Extraction of Uranium from Dilute Solutions using Microbore Tubes

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Abstract

Single-stage micro-scale solvent extraction of uranium from dilute solutions is studied using PTFE microbore tubes. Effects of flow rate, diameter and length of microbore tube on stage efficiency, pressure drop and settling behavior of dispersion are studied to identify the configuration that can ensure high stage efficiency (>90%) with quick settling and low pressure drop (< 2 bar). Two such configurations are put in parallel to demonstrate single-stage extraction at 1 LPH total throughput. Finally, single-stage extraction and stripping experiments with 1N NaHCO₃ as the strippant are carried out to demonstrate the possibility of concentrating uranium in the aqueous phase. Specific extraction rate in the micro-scale extractor based on microbore tubes is estimated to be more than four times of the same in a mixer-settler.

Introduction

Microchannels offer several advantages such as high surface to volume ratio, high specific interfacial area for two-phase reactions and mass transfer operations, small inventories and confident scale-up. These advantages can be harnessed for achieving process intensification. Advantages specific to solvent extraction are controllable quality of dispersion and narrow drop size distributions¹ leading to quick settling, high overall volumetric mass transfer coefficients compared to conventional extractors² and confident scale-up³. Several recent studies carried out at Chemical Engineering Division, BARC highlight potential of microchannels as process intensifying solvent extraction contactors⁴-⁶. In this study, microbore tubes, arguably the cheapest available microchannels are used to study extraction of uranium from dilute streams.

Experimental Work

Phase System

The aqueous phase is a simulated dilute solution having less than 1000 ppm uranium. Acidity of the aqueous phase is 1N. The organic phase is 30% (v/v) TBP in dodecane. Distribution coefficient for extraction is about 6.7. Strippant used is 1 N NaHCO₃ due to its very low distribution coefficient.

Experimental Setup

Fig. 1 shows the experimental setup used in the experiments with single microbore tubes. The setup consists of an opposed T-junction of 750 µm drilled in a PTFE disk having a microbore tube connected to it using a threaded connector. Dispersion generated at the opposed T-junction passes through the microbore tube and gets collected in a glass sample bottle which allows visual observation of settling behavior. The aqueous sample is analyzed for uranium concentration using inductively coupled plasma atomic emission spectrometer (ICP-AES, model ULTIMA-2, Make Jobin Horiba, France). The setup with two microbore tubes in parallel, used for experiments at 1 LPH total throughput, is similar to the setup shown in Fig. 1 but has two additional 2 mm diameter Y-junction distributors drilled in PTFE
disks for splitting of the aqueous and organic streams and a pipe settler (volume 15ml) for settling of dispersion.

Calculations

Equations (1)-(3) are used to quantify the experimental results. To compare the performance of different extractors SER (Specific Extraction Rate) which represents the number of moles extracted per unit time per unit volume of the extractor is used.

\[
\eta = \frac{C_{AE}^{in} - C_{AE}^{out}}{K_D \times 100} \quad (1)
\]

\[
PE = \frac{C_{AE}^{in} - C_{AE}^{out}}{C_{AE}^{in}} \times 100 \quad (2)
\]

\[
SER = \frac{(C_{AE}^{in} - C_{AE}^{out})Q_{AE}}{V} \quad (3)
\]

Where, \( \eta \) and \( PE \) represent percentage stage efficiency and percentage extraction, respectively. \( C_{AE}^{in} \) is the concentration of uranium in the aqueous feed to the extraction stage, \( C_{AE}^{out} \) is the concentration of uranium in the raffinate from the extraction stage, \( C_{OE}^{out} \) is the concentration of uranium in the loaded organic leaving the extraction stage. \( K_D \) is distribution coefficient. \( Q_{AE} \) is the aqueous phase flow rate in the extraction stage. \( V \) is the total volume of the extractor including the settler.

