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 Nakamura, S. , Mori, S. , Yoshimuta, H. , Ito, Y. and Kanno, M.(1988) 'Uranium Adsorption Properties of Hydrous Titanium Oxide Granulated with Polyacrylonitrile', Separation Science and Technology, 23: 6, 731 — 743
To link to this Article: DOI: 10.1080/01496398808057662
URL: http://dx.doi.org/10.1080/01496398808057662

SEPARATION SCIENCE AND TECHNOLOGY, 23(6 & 7), pp. 731-743, 1988

Uranium Adsorption Properties of Hydrous Titanium Oxide Granulated with Polyacrylonitrile

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Abstract

The performance of hydrous titanium oxide (HTO) adsorber granulated with polyacrylonitrile (PAN) has been studied by a batch method using natural seawater. The adsorber was classified into four classes of 24/28, 28/32, 32/35, and 35/48 mesh, and the seawater temperature was varied from 15 to 30°C. The effects of particle size and seawater temperature on the liquid film mass transfer coefficient and the intraparticle diffusion coefficient of the uranium ion were estimated. It was found that the uranium adsorption rate was dependent on both liquid film mass transfer and intraparticle diffusion for the PAN-HTO adsorber. The equilibrium adsorption capacity was in the range of 175 to 127 μg-U/g-AD at 30°C. Particle size of PAN-HTO adsorber had no distinct influence on the adsorption capacity and rates. Both adsorption capacity and rates increased with increasing seawater temperature.

INTRODUCTION

An adsorption method is considered to be the most promising and realistic method to extract uranium from seawater. A wide variety of adsorbers has been developed, and their ability to adsorbing uranium ion has been reported (*1*). To compare the performance of these adsorbers, it is necessary to simulate the engineering performance and provide an economic analysis. Hence, we have developed a simulation program for pumping and fixed-bed plant extracting uranium from seawater (*2*). The adsorber used in the plant was assumed to be hydrous titanium oxide

(HTO) granulated with an organic binder. Uranium adsorption properties of granulated HTO, however, have not been studied in detail. In particular, there have been only a few studies on the kinetics of uranium adsorption (*3–6*).

Therefore we conducted batch measurements on HTO granulated with polyacrylonitrile (PAN-HTO) using an agitated tank and natural seawater. We measured the concentration decay of uranium in seawater in the tank, compared it with the theoretical concentration decay curves, and clarified the rate-determining step of uranium adsorption. An adsorption isotherm was also measured and, the equilibrium adsorption capacity of a PAN-HTO adsorber was determined. The effects of particle size and seawater temperature on the adsorption properties were systematically studied.

EXPERIMENTAL

Experimental and analytical methods of batch measurements using an agitated tank are described elsewhere (*4*, *7*), and only briefly outlined here. An analytical method developed by Suzuki et al. provided theoretical concentration decay curves of uranium in an agitated tank (*7*). The concentration of uranium in the tank was calculated by numerically solving a set of diffusion equations by the finite difference technique. The equations were transformed to dimensionless forms, and the concentration of uranium C was obtained as a function of dimensionless time τ and expressed by the ratio to C_0, i.e., the uranium concentration in natural seawater at $\tau = 0$. The following assumptions are made in the calculation.

(1) The particles are homogeneous spheres of the same radius.
(2) The adsorption isotherm is of the Freundlich type.
(3) The accumulation of uranium in the liquid phase in a particle is negligible.
(4) Adsorption equilibrium is attained locally at each adsorption site.

A set of parameters n, Bi, and C_∞/C_0 gave one theoretical curve. Here n is the Freundlich constant, Bi is the Biot number, and C_∞ is the equilibrated uranium concentration in the seawater of the tank. Bi is defined as

$$\mathrm{Bi} = k_f R/D_e \tag{1}$$

where k_f is the liquid film mass transfer coefficient, R is the particle radius, and D_e is the intraparticle diffusion coefficient. The concentration decay curve obtained by experiments was compared with sets of theoretical curves. If the experimental curve fitted any one of the theoretical curves, we estimated D_e, k_f, and Bi from the curve.

