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3 **Adsorption of Europium(III) with Solvent Impregnated Kapok Fiber**
4 **Containing 2-Ethylhexyl Phosphonic Acid Mono-2-Ethylhexyl Ester**

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13 Solvent impregnated kapok fiber is prepared, employing 2-ethylhexyl phosphonic acid mono-2-ethylhexyl
14 ester as an extractant, and adsorption property of Eu(III) is investigated. The kapok fiber possesses higher
15 impregnation ability for the extractant than conventional solvent impregnated resins, such as crosslinked
16 polystyrene and crosslinked polymethacrylic ester, and thus the solvent impregnated kapok fiber has higher
adsorption ability for Eu(III). The adsorption of Eu(III) with solvent impregnated kapok fiber progresses
with Langmuir adsorption mechanism and the high maximum adsorption amount of 0.685 mmol/g is
obtained.

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1. Introduction

Solvent extraction has been widely used as processes for separation, purification, and recovery of rare metals, due to its simplicity of equipment and operation. The combination of solvent extraction with adsorption and/or ion exchange has been therefore investigated, for the second generation of the extraction system. There are two ways to bridge the gap between the adsorption and the solvent extraction; solvent impregnated resins (SIR) [1-3] and extractant-containing microcapsules [4-5]. The SIR has been therefore actively investigated by many researchers, and a critical review of the works was recently published [6].

The SIR however still has some points which should be improved, and one of the points is lower impregnation capacity of the extractant into polymer resin cause of lower adsorption capacity. Tanaka *et al.* revealed that kapok fiber, a commercial oil sorbent, possesses high impregnation amount of extractant, and solvent impregnated kapok fiber (SIF) was applied for the adsorption of base metals [7] and precious metals [8]. In a present work, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) impregnated kapok fiber is prepared by using two kinds of fibers, and the characteristics of the SIFs are investigated.

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2. Experimental

2.1 Reagents

PC-88A was supplied by Daihachi Chemical Industry Co., kapok fibers (KT-65 and M-4050) were supplied by Kakui Co., and polymer resins (HP20 and HP2MG) were supplied by Nippon Rensui Co. The

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41 compositions of KT-65 and M-4050 styrene/divinylbenzene copolymer resin
42 and HP2MG is methacrylic ester was supplied by Aldrich and all other
43 reagents were supplied by Wako Pure Chemical Industries, as analytical-grade reagents.

44 2.2 Preparation of SIF and SIR

45 The SIF containing PC-88A was prepared by the following method. The kapok fibers were firstly cut
46 into ca. 0.5×0.5 cm pieces, and then were washed with methanol. After drying, the cut fibers were
47 contacted with ethanol solution of PC-88A (0.3 mol/L - 1.0 mol/L as monomeric species) at a ratio of 50
48 mL/g for more than 12 h at 298 K. Ethanol was then removed by evaporation, and the fiber was washed
49 with excess amount of D.I. water at 298 K. The SIR was also prepared by the same
50 manner as the SIF. The impregnation amount of SIF or SIR was determined by the difference
51 of weight of fiber or resin before and after impregnation.

52 2.3 Adsorption of Eu(III)

53 The aqueous solutions were prepared by dissolving $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in D.I. water. The concentration
54 of Eu(III), in the case for time course variation and pH dependency, was set to ca. 1.0 mmol/L, while the
55 concentration was varied from 0.001 mmol/L to 22 mmol/L for the adsorption isotherm experiments. The
56 pH value was adjusted by adding appropriate concentrations of HNO_3 or NaOH solution. A 0.02 g of SIF or
57 a 0.03 g of SIR was added to 10 mL of Eu(III) aqueous solution to be shaken at 298 K for more than 4 h in
58 the case of SIF and for more than 12 h in the case of SIR, which are enough to be reached to equilibrium
59 from preliminary experiments. After filtration, the equilibrium pH was measured by a pH meter (Horiba
60 F-23). The concentrations of Eu were determined by an inductively coupled plasma atomic emission
61 spectrophotometer (ICP-AES; Shimadzu ICPS-7000). The amount of Eu(III) adsorbed, q , is defined by

$$62 \quad q = \frac{([\text{Eu}]_0 - [\text{Eu}]_e) \cdot L}{w} \quad (1)$$

63 where $[\text{Eu}]_0$ and $[\text{Eu}]_e$ are initial and equilibrium concentrations of Eu(III) in the aqueous phase, L is
64 volume of aqueous solution, and w is weight of adsorbent including PC-88A and support. The leakage of
65 PC-88A during adsorption was also determined by measuring phosphorus concentration in the aqueous
66 phase after adsorption.

