Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Heitkamp, D. and Wagener, K.(1990) 'Kinetics of Adsorption of Uranium from Seawater by Humic Acids', Separation Science and Technology, 25: 5, 535 — 546
To link to this Article: DOI: 10.1080/01496399008050348
URL: http://dx.doi.org/10.1080/01496399008050348

SEPARATION SCIENCE AND TECHNOLOGY, 25(5), pp. 535-546, 1990

Kinetics of Adsorption of Uranium from Seawater by Humic Acids

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Abstract

The kinetics of the adsorption of uranium from seawater by humic acids fixed onto a polymer matrix was measured in a fluidized bed as a function of the grain size of the adsorbent and the flow velocity of the seawater. The adsorption rate was found to be governed by the diffusion of the uranium ions through the hydrodynamic surface layer of the adsorbent which is always formed in laminar flows of liquids. The measured rate constants are interpreted in terms of effective diffusion coefficients of 3.6×10^{-5} cm^2/s for uranyl ions and 1.8×10^{-5} cm^2/s for tricarbonatouranate ions in the surface layer. As a consequence of this kinetic behavior, the geometry of the adsorbent as well as the velocity of the water flow are relevant parameters for the amount of adsorbent needed for a projected extraction rate. This conclusion applies to all adsorption processes where diffusion through the hydrodynamic layer is the rate-determining kinetic step.

INTRODUCTION

Adsorption has been extensively considered as a technically feasible procedure for the recovery of uranium from seawater (*1*). For similar reasons, this technique may also serve to decontaminate large quantities of polluted water. In procedures of this kind, costs and performance are generally dominated by the amount of adsorbent needed. This quantity, as well as the associated installations, may be kept relatively small for fast reacting adsorbents. Under these conditions, adsorption kinetics is an important cost-determining property (*2*).

In recent investigations using polymers with amidoxime groups as adsorbents for uranium, the kinetics was found to be controlled by the relatively slow uranium diffusion into the matrix of the adsorbent (*3*, *4*).

In this work, humic acids fixed onto a polymer matrix are shown to have a different kinetic behavior which is governed by the diffusion of the ions to be adsorbed through the hydrodynamic boundary layer formed in laminar currents. This behavior is considered typical for all fluidized bed procedures with fast reacting adsorbents and a basis to optimize the processing of large amounts of water.

Humic acids, a plant degradation product, consist of a mixture of polymers with molecular weights between 10^3 and 10^5 and bearing carboxyl and phenolic hydroxyl groups (*5*). They are known to be effective in adsorbing various metals (*6*, *7*) as well as organic pesticides from aqueous solutions (*8*–*10*).

EXPERIMENTAL

Materials

The adsorption material used in this investigation was extracted from black peat which was stirred in a solution of sodium hydroxide (pH 11) and centrifuged. The remainder was again shaken in sodium hydroxide solution. By repeating this procedure with NaOH solutions of increasing pH, four fractions of humic acids were obtained. The first three fractions (extracted at pH 11, 12, and 13) contained predominantly low molecular weight fulvic and humic acids. They were discarded because of their low adsorbability of uranium. The next three fractions (at pH 14), comprising about 21 wt% of the original dry peat material, were collected and deposited onto a suitable carrier in order to make the adsorbent sufficiently stable in the adsorption and elution media and toward mechanical abrasion. For the kinetic investigations, an anion-exchange resin (Dowex 1×2, grain diameter 0.1–0.5 mm) with quaternary nitrogen as the functional group and 11.5 wt% fixing capacity for humic acids (dry weights) was used as carrier matrix.

Finally, the adsorbent was eluted in 0.5 *M* HCl solution.

Experimental Procedure

The granular adsorbent was contacted with flowing seawater in a fluidized bed. The granules were kept suspended in a column by an upward flow of seawater. By continuously bubbling air through the seawater prior to the adsorption experiment, the carbonate system, which is important for the adsorption of uranium, was maintained in equilibrium with the CO_2 concentration of the air.