The PAN-HTO adsorber used in the present study was supplied by Asahi Chemical Industry Co., Ltd. The adsorber was classified into four classes of 24/28, 28/32, 32/35, and 35/48 mesh. Specific surface area, average particle radius R, and density ρ of the PAN-HTO adsorber are listed in Table 1. The radii of 150 particles were measured for each class and averaged to get the radius in the table. The specific surface area was measured by the one point BET method using an apparatus of Shimadzu Co. Density ρ was determined by displacement of water with a picnometer. Scanning electron microscopic observation of the particle was also performed.

Eight agitated tanks, each of which contained 4 L natural seawater, were kept in a water bath. A constant amount of PAN-HTO adsorber was added into each tank and stirred with a pair of stainless steel blades rotating at 250 rpm. After stirring for a measured period, the uranium concentration in the seawater was measured by using 1 L seawater. Twelve to 16 runs were conducted to get a concentration decay curve. We made our measurements at 5° intervals from 15 to 30°C. This was because the temperature of the Kuroshio Current which supplies fresh uranium-bearing seawater to plants is in the range between 18 and 25°C. The water bath could control the seawater temperature in the agitated tanks with an accuracy of ±0.5°.

The concentration of uranium was measured by a fluorimetric method using a fluorimeter (Aloka FMT 4b) following several chemical concentration processes (*8–10*). An inorganic flux, composed of Na_2CO_3, K_2CO_3, and NaF, was used. The relative error in concentration measurement was checked by using natural seawater. The uranium concentration in the seawater sample was determined to be 3.2 ppb with a relative error of 3%. Centamni et al. reported that the fluorescence intensity was

TABLE 1
Properties of PAN-HTO

Mesh no.	24/28	28/32	32/35	35/48
Average radius R (mm)	0.38	0.32	0.28	0.24
Specific surface area (m^2/g)	176	199	184	181
Density ρ (g/cm^3)	2.70	2.80	—	2.77

increased by the addition of a small amount of LiF to the flux, and that reproducibility was improved at the same time (*11*). We examined the reproducibility and found that the addition of LiF incrased the fluorescence intensity but decreased the reproducibility. Therefore, the flux without LiF was used in our experiment. The seawater was supplied by the Seaside Laboratory of Niigata University, located on the north coast of Sado Island in the Sea of Japan.

RESULTS AND DISCUSSION

Effects of Particle Size

The effects of particle size on equilibrium adsorption capacity q_0 and adsorption rates were studied at 30°C. Figure 1 shows a uranium uptake curve at 30°C for a PAN-HTO adsorber of 28/32 mesh. The slope of the curve at the initial stage decreased with increasing particle size. The adsorption time required to reach equilibrium between the adsorber and seawater was about 7 to 9 d. It became longer as the particle size increased.

The amount of adsorber added to 4 L seawater was varied from 30 to 400 mg and agitated for about 9 d until equilibrium was attained. From

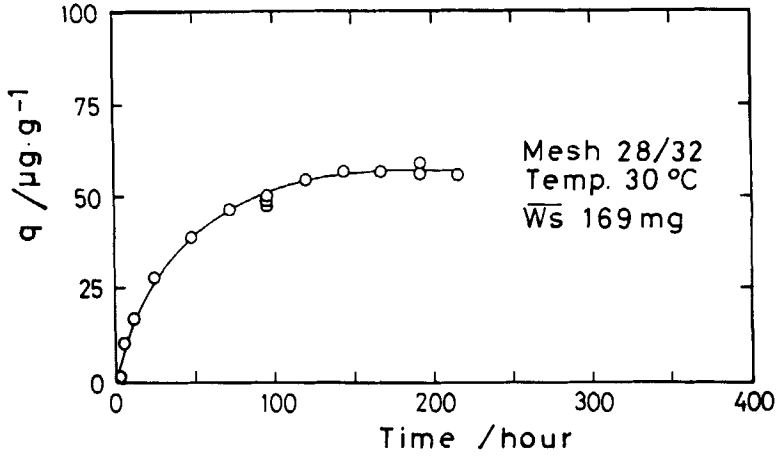

FIG. 1. Uranium uptake curve for PAN-HTO.