Experiments with Single Microbore Tubes

Effect of Flow Rate

Experiments were carried out to find out the maximum flow rate a single microbore tube can handle while giving quick phase separation (instantaneous phase separation with clear aqueous and organic phases and no dispersion band seen in glass sample bottle). This maximum flow rate is expected to reduce with reduction in diameter as increased velocities will make the dispersion finer, leading to difficult settling. Thus of the three available diameters (300 µm, 500 µm and 800 µm) 800 µm microbore tube was chosen for these experiments. O/A ratio was 1. Total flow rate was varied in the range 0.03-1.2 LPH. Settling was slow for flow rates more than 0.6 LPH. The flow patterns observed in 800 µm microbore tubes for the same phase system sans uranium and corresponding settling behavior are shown in Fig. 2. The dispersion becomes finer as the flow rate increases leading to difficult phase separation. For the system containing uranium, quick settling was observed up to 0.6 LPH total flow rate at O/A = 1. Fig. 3 shows the variation of stage efficiency and percentage extraction with flow rate. From 0.03 LPH to 0.6 LPH, stage efficiency reduces monotonically. In this range flow pattern is slug flow and reduction in stage efficiency is due to reduction in contact time. When flow rate is
increased beyond 0.6 LPH, oscillatory trends, attributable to transitions in flow pattern and combined effect of increase in specific interfacial area and reduction in contact time, are observed. Though for flow rates less than 0.6 LPH higher stage efficiencies are observed, choosing a flow rate lower than 0.6 LPH will reduce the capacity. Lower stage efficiency at 0.6 LPH can be increased by using longer tubes. Thus 0.6 LPH is taken as the maximum flow rate microbore tube of 800 µm diameter can handle.

**Effect of Microbore Tube Diameter**

Further experiments were done to check if 0.6 LPH flow rate can also be handled by microbore tubes of smaller diameters. Fig. 4 shows that stage efficiency increases with reduction in microbore tube diameter. Table 1 documents the pressure drop and settling behavior observed for microbore tubes of different diameters and shows that 300 µm microbore tube cannot be used despite giving the

<table>
<thead>
<tr>
<th>d (µm)</th>
<th>L (cm)</th>
<th>Q (LPH)</th>
<th>t (s)</th>
<th>O/A</th>
<th>η</th>
<th>PE</th>
<th>∆P (bar)</th>
<th>Settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>120</td>
<td>0.6</td>
<td>0.5</td>
<td>1/1</td>
<td>80</td>
<td>71</td>
<td>21</td>
<td>Very slow</td>
</tr>
<tr>
<td>500</td>
<td>43</td>
<td>0.6</td>
<td>0.5</td>
<td>1/1</td>
<td>49</td>
<td>46</td>
<td>4</td>
<td>Fast</td>
</tr>
<tr>
<td>800</td>
<td>18</td>
<td>0.6</td>
<td>0.5</td>
<td>1/1</td>
<td>46</td>
<td>43</td>
<td>1</td>
<td>Fast</td>
</tr>
</tbody>
</table>
highest stage efficiency as pressure drop is very high and settling is very slow. For 500 μm microbore tube also pressure drop is more than 2 bar, the maximum admissible limit set by us. Thus of the three diameters 800 μm is considered as the one capable of handling high throughput with quick settling and low pressure drop. d, L, Q, τ and ∆P in Table 1 represent diameter of the microbore tube, length of the microbore tube, total flow rate, contact time and pressure drop, respectively.

**Effect of Length of Microbore Tube**

Further experiments were carried out to find out to what extent stage efficiency can be improved by increasing the length without breaching the upper limit on the pressure drop. Changing of contact time by changing length of microbore tube ensures that the quality of dispersion remains same and thus settling is not affected. Fig. 5 shows the effect of length of microbore tube on stage efficiency and percentage extraction. Table 2 compiles the data resulting from this set of experiments. Stage efficiency increases with increase in the length of microbore tube when it is increased from 16 cm to 67 cm, thereafter the increase is not significant. Pressure drop is not more than 2 bar despite increase in length. Thus the optimum configuration, highlighted in bold font in Table 2, giving high stage efficiency, quick settling and low pressure drop consists of a 67 long microbore tube of diameter 800 μm connected to an opposed T-junction of 750 μm diameter. The maximum capacity of the configuration is 0.6 LPH and stage efficiency obtained at O/A = 1/1 is 95% in contact time of 2 sec.