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68 3. Results and Discussion

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69 3.1 Preparation of SIF

70 Impregnation abilities of PC-88A into kapok fibers and conventional resins are investigated by
71 changing concentrations of PC-88A at the impregnation procedure. Table 1 shows the impregnation amount
72 of PC-88A in each support. In all support systems, impregnation amount is almost saturated with 0.3 mol/L
73 of PC-88A, and the impregnation amount is hardly changed by increasing in PC-88A concentration.
74 Impregnation is therefore conducted with 0.3 mol/L of PC-88A hereafter. Kapok fibers have much higher
75 impregnation abilities than both of conventional resins. Among two kapok fibers, M-4050 possesses
76 slightly higher impregnation ability than KT-65. This may be due to the content of kapok, as shown in
77 Table 1.

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Table 1. Impregnation amount of PC-88A on polymer resins.

[PC-88A] (mol/L)	Impregnation amount (mmol/support-g)			
	Sample A	Sample B	Sample C	Sample D
0.1	2.00	2.10	1.90	1.80
0.2	2.00	2.10	1.90	1.80

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3.2 Adsorption behavior of Eu(III)

82 Figure 1 shows time course variations of adsorption of Eu(III) with SIFs. The adsorption reaches
83 equilibrium within 3 h in both systems. Figure 2 shows the effect of pH on adsorption amount of Eu(III),
84 together with leakage of PC-88A. In all systems, the adsorption increases with increase in pH, as same as in
85 the solvent extraction system. Comparing the adsorption
86 behavior with SIF and SIR, much higher adsorption
87 amount is obviously obtained in SIF systems.
88 Comparing the support fiber of SIF, KT-65 and M-4050,
89 the adsorption amount of Eu(III) with SIF prepared by
90 M-4050 is lower than that by KT-65 at higher pH region,
91 in spite of higher impregnation amount of PC-88A by
92 M-4050. The leakage of PC-88A from SIF by M-4050 is
93 much higher than that from SIF by KT-65 as well as the
94 conventional SIRs. The smaller adsorption ability of SIF
95 by M-4050 is caused by the leakage of PC-88A from SIF.
96 The KT-65 is therefore concluded to
97 for PC-88A than M-4050 and also compared with
98 resins. The maximum adsorption amount with SIF is 3.6
99 times higher than the conventional SIR. The kapok fiber
100 is therefore expected as a new support for impregnating
101 the extractant.
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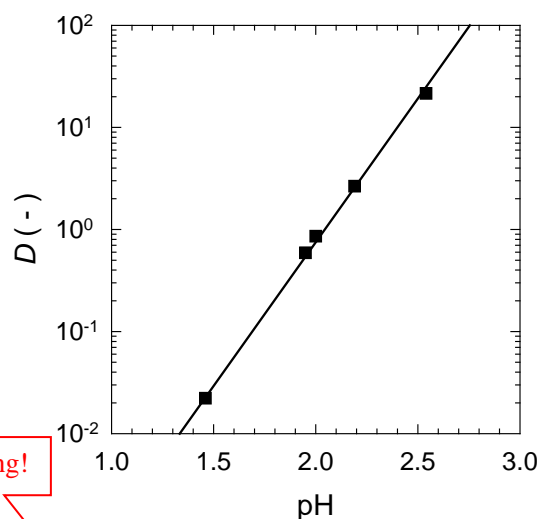


Figure 1. Effect of pH on the distribution ratio of Eu(III) and leakage of PC-88A.

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4. Conclusion

105 The abbreviation of Solvent Extraction Research and Development, Japan (SERDJ) is Solvent Extr.
106 Res. Dev., Jpn. The solvent impregnated kapok fiber is prepared, using PC-88A as an extractant, and the
107 adsorption property of Eu(III) with the SIF is investigated. KT-65 possesses higher adsorption ability for
108 Eu(III) than M-4050 due to less leakage of the extractant from SIF during the adsorption. The KT-65 has
109 also ca. 35 % higher impregnation ability of PC-88A than conventional polymer resins, HP20 and HP2MG,
110 and the maximum adsorption amount of 0.685 mmol/g of Eu(III), which is 3.6 times higher than HP20, is
111 obtained.

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