the uranium concentration of seawater, we could determine the equilibrated concentration of uranium in the adsorber and seawater, i.e., q^* and C^*. Thus, we obtained uranium adsorption isotherms for PAN-HTO adsorbers of different particle sizes as illustrated in Fig. 2. The adsorption isotherms were represented by Freundlich's Eq. (2) with the adsorption constants n between 1.3 and 1.7:

$$q^* = kC^{*1/n} \tag{2}$$

The constants obtained by Freundlich's Eq. (2) are shown in Table 2, where the adsorber weight was measured after drying. The average value of n was 1.5, and the theoretical curves were calculated using this value of n. These values are in close agreement with those reported for HTO powder (*12*). We calculated the equilibrium adsorption capacity q_0 by using Eq. (2) with $C_0 = 3.2$ ppb. Figure 3 shows plots of q_0 versus the inverse of the particle radius. Kanno et al. (*13*) reported that q_0 is proportional to $1/R$ of the HTO adsorber granulated by pressing. However, $1/R$ dependence of q_0 was not obvious for the PAN-HTO adsorber. One of the reasons is that the specific surface area of the PAN-HTO adsorber does not have a proportional relationship to $1/R$, as shown in Table 1. In addition, q_0 is not only influenced by the specific surface area but also by the accumulated pore volume and the preparation

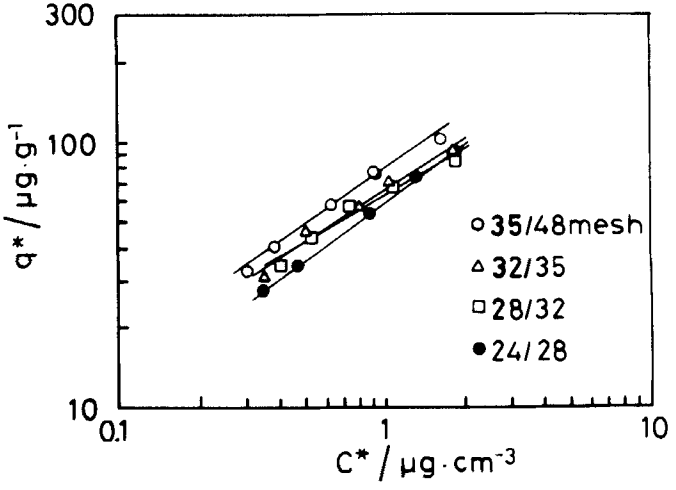

FIG. 2. Uranium adsorption isotherms for PAN-HTO of four different particle sizes at 30°C.

TABLE 2
Freundlich Constants of PAN-HTO[a]

Mesh no.	$2R$ (10^{-2} cm)	k	n	C_0 (ppb)	q_0 (μg/g)
35/48	4.8	78	1.4	3.2	175
32/35	5.6	65	1.5	3.2	139
28/32	6.3	62	1.7	3.2	127
24/28	7.6	58	1.4	3.2	137

[a]Temperature: 30°C.

conditions of the adsorber. Therefore, we consider that the relationship between q_0 and the physical properties of the adsorber particle are not simple.