After passing the column, the seawater was collected in equal portions of one liter and analyzed with respect to its uranium concentration. For analysis, the uranium of each portion was preconcentrated via a silica gel column and then determined by fluorometry. As a control of the seawater analyses, the uranium content of the adsorbent itself was determined, too. For this purpose, ~150–300 mg (dry weight) of the adsorber was taken from the column after the adsorption experiment, heated, solved in nitric acid, and analyzed fluorometrically.

At the time t_i, i portions have passed the column. Then the uranium concentration of the humic acids is

$$C_{Uh}(t_i) = \frac{M_{si}}{M_h} \sum_{j=0}^{j=i} [C_{Us} - C_{Us}(t_j)] \qquad (1)$$

C_{Us} denotes the original uranium concentration of the seawater; $C_{Us}(t_i)$ and M_{si} represent the uranium concentration and the mass, respectively, of the ith portion of the seawater; and M_h is the total mass of the humic acids in the column.

The experimental uranium accumulation of the humic acids is now given by

$$A_h(t_i) = \frac{C_{Uh}(t_i)}{C_{Us}} \qquad (2)$$

RESULTS AND DISCUSSION

Experimental Findings

The A_h values of the humic acids deposited on an anion-exchange resin have been measured for different grain sizes of the resin and flow velocities of the seawater. A survey of the experimental conditions is given in Table 1. The experimental results are presented in Figs. 1 and 2 in terms of the function $f(t) = \ln(1 - A_h/A_\infty)$, with $A_\infty = A_h(\infty)$.

Kinetics of the Reaction Steps

The adsorption of uranium on the humic acids may involve up to four reaction steps (1)–(4).

(1) Transport of the uranium to the adsorbent: In a laminar liquid flow, solid material is always surrounded by a hydrodynamic layer due to internal friction. A simple calculation for a procedure involving a laminar flow of the seawater through the adsorber column shows that the transport of the uranium to this layer is a fast process compared to the diffusion of the uranium ions through the layer of the adsorber granules. The thickness of this layer may be estimated to be (*11*)

$$\delta = (\nu\lambda/(\rho_s w))^{1/2} \tag{3}$$

where w, λ, and ρ_s represent the flow velocity, viscosity, and density, respectively, of the seawater in the column. The quantity ν in Eq. (3) is a

TABLE 1
Experimental Conditions[a]

Experiment	r (cm)	w (cm/s)	T (°C)	$\rho_s C_{Usr}$ (μg U/L)	M_h (g)	M_{m+h} (g)
H2	0.0175	0.33	18	2.6	0.4	3.5
H3	0.025	0.33	18	1.4	2.3	20
H4	0.0175	0.16	18	2.3	0.7	6.1
H5	0.0125	0.16	18	2.4	0.4	3.5
H6	0.0175	0.19	18	2.6	0.4	3.5

[a] r = mean radius of the adsorber granules.
w = flow velocity of the seawater in the fluidized bed.
T = temperature.
C_{Usr} = uranium concentration in the seawater which has passed the column.
M_h = mass of humic acids in the fluidized bed.
M_{m+h} = mass of humic acids including carrier matrix.

