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

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(Received December 25, 2015; Accepted February 1, 2016)

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Solvent impregnated kapok fiber is prepared, employing 2-ethylhexyl phosphonic acid mono-2-ethylhexy ester as an extractant, and adsorption property of Eu(III) is investigated. The kapok fiber possesses higher impregnation ability for the extractant than conventional solvent impregnated resins, such as crosslinked 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 compositions of KT-65 and M-4050 are shown in Table 1. HP20 is styrene/divinylbenzene copolymer resin and HP2MG is methacrylic ester copolymer resin. Eu(NO3)3•6H2O was supplied by Aldrich and all other reagents were supplied by Wako Pure Chemical Industries, as analytical-grade reagents.

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## 2.2 Preparation of SIF and SIR

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The SIF containing PC-88A was prepared by the following method. The kapok fibers were firstly cut into ca. 0.5 × 0.5 cm pieces, and then were washed with methanol. After drying, the cut fibers were contacted with ethanol solution of PC-88A (0.3 mol/L - 1.0 mol/L as monomeric species) at a ratio of 50 mL/g for more than 12 h at 298 K. Ethanol was then removed by evaporation, and the fiber was washed with excess amount of D.I. water and dried for overnight at 353 K. The SIR was also prepared by the same manner as the SIF. The impregnated amount of PC-88A in the SIF or SIR was determined by the difference of weight of fiber or resin before and after impregnation.

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## 2.3 Adsorption of Eu(III)

The aqueous solutions were prepared by dissolving Eu(NO3)3·6H2O in D.I. water. The concentration of Eu(III), in the case for time course variation and pH dependency, was set to ca. 1.0 mmol/L, while the concentration was varied from 1.0 × 10–6 mol/L to 22 mmol/L for the adsorption isotherm experiments. The pH value was adjusted by adding appropriate concentrations of HNO3 or NaOH solution. A 0.02 g of SIF or a 0.03 g of SIR was added to 10 mL of Eu(III) aqueous solution to be shaken at 298 K (25 °C) for more than 4 h in the case of SIF and for more than 12 h in the case of SIR, which are enough to be reached to equilibrium from preliminary experiments. After filtration, the equilibrium pH was measured by a pH meter (Horiba F-23). The concentrations of Eu were determined by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES; Shimadzu ICPS-7000). The amount of Eu(III) adsorbed, *q*, is defined by eq. (1).

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 (1)  
where [Eu]0 and [Eu]e are initial and equilibrium concentrations of Eu(III) in the aqueous phase, *L* is volume of aqueous solution, and *w* is weight of adsorbent including PC-88A and support. The leakage of PC-88A during adsorption was also determined by measuring phosphorus concentration in the aqueous phase after adsorption.

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# 3. Results and Discussion

## 3.1 Preparation of SIF

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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 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  Always full spelling! | 2.00 | 2.10 | 1.90 | 1.80 |

## 3.2 Adsorption behavior of Eu(III)

Figure 1 shows time course variations of adsorption of Eu(III) with SIFs. The adsorption reaches equilibrium within 3 h in both systems. Figure 2 shows the effect of pH on adsorption amount of Eu(III), together with leakage of PC-88A. In all systems, the adsorption increases with increase in pH, as same as in the solvent extraction system. Comparing the adsorption behavior with SIF and SIR, much higher adsorption amount is obviously obtained in SIF systems. Comparing the support fiber of SIF, KT-65 and M-4050, the adsorption amount of Eu(III) with SIF prepared by M-4050 is lower than that by KT-65 at higher pH region, in spite of higher impregnation amount of PC-88A by M-4050. The leakage of PC-88A from SIF by M-4050 is much higher than that from SIF by KT-65 as well as the conventional SIRs. The smaller adsorption ability of SIF by M-4050 is caused by the leakage of PC-88A from SIF. The KT-65 is therefore concluded to be suitable support for PC-88A than M-4050 and also conventional polymer resins. The maximum adsorption amount with SIF is 3.6 times higher than the conventional SIR. The kapok fiber is therefore expected as a new support for impregnating 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

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

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# Acknowledgement

This study was supported by a Grant-in-Aid for Scientific Research (No. xxxx) of the Ministry of Education, Science, Sports and Culture of Japan.

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# Declaration

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