**Experiments with Parallel Microbore Tubes**

**Experiments at Total Throughput of 1 LPH**

To achieve higher throughputs multiple optimum configuration can be arranged in parallel. Number of parallel paths can be decided considering that flow through each path should not exceed 0.6 LPH. For 1 LPH total throughput, experiments were conducted using two parallel paths. Table 3 summarizes the results and shows that high stage efficiency (90-100%) can be achieved with short contact time of 2.5 sec for O/A ratio ranging from 1/2 to 2/1 at total throughput of 1 LPH.

**Comparison of Micro-scale Extractor with a Mixer-settler**

Table 4 shows comparison of the micro-scale extractor and a mixer-settler. V_m and V_s represent mixer and settler volumes, respectively. For the micro-scale extractor data given in the second row of Table 3 are used. Contact time in the micro-scale extractor is very small (2.5 sec) causing inventory of

<table>
<thead>
<tr>
<th>d (µm)</th>
<th>L (cm)</th>
<th>Q (LPH)</th>
<th>τ (s)</th>
<th>O/A</th>
<th>η</th>
<th>PE</th>
<th>∆P (bar)</th>
<th>Settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>16</td>
<td>0.6</td>
<td>0.5</td>
<td>1/1</td>
<td>22</td>
<td>21</td>
<td>1</td>
<td>Fast</td>
</tr>
<tr>
<td>800</td>
<td>34</td>
<td>0.6</td>
<td>1.0</td>
<td>1/1</td>
<td>68</td>
<td>60</td>
<td>1</td>
<td>Fast</td>
</tr>
<tr>
<td>800</td>
<td>50</td>
<td>0.6</td>
<td>1.5</td>
<td>1/1</td>
<td>88</td>
<td>78</td>
<td>1</td>
<td>Fast</td>
</tr>
<tr>
<td><strong>800</strong></td>
<td><strong>67</strong></td>
<td><strong>0.6</strong></td>
<td><strong>2.0</strong></td>
<td><strong>1/1</strong></td>
<td><strong>95</strong></td>
<td><strong>84</strong></td>
<td><strong>1</strong></td>
<td><strong>Fast</strong></td>
</tr>
<tr>
<td>800</td>
<td>135</td>
<td>0.6</td>
<td>4.0</td>
<td>1/1</td>
<td>95</td>
<td>84</td>
<td>2</td>
<td>Fast</td>
</tr>
</tbody>
</table>
Table 3: Results of experiments carried out at 1 LPH total throughput

<table>
<thead>
<tr>
<th>d (µm)</th>
<th>L (cm)</th>
<th>Q (LPH)</th>
<th>τ (s)</th>
<th>O/A</th>
<th>η</th>
<th>PE</th>
<th>ΔP (bar)</th>
<th>Settling</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>67</td>
<td>1.0</td>
<td>2.5</td>
<td>1/2</td>
<td>100</td>
<td>67</td>
<td>1</td>
<td>Fast</td>
</tr>
<tr>
<td>800</td>
<td>67</td>
<td>1.0</td>
<td>2.5</td>
<td>1/1</td>
<td>96</td>
<td>87</td>
<td>1</td>
<td>Fast</td>
</tr>
<tr>
<td>800</td>
<td>67</td>
<td>1.0</td>
<td>2.5</td>
<td>2/1</td>
<td>93</td>
<td>97</td>
<td>1</td>
<td>Fast</td>
</tr>
</tbody>
</table>