Curve fitting of the experimental concentration decay curve to the theoretical curve is illustrated in Fig. 4. The best fitted theoretical curve was for Bi = 2. The other parameters were obtained from the experiment. A value of dimensionless time τ and the corresponding real adsorption time t could be determined from Fig. 4, where τ is defined as

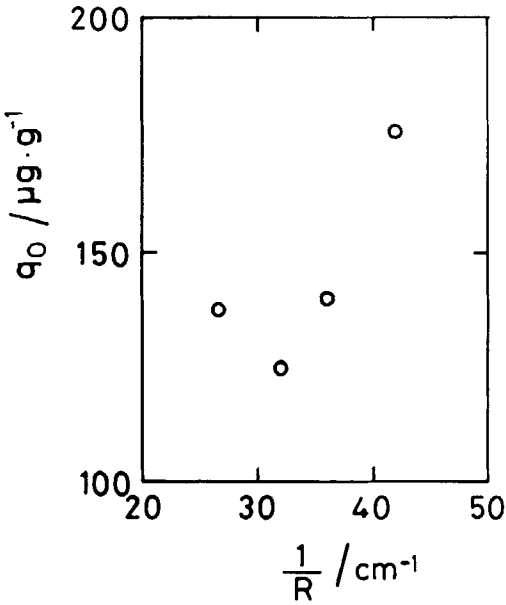

FIG. 3. Plots of equilibrium adsorption capacity q_0 versus inverse of particle radius R at 30°C.

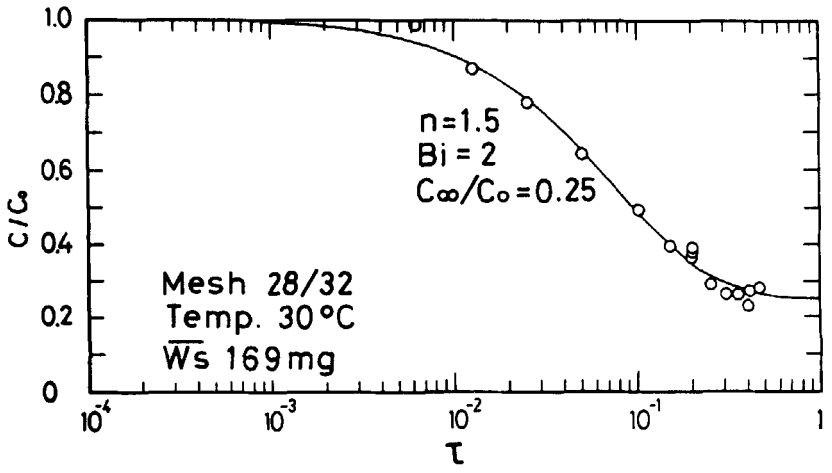

FIG. 4. Fitting of concentration decay curve. (O) Experimental results. (——) Theoretical curve.

$$\tau = (D_e t/R^2)(C_0/\rho_p q_0) \tag{3}$$

Therefore, we could calculate D_e using Eq. (3). The Biot number was determined to be 2 in this case, and we calculated k_f from D_e and Bi.

The uranium adsorption process is purely intraparticle diffusion controlled when Bi = ∞ and purely liquid film mass transfer controlled when Bi = 0. Biot numbers determined from the experiments were 2 for most cases and 4 for one case. This suggests that the rates of liquid film mass transfer and intraparticle diffusion are of comparable magnitude, and that both processes contributed to the adsorption kinetics of the PAN-HTO adsorber.

Figure 5 shows plots of D_e and k_f versus particle size of the PAN-HTO adsorber at 30°C. k_f and D_e seem to decrease with increasing R, but these tendencies are not clear because of experimental uncertainties.

D_e obtained here was of the order of 10^{-5} cm^2/s, and 1 to 2 orders of magnitude larger than those reported previously for HTO adsorbers (*3*, *4*). We consider that the discrepancy arises from the following reason. The adsorber was assumed to be a homogeneous sphere in the calculation. This assumption was the same as for the case in the simulation model where the particle radius was used as the adsorber radius (*2*). The PAN-HTO particle used, however, was not homogeneous. Figure 6 shows SEM photographs of a PAN-HTO particle and its cross section. The particle has a crust of PAN, and the crust has many holes