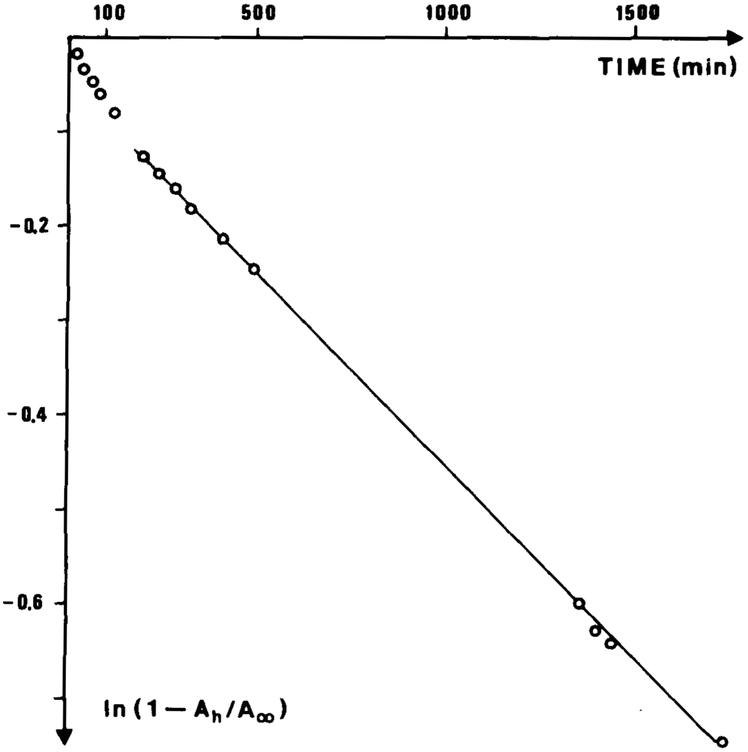

FIG. 1. Adsorption of uranium from seawater by humic acids on a polymer matrix: one day experiment at conditions compiled in Table 1 (H3).

characteristic length which has the order of magnitude of the radius r of the adsorber granules. Writing ν as f^2r, with f as a proportionality factor, yields

$$\delta = f(r\lambda/(\rho_s w))^{1/2} \tag{3a}$$

The mean diffusion length of the uranium ions in the liquid layer of the adsorbent during the time $\pi r/w$ when the uranium ions are in direct contact with this layer is

$$\xi \approx (2D\pi r/w)^{1/2} \tag{4}$$

where D denotes the diffusion coefficient.

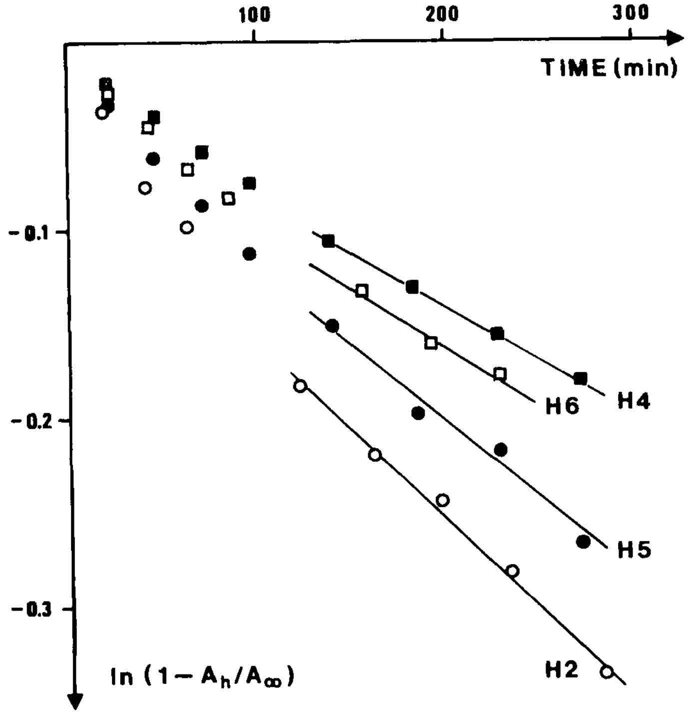

FIG. 2. Adsorption of uranium from seawater by humic acids on a polymer matrix: experiments at different grain sizes and flow velocities (see Table 1).

For $D = 1.8 \times 10^{-5}$ cm^2/s, $\lambda(18°\text{C}) = 1.15 \times 10^{-2}$ g · cm^{-1} · s^{-1} (*12*) and $\rho_s(18°\text{C}) = 1.03$ g/cm^3, δ is about 10 times larger than ξ, independent of the grain size of the adsorber and the flow velocity of the seawater in the column. This means that the uranium transport to the adsorbent is always much faster than the penetration of the hydrodynamic layer and thus does not determine the adsorption rate.

