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

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Solvent impregnated kapok fibers are prepared, employing 2-ethylhexyl phosphonic acid mono-2-ethylhexy ester as the extractant, and the adsorption property of Eu(III) are investigated. Kapok fibers possess a higher impregnation ability for the extractant than conventional solvent impregnated resins, such as crosslinked polystyrene and crosslinked polymethacrylic ester, and thus solvent impregnated kapok fibers have a higher adsorption ability for Eu(III). The adsorption of Eu(III) with solvent impregnated kapok fibers progresses via a Langmuir adsorption mechanism and a high maximum adsorption of 0.685 mmol/g is obtained.

1. Introduction

Solvent extraction has been widely used as a process for separation, purification, and recovery of rare metals, due to its simplicity of equipment and operation. The disadvantage of solvent extraction, such as the requirement of large amounts of organic solvent, has however been recently recognized, since the organic solvent may be lost to the aqueous phase, owing to its solubility in aqueous solutions. The combination of solvent extraction with adsorption and/or ion exchange has been therefore investigated, for the second generation of such extraction systems. There are two ways to bridge the gap between adsorption and solvent extraction; solvent impregnated resins (SIR) [1-3] and extractant-containing microcapsules [4-5]. Comparing these two methods, SIR possess the advantage of easy preparation, because the SIR are usually prepared by just treating the polymer resin with the organic solvent containing the extractant. The SIR have been therefore actively investigated by many researchers, and a critical review of all this work was recently published [6].
The SIR however can still be improved, one problem being the lower impregnation capacity of the polymer resin for the extractant, thus causing a lower adsorption capacity. Alternative impregnation supports for extractants are therefore being investigated. Tanaka et al. revealed that kapok fibers, used as commercial oil sorbents, possess a high impregnation capacity for extractants, and solvent impregnated kapok fibers (SIF) were applied for the adsorption of base metals [7] and precious metals [8]. Although the potential of SIF as metal adsorbents has been elucidated, further potential of SIF remains to be investigated. In the present work, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC-88A) impregnated kapok fibers are prepared by using two types of fibers, and the characteristics of the SIF have been investigated. Then, the impregnation ability of the fibers for PC-88A and the adsorption of Eu(III) with the SIF are investigated.

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 a styrene/divinylbenzene copolymer resin and HP2MG is a 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.

<table>
<thead>
<tr>
<th></th>
<th>Kapok</th>
<th>Cotton</th>
<th>Polypropylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>KT-65</td>
<td>43 %</td>
<td>28 %</td>
<td>29 %</td>
</tr>
<tr>
<td>M-4050</td>
<td>70 %</td>
<td>–</td>
<td>30 %</td>
</tr>
</tbody>
</table>

2.2 Preparation of SIF and SIR

The SIF containing PC-88A were 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 an 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. The ethanol was then removed by evaporation, and the fibers were washed with an excess amount of D.I. water and dried overnight at 353 K. The SIR were 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 in weight of the fibers or resins before and after impregnation.

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), for the adsorption rate and pH dependency experiments, was set at ca. 1.0 mmol/L, while the concentration was varied from 0.001 mmol/L to 22 mmol/L for the adsorption isotherm experiments. The pH value was adjusted by adding appropriate concentrations of HNO₃ or NaOH solution. SIF (0.02 g) or SIR (0.03 g) were added to 10 mL of Eu(III) aqueous solution and shaken at 298 K for more than 4 h in the case of the SIF and for more than 12 h in the case of the SIR, which from preliminary experiments is sufficient to achieve equilibrium respectively. After filtration, the equilibrium pH was measured using a pH meter (Horiba F-23). The concentrations of Eu were determined using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES; Shimadzu ICPS-7000). The amount of Eu(III) adsorbed, \( q \), is defined by

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

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

3. Results and Discussion

3.1 Preparation of SIF

The impregnation abilities of PC-88A into kapok fibers and conventional resins were investigated by changing the concentration of PC-88A in the impregnation procedure. Table 2 shows the impregnation amount of PC-88A in each support.

