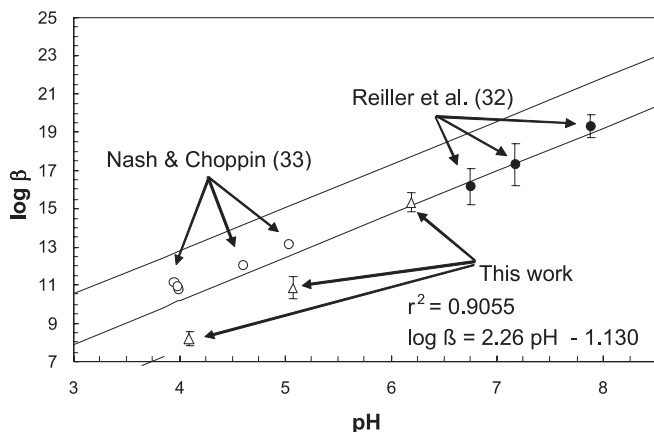


Fig. 4. Comparison of the $\log \beta_{\text{ThHA}}$ values obtained in this study with other constants sets Th(IV) hydrolysis data from [14]. White triangle this work.

It is interesting to compare our results with other values from the literature [32, 33], providing that the hydrolysis constants are the same. The $\log \beta_{\text{ThHA}}$ values, calculated from the procedure of Baes and Mesmer [34], are reported in Fig. 4. It can be seen that there is a satisfactory agreement between the three independent data sets.

Conclusions

The ready synthesis of SiO_2 -HA has been established. The potential of such materials to complex cations such as Th^{4+} has been demonstrated. From an examination of the sorption isotherms of Th(IV) at different pHs it is apparent that conditional stability constants of Th^{4+} ($\log \beta_{\text{ThHA}}$) can be easily calculated. This investigation indicates that humic acid materials such as SiO_2 -HA are likely to be of value for modelling the role of humates in interacting with transuranic species, such as Pu^{4+} , in groundwater.

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