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

Desorption of Uranium from Amidoxime Fiber Adsorbent

Akira Goto[a]; Shigeharu Morooka[a]; Masakazu Fukamachi[a]; Katsuki Kusakabe[a]; Tokihiro Kago[b]
[a] Department of Chemical Science and Technology, Kyushu University, Fukuoka, Japan [b] Department of Applied Chemistry, Towa University, Fukuoka, Japan

To cite this Article Goto, Akira , Morooka, Shigeharu , Fukamachi, Masakazu , Kusakabe, Katsuki and Kago, Tokihiro(1993) 'Desorption of Uranium from Amidoxime Fiber Adsorbent', Separation Science and Technology, 28: 13, 2229 — 2235
To link to this Article: DOI: 10.1080/01496399308016745
URL: http://dx.doi.org/10.1080/01496399308016745

SEPARATION SCIENCE AND TECHNOLOGY, **28**(13&14), pp. 2229–2235, 1993

Desorption of Uranium from Amidoxime Fiber Adsorbent

AKIRA GOTO, SHIGEHARU MOROOKA, MASAKAZU FUKAMACHI, and KATSUKI KUSAKABE
DEPARTMENT OF CHEMICAL SCIENCE AND TECHNOLOGY
KYUSHU UNIVERSITY
FUKUOKA 812, JAPAN

TOKIHIRO KAGO
DEPARTMENT OF APPLIED CHEMISTRY
TOWA UNIVERSITY
FUKUOKA 815, JAPAN

ABSTRACT

An amidoxime fibrous adsorbent is contacted with uranium-enriched seawater (10 ppm); about 10 mg uranium is loaded per 1 g dry fiber. Then the rate and yield of uranium desorption from the fiber are determined with various eluents. Acid solutions are superior to alkali carbonate solutions as eluents. With a 0.1 $mol \cdot L^{-1}$ HCl solution, desorption is completed in 2 hours regardless of the presence of uranium in the leaching solution up to 15 ppm ($\approx 6 \times 10^{-5}$ $mol \cdot L^{-1}$). Serial operation of the adsorption–desorption cycle four times does not affect desorption efficiency, but the addition of heavy metal ions to the eluent at a level of 1.8×10^{-3} $mol \cdot L^{-1}$ significantly decreases desorption efficiency.

INTRODUCTION

The recovery of uranium from seawater has been tested with various adsorbents (1, 2). Fibrous adsorbents are superior to granular ones because of their higher adsorption rate and a lower probability of entrainment from the adsorption unit. Amidoxime adsorbents prepared with commercial poly(acrylonitrile) fiber are especially promising and can collect uranium from seawater up to 1–10 g uranium per kg dry fiber (3–10). This concentration is of the same order of magnitude as that in lean uranium ores. The process of uranium desorption from seawater has the merit

that it produces much less waste than does ore processing. The uranium-enriched eluate can be treated by conventional separation systems.

On the other hand, feasibility testing of uranium desorption from amidoxime adsorbent is still insufficient. The desorption rate increases with increasing eluent acidity (11). Hirotsu et al. (12) investigated the separative elution of uranium from amidoxime polymer beads packed in a column and found that the uranium concentration in the eluate was increased by the step elution method, changing the HCl concentration from 0.1 to 1.0 $mol \cdot L^{-1}$. However, the lower the acid concentration, the smaller the damage to the fiber. Changes in adsorption rate and fiber strength after contacting fiber with eluent in the desorption step should be evaluated from the viewpoint of fiber durability. There must be an optimum eluent acidity. Furthermore, metal ions coadsorbed with uranium affect the desorption yield.

In the present study, the rate and yield of uranium desorption from amidoxime fiber adsorbent are determined with various eluents. Repetitive tests of adsorption and desorption are carried out. The effects of the types of eluent and the concentrations of uranium and other metal ions in the eluent on the desorption efficiency are also examined.