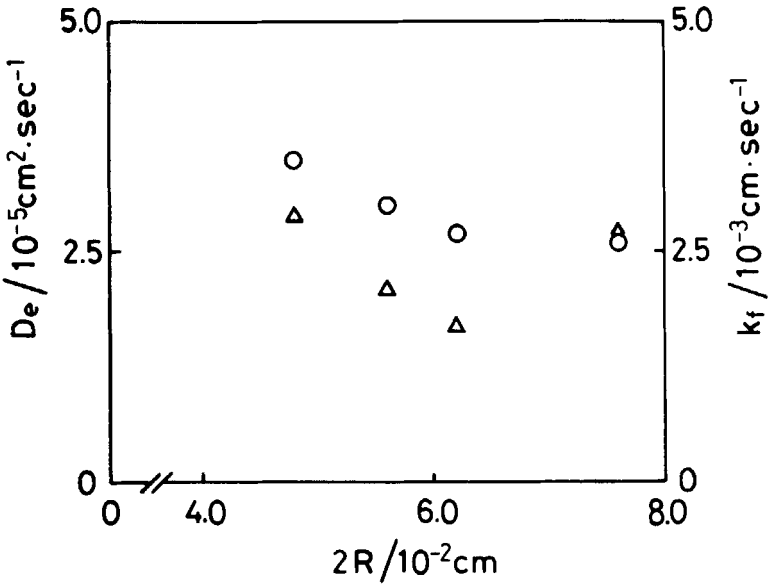

FIG. 5. Plots of D_e (O) and k_f (Δ) versus particle size at 30°C.

through it. The particle consists of small HTO particles of about 5 μm diameter which tend to form a cluster of 50 to 100 μm. The particle is porous, and the pore sizes are not homogeneous. The pore size of the inner part was larger than that near the surface, and the particle was denser near its surface. Thus, the diffusion distance of uranium in the calculation was much longer than the actual one, and a greater D_e might be resulted. It would be not proper to use the particle size R as the adsorber radius in calculation of the theoretical decay curve. The granulated PAN-HTO adsorber, however, can be considered as an adsorber which has the D_e and k_f values obtained here with the radius R used in the calculation. This is because the basic assumptions in the theoretical calculation of the decay curve and the simulation of engineering performance are essentially the same. Therefore, the values of D_e and k_f or radius R must be considered as apparent values.

Effects of Temperature

A series of experiments was carried out at four different temperatures, 15, 20, 25, and 30°C, to elucidate the effects of temperature on uranium