Table 4: Comparison of the micro-scale extractor with a mixer-settler

<table>
<thead>
<tr>
<th>Micro-scale extractor</th>
<th>Mixer-settler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis</td>
<td>Value</td>
</tr>
<tr>
<td>Q (LPH)</td>
<td>Experiment</td>
</tr>
<tr>
<td>τ (sec)</td>
<td>Experiment</td>
</tr>
<tr>
<td>Vm (ml)</td>
<td>Vm = τ Q</td>
</tr>
<tr>
<td>Vs (ml)</td>
<td>Experiment</td>
</tr>
<tr>
<td>SER (mol sec⁻¹ m⁻³)</td>
<td>0.027</td>
</tr>
</tbody>
</table>

Liquid in it to be very small compared to a mixer-settler. Values used to estimate SER for a mixer-settler (τ = 60 sec, Vs = 3Vm) are typical values used for mixer-settler. As shown in Table 4, SER in the micro-scale extractor is estimated to be more than four times of the same in a mixer-settler.

**Extraction and Stripping Experiments**

In these experiments uranium from a dilute aqueous stream is first extracted using 30% TBP in dodecane in a single-stage contact in the micro-scale extractor. The loaded organic is then stripped using 1N NaHCO₃ in a single-stage contact in the micro-scale extractor. The results obtained from these experiments are summarized in Table 5. Cₐₑₑ represents the concentration of uranium in the aqueous product stream from the stripping stage. With O/A = 1 in extraction and O/A = 2 in stripping the concentration of uranium in the raffinate and the product was 68 and 1260 ppm, respectively. With O/A = 2 in extraction and O/A = 4 in stripping, the concentration of uranium in the raffinate and the product was 30 and 1159 ppm respectively. These concentrations of uranium in the aqueous product stream from the stripping stage may not be enough for direct precipitation. For higher uranium concentration in the aqueous product stream obtained from the stripping stage, a two-step procedure can be adopted. In the first step uranium can be concentrated in the organic phase by keeping

Table 5: Results of extraction and stripping experiments (feed concentration = 734 ppm)

<table>
<thead>
<tr>
<th>Extraction O/A</th>
<th>Stripping O/A</th>
<th>Cₑₑₑₑ (ppm)</th>
<th>Cₐₐₐₐ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>68</td>
<td>1260</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
<td>30</td>
<td>1159</td>
</tr>
<tr>
<td>1/2</td>
<td>4</td>
<td>173</td>
<td>3620</td>
</tr>
</tbody>
</table>
low O/A in the extraction stage. In the second step uranium should be concentrated in the strippant by keeping high O/A ratio in stripping. For O/A = ½ in extraction stage and O/A = 4 in the stripping stage a high uranium concentration of 3620 ppm could be achieved in the aqueous product stream from the stripping stage. But, due to low O/A in the extraction stage, concentration of uranium in the raffinate was 173 ppm. In this study only single-stage experiments are carried out. However, it is expected that in a multistage contact with O/A = ½ in extraction and O/A = 4 in stripping, low concentration of uranium in raffinate as well as high concentration of uranium in the aqueous product stream from stripping can be achieved.

Conclusions

Micro-scale extraction of uranium from dilute solutions is studied using microbore tubes. A configuration consisting of a 750 µm opposed T-junction having microbore tube of diameter 800 µm and length 67 cm on its down stream side is identified as the optimum configuration that can handle a total throughput of 0.6 LPH while giving 95% stage efficiency in contact time of 2 sec with quick settling of resulting dispersion and less than 1 bar pressure drop. Micro-scale solvent extraction at total throughput of 1 LPH is demonstrated using two parallel paths of this optimum configuration. Using single-stage extraction and strippiing, high concentration of uranium in the product could be obtained. Specific extraction rate in the micro-scale extractor is estimated to be more than 4 times of the same in a mixer-settler. The study highlights possibility of intensification and confident scale-up of solvent extraction process for recovery of uranium from dilute solutions by using micro-scale extractors.

References