EXPERIMENTAL

Materials

A commercial poly(acrylonitrile) bicomponent fiber of 6 denier was obtained from Mitsubishi Rayon Co. The fiber was composed of a part blended with 5.8 wt% methyl acrylate and 0.4 wt% sodium methallylsulfonate and a part blended with 1.2 wt% sodium methallylsulfonate. The cross section of the solid-shaped dry fiber is shown in Fig. 1. The fiber was treated in a 1.5 wt% methanolic solution of NH_2OH at 353 K for 9 hours, then modified in a 0.1 $mol \cdot L^{-1}$ NaOH solution at 353 K for 45 minutes. Details of the treatment and the properties of the fiber prepared

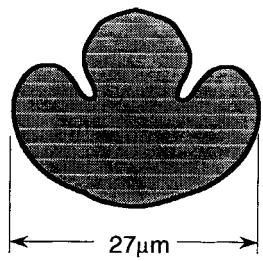

FIG. 1 Cross-sectional shape of dry fiber.

are described in previous papers (9, 10). Adsorption sites (mostly the amidoxime group) were homogeneously formed in the fiber (9). The intrinsic adsorption rate of uranium in seawater, excluding the liquid–solid mass transfer resistance, was about 300 mg/kg dry fiber per day.

Adsorption

The potassium salt of uranyl tricarbonate [$K_4UO_2(CO_3)_3 \cdot 2H_2O$] was dissolved in seawater at a uranium concentration of 10 ppm. Uranium-loaded fibers for the desorption experiment were prepared by agitating the amidoxime fiber in the uranium-enriched solution for 24 hours. The amount of uranium adsorbed was determined from the difference in uranium concentration measured by ICP spectroscopy before and after adsorption. The uranium adsorbed was about 10 g/kg dry fiber throughout the present study.

Desorption

Hydrochloric acid (0.01–1 mol·L^{-1}), nitric acid (0.01–0.5 mol·L^{-1}), sulfuric acid (0.1 mol·L^{-1}), sodium carbonate (0.5–2 mol·L^{-1}), and sodium hydrogen carbonate (0.5 mol·L^{-1}) solutions were used as the eluents. To check the effect of uranium dissolved in the eluent on the desorption rate, the initial uranium concentration was varied between 0 and 15 ppm in a 0.1 mol·L^{-1} HCl solution. The effect of foreign ions, Mg(II), Ca(II), Fe(III), Cu(II), and Zn(II), was also evaluated. The species were chosen on the basis of the results of Hirotsu et al. (12), who reported the major adsorbates of an amidoxime adsorbent from seawater.

Uranium-loaded amidoxime fiber (0.05 g) was mixed in 50 mL eluent, and the mixture was shaken at 303 K. After 500-fold dilution, the uranium concentration was determined by ICP mass spectroscopy. The desorption yield is defined as

$$\text{Desorption yield} = \frac{\text{amounts of U desorbed into eluent}}{\text{amounts of U loaded on fiber}} \quad (1)$$

RESULTS AND DISCUSSION

Figure 2 shows the evolution of desorption yield with different leaching solutions. The rates of desorption by mineral acid solutions were faster than those by carbonate and hydrogen carbonate solutions. After 6 hours of leaching, desorption was completed for the 0.05 mol·L^{-1} HCl solution. The desorption yields for 0.5 mol·L^{-1} Na_2CO_3 and $NaHCO_3$ after 10 hours of leaching were only 60 and 45%, respectively. Since a uranyl ion

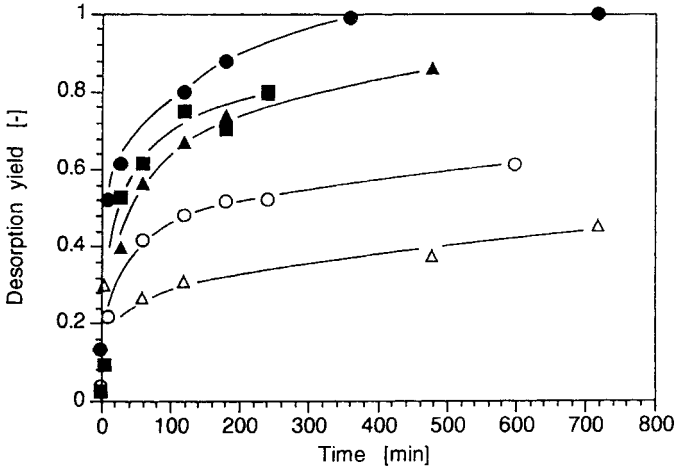

FIG. 2 Effect of leaching solution on desorption yield: (●) 0.05 mol·L^{-1} HCl, (▲) 0.05 mol·L^{-1} HNO_3, (■) 0.05 mol·L^{-1} H_2SO_4, (○) 0.5 mol·L^{-1} Na_2CO_3, (△) 0.5 mol·L^{-1} $NaHCO_3$.

forms a stable complex with three carbonate ions (13), a concentrated carbonate salt solution is an eluent candidate. Even when the concentration of Na_2CO_3 was increased to 2 mol·L^{-1}, the desorption yield remained unchanged at a low level.