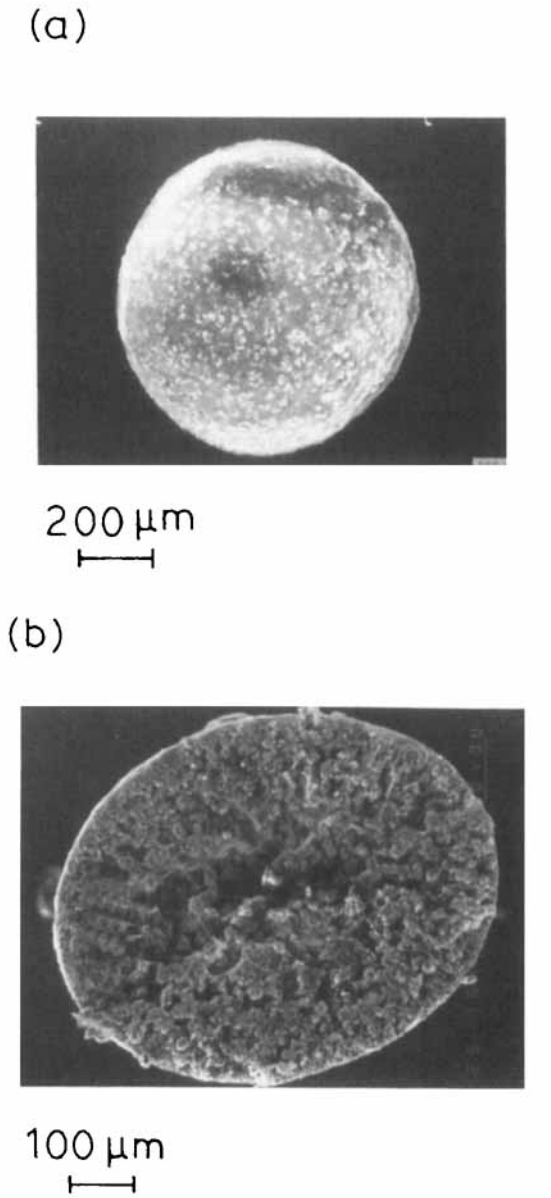

FIG. 6. Photographs by SEM of a PAN-HTO particle. (a) PAN-HTO particle. (b) Cross section.

adsorption by an PAN-HTO adsorber. The adsorption time required to reach equilibrium between the adsorber and seawater was about 18 to 9 d. It became shorter as temperature increased. Adsorption isotherms at each temperature are shown in Fig. 7. Freundlich's equation holds at every temperatures examined here; n values ranged from 1.3 to 1.6 and were nearly independent of the temperature. The constants obtained by Freundlich's Eq. (2) are shown in Table 3. The q_0 value at each temperature was calculated from Fig. 7 and is presented in Fig. 8. q_0 tended to increase with increasing temperature.

Concentration decay curves were also determined at each temperature, and Bi, D_e, and k_f were obtained. D_e and k_f are plotted versus temperature in Fig. 9. D_e appreciably increased with increasing temperature. k_f gradually increased with increasing temperature except for 25°C; but the reason for this tendency is not clear. Bi was 4 at higher temperatures and 10 at lower temperatures. This suggests that the uranium adsorption rate is dependent on both liquid film mass transfer and intraparticle diffusion in the range of 15 to 30°C.

CONCLUDING REMARKS

Batch measurements were carried out on the adsorption of uranium in natural seawater using agitated tanks, and the effects of the particle size

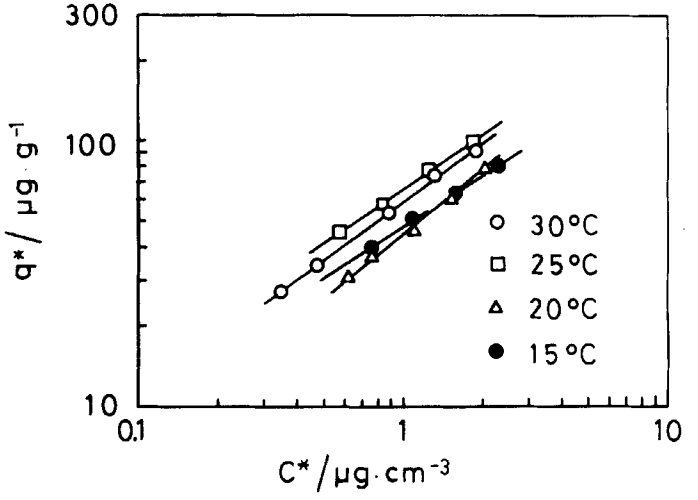

FIG. 7. Uranium adsorption isotherms for PAN-HTO of 24/28 mesh at four different temperatures.

TABLE 3
Temperature Dependence of Freundlich Constants[a]

Temperature (°C)	$2R$ (10^{-2} cm)	k	n	C_0 (ppb)	q_0 (μg/g)
30	7.6	58	1.4	3.2	137
25	7.6	66	1.5	3.3	149
20	7.6	45	1.3	3.3	114
15	7.6	48	1.6	3.3	103

[a]Mesh no. 24/28.

of PAN-HTO adsorbers and seawater temperature on the adsorption properties were systematically studied.

The results are summarized as follows:

(1) The uranium adsorption process of an PAN-HTO adsorber has two steps with comparable rates, i.e., liquid film mass transfer and intraparticle diffusion.
(2) The size of the PAN-HTO adsorber has no distinct influence on the adsorption capacity and rates.