(2) Penetration of the hydrodynamic layer: According to Fick's first law, the diffusion flow of uranium ions through the hydrodynamic layer adhering to the surface of the adsorber particles in the column is given by

$$j(t) = n_a 4\pi r^2 D \rho_s \frac{1}{\delta} [C_{Us} - C_{Usp}(t)] \tag{5}$$

where $C_{Usp}(t)$ is the uranium concentration at the boundary between a particle and the adhering layer, and n_a is the number of adsorber particles in the column. Provided that the diffusion of the uranium through the boundary layer proceeds much slower than the subsequent adsorption reaction, we may assume that the uranium concentrations of the seawater directly at the surface of the adsorbent, $C_{Usp}(t)$, and of the humic acids, C_{Uh}, are always in equilibrium with each other, i.e.,

$$\frac{C_{Uh}(t)}{C_{Usp}(t)} = A_\infty \tag{6}$$

If the adsorption rate is exclusively determined by the uranium flow $j(t)$ through the hydrodynamic layer, we may write

$$M_h \frac{dC_{Uh}(t)}{dt} = j(t) \tag{7}$$

Taking into account Eqs, (2), (5), and (6), Eq. (7) leads to

$$\frac{dA_h(t)}{dt} = k_2(A_\infty - A_h(t)) \tag{8}$$

with the rate constant

$$k_2 = \frac{3\rho_s D}{r\delta\varepsilon_h \rho_{m+h} A_\infty} \tag{9}$$

Here, ρ_{m+h} denotes the mean density of the humic acids and the carrier matrix, and ε_h is the mass fraction M_h/M_{m+h} of the humic acids with respect to the total mass of the adsorbent including the carrier. Equation (8), with the boundary condition $A_h = 0$ for $t = 0$, has the solution

$$A_h(t) = A_\infty[1 - \exp(-k_2 t)] \tag{10}$$

(3) Diffusion into the adsorbent: If this step is involved in the adsorption process and dominates the kinetics, $A_h(t)$ is initially proportional to the square root of time (*13*). Since diffusion into the polymer matrix is generally much slower than in the liquid layer, the reaction rate is anticipated to be considerably smaller than in Case (2).

(4) Adsorption reaction: The net rate of the chemical reaction step of uranium adsorption is given by the difference of the rates of the adsorption and desorption reactions (*13*):

$$\frac{dC_{Uh}(t)}{dt} = \overrightarrow{\mathbf{k}} \cdot C_{Us} \cdot C_b(t) - \overleftarrow{\mathbf{k}} \cdot C_{Uh}(t) \cdot C_c \tag{11}$$

where $\overrightarrow{\mathbf{k}}$ and $\overleftarrow{\mathbf{k}}$ are the corresponding specific rate constants. $C_b(t)$ and C_c represent the concentrations of the adsorbent's free places to bind uranium ions and of the counterions in the liquid phase in contact with the adsorbent, respectively. Equation (11) is independent of the mechanisms of the adsorption and desorption reactions. C_c may be regarded as practically constant. Taking into account that $C_{Uh}(t) + C_b(t)$ equals the (constant) concentration, C, of all functional groups of the humic acids for binding uranium, one may write

$$\frac{dC_{Uh}(t)}{dt} = -C_{Uh}(t)\,(\overrightarrow{\mathbf{k}} \cdot C_{Us} + \overleftarrow{\mathbf{k}} \cdot C_c) + \overrightarrow{\mathbf{k}} \cdot C \cdot C_{Us} \tag{12}$$

At the steady state, for $C_{Uh}(\infty) = C_{Uh\infty}$, the adsorption rate equals zero, or

$$C_{Uh\infty} = \overrightarrow{\mathbf{k}} \cdot C_{Us} \cdot C/(\overrightarrow{\mathbf{k}} \cdot C_{Us} + \overleftarrow{\mathbf{k}} \cdot C_c) \tag{13}$$