<table>
<thead>
<tr>
<th>[PC-88A] (mol/L)</th>
<th>KT-65</th>
<th>M-4050</th>
<th>HP20</th>
<th>HP2MG</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>2.54</td>
<td>2.64</td>
<td>1.85</td>
<td>1.88</td>
</tr>
<tr>
<td>0.4</td>
<td>2.50</td>
<td>2.71</td>
<td>1.92</td>
<td>1.68</td>
</tr>
<tr>
<td>0.8</td>
<td>2.58</td>
<td>2.72</td>
<td>1.96</td>
<td>1.75</td>
</tr>
<tr>
<td>1.0</td>
<td>2.53</td>
<td>2.79</td>
<td>1.89</td>
<td>1.91</td>
</tr>
</tbody>
</table>

In all the support systems, the amount of impregnation is almost at saturation with 0.3 mol/L of PC-88A, and the impregnation amount hardly changes on increasing the PC-88A concentration. Impregnation was therefore carried out using 0.3 mol/L of PC-88A hereafter. Kapok fibers have much higher impregnation abilities than both of the conventional resins. Of the two kapok fibers, M-4050 possesses a slightly higher impregnation ability than KT-65. This may be due to the content of kapok, as shown in Table 1.
3.2 Adsorption behavior of Eu(III)

The SIF and SIR were used for the adsorption of Eu(III). Figure 1 shows the rate of adsorption of Eu(III) with the SIF. The adsorption reached equilibrium within 3 h in both systems. Figure 2 shows the effect of pH on the amount of Eu(III) adsorbed, together with the leakage of PC-88A. In all systems, adsorption increases with increasing pH, just as in the solvent extraction system. Comparing the adsorption behavior of SIF with SIR, much higher adsorption is obviously obtained in the SIF systems. Comparing the SIF support fibers, KT-65 and M-4050, the amount of adsorption of Eu(III) with the SIF prepared using M-4050 is lower than that for KT-65 at higher pH values, in spite of M-4050 containing more impregnated PC-88A. Leakage of PC-88A from the SIF during adsorption is also shown in Figure 2. The leakage of PC-88A from the M-4050 SIF is much higher than that from the KT-65 SIF as well as the conventional SIR. The smaller adsorption ability of the M-4050 SIF is caused by the leakage of PC-88A from the SIF. KT-65 is therefore concluded to be a more suitable support for PC-88A than M-4050 or the conventional polymer resins.

![Figure 1. Rate of adsorption of Eu(III) with SIF. Shaking rate = 180 rpm; [Eu(III)]_initial = 1.16 mmol/L (KT-65) and 0.932 mmol/L (M-4050), and pH_initial = 1.64 (KT-65) and 2.34 (M-4050).](image1)

![Figure 2. Effect of pH on the adsorption of Eu(III) and leakage of PC-88A by SIF and SIR; [Eu]_initial = 1.15 mmol/L (KT-65), 1.04 mmol/L (M-4050), 0.996 mmol/L (HP-20), and 0.996 mmol/L (HP-2MG).](image2)
Figure 3(a) shows the adsorption isotherms for Eu(III) with SIF and (b) Langmuir linear relationships for the on the KT-65 SIF at pH = 2.52 ± 0.02 and the HP20 SIR at pH = 2.47 ± 0.03.

Figure 3(a) shows the adsorption isotherms for the KT-65 SIF and HP20 SIR at pH = ca. 2.5. The adsorption of Eu(III) with both adsorbents is shown to progress via the Langmuir mechanism as shown in Figure 3(b). Maximum adsorption amounts are 0.685 mmol/g for KT-65 and 0.192 mmol/g for HP20. The maximum adsorption amount with SIF is 3.6 times higher than the conventional SIR. Kapok fibers are therefore good candidates as new supports for impregnating the extractant.

4. Conclusion

Solvent impregnated kapok fibers were prepared, using PC-88A as the extractant, and the adsorption properties for Eu(III) with the SIF have been investigated. KT-65 possesses a higher adsorption capacity for Eu(III) than M-4050 due to less leakage of the extractant from the SIF during adsorption. KT-65 has also ca. 35 % higher impregnation capacity for PC-88A than the conventional polymer resins, HP20 and HP2MG, and a maximum adsorption capacity of 0.685 mmol/g for Eu(III), which is 3.6 times higher than HP20, was obtained.

References
4) S. Nishihama, N. Sakaguchi, T. Hirai, I. Komasawa, Hydrometallurgy, 64, 35-42 (2002).