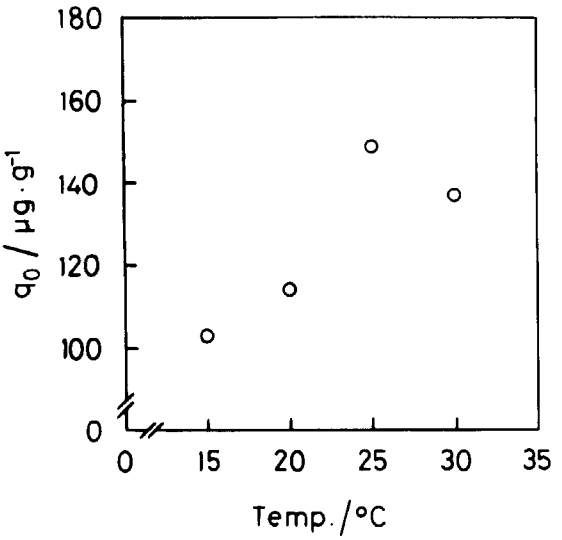

FIG. 8. Plots of equilibrium adsorption capacity q_0 versus temperature for PAN-HTO of 24/28 mesh.

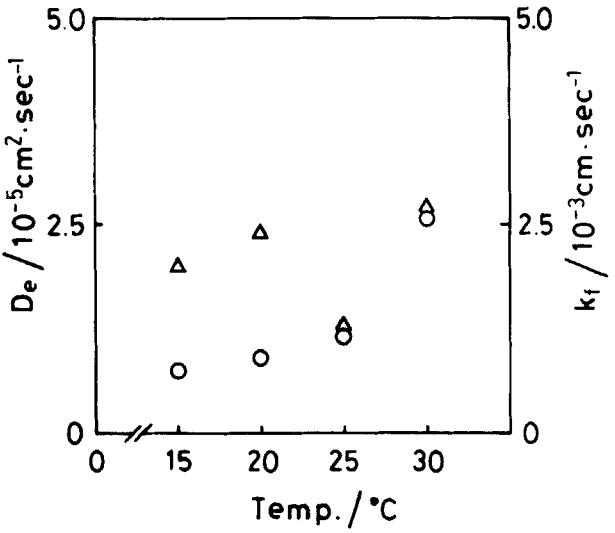

FIG. 9. Plots of D_e (○) and k_f (△) versus temperature for PAN-HTO of 24/28 mesh.

(3) Both adsorption capacity and rates increase with increasing seawater temperature.

SYMBOLS

Bi	Biot number = $k_f R/D_e$ (−)
C_0	initial concentration of uranium (μg/cm^3)
C^*	concentration of uranium in equilibrium to q^* (μg/cm^3)
C_∞	concentration of uranium in equilibrium (μg/cm^3)
D_e	intraparticle diffusion coefficient (cm^2/s)
k_f	liquid film mass transfer coefficient (cm/s)
k	constant in Freundlich equation
n	Freundlich constant (−)
q	amount of uranium adsorbed at t (μg/g)
q_0	amount of uranium adsorbed in equilibrium with C_0 (μg/g)
q^*	amount of uranium adsorbed in equilibrium with C^* (μg/g)
R	average radius of adsorber (cm)
τ	dimensionless time = $(D_e t/R^2)(C_0/\rho_p q_0)$ (−)
t	adsorption time (s)
ρ_p	apparent density of adsorber (dry) (g/cm^3)
ρ	adsorber density (g/cm^3)

Acknowledgments

This study was supported by the Special Project Research on Energy (Recovery of uranium from seawater) under Grant-in-Aid of Scientific Research of the Ministry of Education, Science and Culture.

The authors are grateful to Prof M. Suzuki, University of Tokyo, for supplying the calculation program of theoretical concentration decay curves; Asahi Chemical Industry Co., Ltd., for supplying PAN-HTO adsorbers; and Seaside Laboratory of Niigata University for supplying the seawater.

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Received by editor September 3, 1987