Introducing Eqs. (2) and (13) into Eq. (12) leads to

$$\frac{dA_h(t)}{dt} = k_4(A_\infty - A_h(t)) \tag{14}$$

with the rate constant

$$k_4 = \overrightarrow{\mathbf{k}} \cdot C_{Us} \cdot C/C_{Uh\infty} \tag{15}$$

With the boundary condition $A_h = 0$ for $t = 0$, the solution of Eq. (14) is

$$A_h(t) = A_\infty[1 - \exp(-k_4 t)] \tag{16}$$

Comparison with the Experimental Results

The function $f(t) = \ln(1 - A_h/A_\infty)$ shows different behavior in two subsequent time intervals (Figs. 1 and 2), in accord with earlier investigations (*14*), and turns out to be linear for $t >$ ~150 min (Phase II). A linear behavior is anticipated if the adsorption of uranium by the humic acids from seawater is governed either by diffusion of the uranium ions through the boundary layer (Eq. 10) or by the chemical reaction itself (Eq. 16).

To differentiate between these two reactions, which are both first order, the rate constants need to be considered in detail. If the diffusion through the liquid layer is the rate-determining step (Case 2), the experimental rate constants are expected to be comparable to k_2 (Eq. 9) and to depend in a characteristic way on the flow velocity of the seawater and the size of the adsorber granules.

In Table 2 the rate constants, k_{II}, obtained from the slopes of $\ln(1 - A_h/A_\infty)$ in Phase II of the adsorption experiments presented in Figs. 1 and 2 are compiled. Within experimental error, they agree with the rate con-

TABLE 2

Kinetics of Uranium Adsorption from Seawater by Humic Acids. Experimental and Theoretical Rate Constants under Different Conditions

	Experimental data[a]			Data after Eqs. (9) + (3a)[b]	
Experiment	k_I (h^{-1})	k_{II} (h^{-1})	$\frac{k_I}{k_{II}}$	k_{2I} (h^{-1})	k_{2II} (h^{-1})
H2	0.119	0.056 ±0.003	2.12	0.094	0.047 ±0.007
H3	0.052	0.025 ±0.0002	2.08	0.055	0.027 ±0.004
H4	0.062	0.034 ±0.0004	1.83	0.065	0.032 ±0.005
H5	0.092	0.052 ±0.003	1.78	0.108	0.054 ±0.008
H6	0.075	0.038 ±0.005	1.98	0.071	0.035 ±0.005

[a] From Figs. 1 and 2 (method of least squares).

[b] Calculated with $D_I = 3.6 \times 10^{-5}$ cm²/s, $D_{II} = 1.8 \times 10^{-5}$ cm²/s, $\rho_s(18°C) = 1.03$ g/cm³, $\rho_{m+h} = 1.1$ g/cm³, $\lambda(18°C) = 1.15 \times 10^{-2}$ g·cm^{-1}·s^{-1}, $A_\infty = 7.94 \times 10^4$, $f = 1$, and the measured values of $r \pm 10\%$, $w \pm 5\%$ and $\varepsilon_h = 0.115 \pm 0.001$ (Table 1).

stants, k_{2II}, calculated on the basis of Eqs. (9) and (3a), assuming $f = 1$ and an effective diffusion coefficient $D_{II} = 1.8 \times 10^{-5}$ cm^2/s for the diffusion of $[UO_2(CO_3)_3]^{4-}$ ions through the adhering layer of the adsorber granules. These complex ions are likely to be the most abundant uranium ions in natural seawater (*15, 16*).