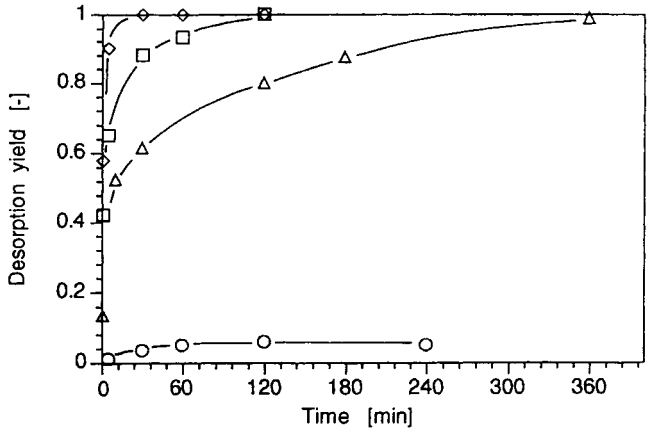

FIG. 3 Effect of HCl concentration on desorption yield: (○) 0.01 mol·L^{-1} HCl, (△) 0.05 mol·L^{-1}, (□) 0.1 mol·L^{-1}, (◇) 0.2 mol·L^{-1}.

Figure 3 reveals the effect of HCl concentration on desorption yield. The desorption rate was accelerated by increasing the acid concentration, and complete desorption was achieved within 30 minutes with a 0.5 mol·L^{-1} HCl solution. Hirotsu et al. (12) studied the elution of uranium from an amidoxime polymer with a hydrochloric acid solution, and they showed that UO_2^{2+} begins to elute at pH 2–3. As shown in Fig. 3, the desorption yield was equilibrated at about 5% in the 0.01 mol·L^{-1} HCl solution, which agrees with their result.

A high uranium concentration in an eluate is desirable for the downstream separation process, and it can be attained by repeating the desorption with the same solution. Figure 4 shows the desorption yield with 0.1 mol·L^{-1} HCl solutions containing different amounts of uranium. The desorption rate was independent of the initial uranium concentration up to 15 ppm in the eluent, and the yield reached 100% after 120 minutes. This concentration is more than that in the eluent from uranium ores, and it is easily enriched by conventional methods.

The adsorption–desorption cycle was carried out four times with the same solution and the reloaded fiber. Each desorption period was 120 minutes. As indicated in Fig. 5, the desorption yield after each cycle was virtually 100%. The adsorption capacity of the amidoxime fiber was at the same level for each cycle. Thus, the undamaged fiber could be reused after each repetition.

Table 1 indicates the desorption yield by the eluents containing metal ions as well as uranium (10 ppm) in the 0.1 mol·L^{-1} HCl solution. Eluent 2 simulates the composition of the corresponding species in seawater. The results with two paired eluents, 1 and 2, 3 and 4, show that no significant change in desorption yield is caused by the addition of a large quantity

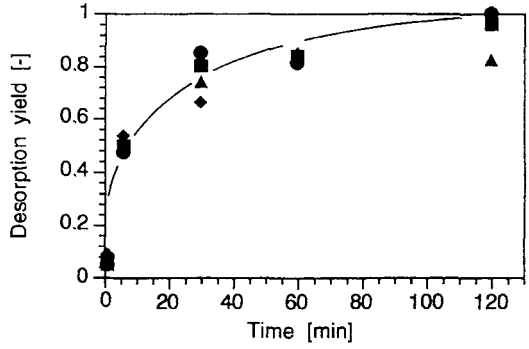

FIG. 4 Effect of initial uranium concentration in 0.1 mol·L^{-1} HCl solution on desorption yield: (●) 0 ppm, (■) 5 ppm, (▲) 10 ppm, (◆) 15 ppm.

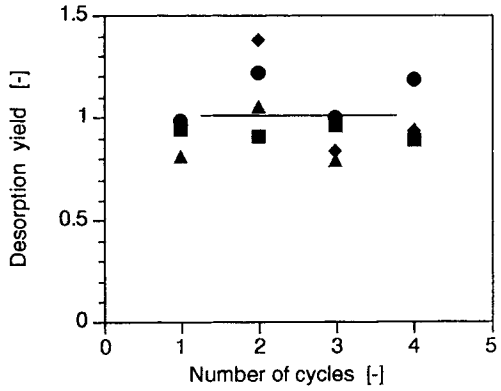

FIG. 5 Change in desorption yield by number of cycles: (●) initial uranium concentration = 0 ppm, (■) 5 ppm, (▲) 10 ppm, (◆) 15 ppm.

TABLE 1
Desorption Yield by Eluents Containing Metal Ions

	Eluent 1	Eluent 2	Eluent 3	Eluent 4
Metal ion concentration in 0.1 mol·L^{-1} HCl solution:				
Fe(III)	4.7×10^{-4}	4.7×10^{-4}	9.3×10^{-4}	9.3×10^{-4}
Zn(II)	3.6×10^{-4}	3.6×10^{-4}	7.2×10^{-4}	7.2×10^{-4}
Cu(II)	6.8×10^{-5}	6.8×10^{-5}	1.4×10^{-4}	1.4×10^{-4}
Mg(II)	—	5.6×10^{-2}	—	1.1×10^{-1}
Ca(II)	—	3.4×10^{-2}	—	6.8×10^{-2}
Desorption yield after 120 minutes (%)	87.6	90.2	64.4	68.0

of magnesium and calcium ions. When the total concentration of such heavy metal ions as Fe(III), Zn(II), and Cu(II) was doubled to 1.8×10^{-3} mol·L^{-1} (Eluents 2 and 4), however, the desorption yield after 120 minutes fell to 64–68%. When the acid concentration was increased from 0.1 to 1 mol·L^{-1} at the same metal ion concentration, the desorption yield was improved to ~90% in spite of the presence of heavy metal ions.

CONCLUSION

The desorption of uranium ion from amidoxime fiber adsorbent was studied with various eluents. Hydrochloric acid was superior to Na_2CO_3 and $NaHCO_3$ solutions. After 2 hours of leaching in a 0.1 mol·L^{-1} HCl

solution containing 0–15 ppm uranium, desorption was virtually completed. Serial operation (four cycles) resulted in no reduction of the desorption yield. The effect of heavy metal ions on elution was significant when a 0.1 mol·L^{-1} HCl solution was used.

ACKNOWLEDGMENTS

This work was partially supported by a Grant-in-Aid on Priority Area Research received from the Ministry of Education, Science and Culture, Japan (Grant 03203105) and the Salt Science Research Foundation (Grant 9116). ICP mass measurements were made at the Center of Advanced Instrument Analysis, Kyushu University.

REFERENCES

1. L. Astheimer, H. J. Schenk, E. G. Witte, and K. Schwochau, *Sep. Sci. Technol.*, *18*, 307 (1983).
2. H. Egawa, *Bull. Soc. Sea Water Sci. Jpn.*, *41*, 235 (1988).
3. S. Katoh, K. Sugasaka, K. Sakane, N. Takai, H. Takahashi, Y. Umezawa, and Y. Itagaki, *Nippon Kagaku Kaishi*, p. 1455 (1982).
4. H. Omichi, A. Katakai, T. Sugo, and J. Okamoto, *Sep. Sci. Technol.*, *20*, 163 (1985).
5. K. Saito, K. Uezu, T. Hori, S. Furusaki, T. Sugo, and J. Okamoto, *AIChE J.*, *34*, 411 (1988).
6. T. Shirotsuka, K. Onoe, and S. Mochizuki, *Bull. Soc. Sea Water Sci. Jpn.*, *42*, 15 (1988).
7. N. Takagi, T. Hirotsu, J. Sakakibara, S. Katoh, and K. Sugasaka, *Ibid.*, *42*, 279 (1989).
8. Y. Kobuke, T. Aoki, H. Tanaka, I. Tabushi, T. Kamaishi, and I. Hagiwara, *Ind. Eng. Chem. Res.*, *29*, 1662 (1990).
9. T. Kato, T. Kago, K. Kusakabe, S. Morooka, and H. Egawa, *J. Chem. Eng. Jpn.*, *23*, 744 (1990).
10. T. Kago, A. Goto, K. Kusakabe, and S. Morooka, *Ind. Eng. Chem. Res.*, *31*, 204 (1992).
11. T. Hirotsu, S. Katoh, K. Sugasaka, M. Seno, and T. Itagaki, *Sep. Sci. Technol.*, *21*, 1101 (1986).
12. T. Hirotsu, S. Katoh, K. Sugasaka, N. Takai, M. Seno, and T. Itagaki, *Ibid.*, *22*, 1725 (1987).
13. T. Aihara, A. Goto, T. Kago, K. Kusakabe, and S. Morooka, *Ibid.*, *27*, 1655 (1992).