In Phase I ($t < \sim 150$ min) the slope of ln $(1 - A_h/A_\infty)$ is larger than in Phase II but gradually decreases. This behavior may be interpreted in terms of a varying effective diffusion coefficient of the uranium ions. At the beginning of the adsorption process, due to H^+ ions from the humic acids, the pH of the hydrodynamic layer is reduced such that most of the tricarbonatouranate ions entering this layer decay to uranyl ions which, as smaller ions, diffuse faster than the complex ions. This leads to higher rate constants. With the decreasing supply of H^+ ions, however, the concentration of the tricarbonatouranate ions again rises until it has reached the value of natural seawater. As a result, the effective diffusion coefficient of all uranium ions in the hydrodynamic layer gradually decreases until the reaction is solely controlled by the diffusion of the complex ions (Phase II). This interpretation is supported by the finding that the initial slopes of ln $(1 - A_h/A_\infty)$, denoted by k_I in Table 2, are, in all experiments, about two times larger than the corresponding slopes, k_{II}, in Phase II, a result which indicates that the effective diffusion coefficient of the uranyl ions, D_I, is about $2\,D_{II}$ or 3.6×10^{-5} cm^2/s. With this value the calculated initial rate constants in Phase I, k_{2I}, are in good agreement with the measured k_I data.

Independent of f in Eq. (3a) and the absolute values of the uranium diffusion coefficients, the effect of parameters like w and r on the adsorption rate further supports the conclusion that the layer diffusion is the rate-determining step of the uranium adsorption by humic acids. The quotients of the rate constants of two adsorption experiments i and j differing in *one* parameter are, according to Eqs. (9) and (3a), for constant T and r:

$$\left.\frac{k_2(w_i)}{k_2(w_j)}\right|_{T,r} = \left[\frac{w_i}{w_j}\right]^{1/2} \tag{17a}$$

and for constant T and w:

$$\left.\frac{k_2(r_i)}{k_2(r_j)}\right|_{T,w} = \left[\frac{r_j}{r_i}\right]^{3/2} \tag{17b}$$

A comparison between the experimental and theoretical values of these ratios in Phase II shows, within experimental error, good agreement (Table 3).

TABLE 3
Ratios of Rate Constants in Phase II

	For constant T and r		For constant T and w	
	$\frac{k_{(H2)}}{k_{(H6)}}$	$\frac{k_{(H2)}}{k_{(H4)}}$	$\frac{k_{(H3)}}{k_{(H2)}}$	$\frac{k_{(H4)}}{k_{(H5)}}$
Experimental data[a]	1.47	1.65	0.45	0.65
After Eqs. (17)[b]	1.34	1.47	0.58	0.60

[a] From Figs. 1 and 2.
[b] Using the experimental values of r and w (Table 1).

CONCLUSIONS

The output of a technical adsorption plant, defined as the amount of material adsorbed per unit of time, is proportional both to the amount of adsorbent, M, and the adsorption rate. At a projected output, fast kinetics helps, therefore, minimizing M (*2*). On technical scale, this is important, since M essentially determines the dimension of the adsorption plant and is one of the crucial cost elements.

The result of the investigations on uranium adsorption by humic acids underlines the kinetic significance of the hydrodynamic layer in the fluidized bed technique. For uranium adsorption from seawater by humic acids, the penetration of this layer is the rate-determining kinetic step for an adsorption time of about one day.

In all fluidized bed techniques using adsorbents which display this kind of kinetic behavior, M can minimized decisively by a proper choice of the flow velocity and the geometry of the adsorbent. Reducing the effective diameter of the adsorbent by a factor of 4 would lead to an increase of the adsorption rate by a factor of 8 or, for a projected adsorption rate of the plant, to a reduction of M by the same factor. For this reason, adsorbents consisting of small grains or thin fibrous material with thin hydrodynamic layers in laminar currents would be preferable in processing large amounts of polluted water.

Acknowledgments

The assistance of Mrs. G. Putral and Mr. F. Ringelmann in carrying out the experiments is gratefully acknowledged. We also thank the Biological

Institute at Helgoland and the Uranium Mining Company, Ltd., Bonn, for their permission to use the adsorption plant at Helgoland.

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Recieved by editor April 20, 1989