NON-DISPERSE SOLVENT EXTRACTION OF NEODYMIUM (III) USING A HOLLOW FIBER CONTACTER WITH TODGA AS THE EXTRACTANT

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Abstract
Membrane based non-dispersive solvent extraction (NDSX) of Nd(III) from aqueous nitric acid medium was carried out using a commercial liquid-liquid extraction system consisting of an extra-flow hollow fiber module with about 10,000 microporous hydrophobic polypropylene capillaries with an effective surface area of 1.4 m². The NDSX operation was carried out by pumping about 1 g/L Nd(III) solutions at a fixed nitric acid concentration of 3.57 M through the tube side and organic solvent (tetra-n-octyl-3-oxapentane-diamide (TODGA) in normal paraffin hydrocarbon (NPH)) through the shell side of the hollow fiber capillaries. Mass transfer modeling was reported in the present paper.

Introduction
Hollow fiber membrane based separation studies include operations in the (i) supported liquid membrane (SLM) mode where the organic phase is impregnated in the pores of the hollow fibers, (ii) strip dispersion mode where the feed solution is passed from one side and the organic phase dispersed in strip phase is passed from the other side of the module, and (iii) non-dispersive solvent extraction (NDSX) mode where the organic and aqueous phases are passed through the two sides of the module. In NDSX mode, the organic and aqueous phases come into contact without being dispersed, and hence have the advantages of solvent extraction without the need of phase separation [1].

In the present work the NDSX of Nd(III) was carried out by 0.1M TODGA + 0.5M DHOA in NPH employing hollow fiber membrane technique. Mass transfer modeling was also done to understand the mechanism of Nd(III) extraction.

Experimental
TODGA and DHOA were synthesized indigenously as reported earlier [2]. All the chemicals used were of analytical reagent grade. A 28.25cm long module with 6.65cm diameter was employed in the present studies. The total effective surface area was 1.4 square meters with ~10,000 fibers. The internal diameter of the hollow fiber (lumen) was 220mm having 40% porosity. The specifications of the hollow fiber contactor are given in Table 1. To avoid the mixing of two phases, aqueous phase was passed through the lumen side at a pressure of 3 psi and the organic phase through shell side in counter current mode. The organic phase used was 0.1M TODGA + 0.5M DHOA dissolved in NPH. The flow rates of both the phases were maintained constant with the help of gear pumps equipped with precise flow control. A schematic representation of the non-dispersive extraction set up is shown in Fig. 1. All the experiments were performed in the recycling mode of operation as mentioned earlier [3].
Results and Discussion

The organic phase (0.1 M TODGA + 0.5 M DHOA in NPH) flow rate varied in the range 100 mL/min to 500 mL/min in co-current as well as counter-current mode at constant flow rate (300 mL/min) of aqueous phase (1 g/L Nd at 3.57 M HNO₃) indicated that increasing the organic phase flow rate had no significant variation in the percent extraction where >99% extraction of Nd was achieved in about 30 minutes at all the flow rates. Similarly, the aqueous flow rate variation experiments carried out at constant organic phase flow rate (300 mL/min) indicated that increasing the aqueous phase flow rate has a positive influence on the NDSX of Nd. A plateau was observed in almost all the cases other than 50 mL/min for an operation time of 20 minutes or more.

Mass transfer modeling

The steps in the NDSX process were assumed to be as: (1) the metal ion/metal species in the feed phase diffused from the bulk to the feed-membrane interface (inside wall of fiber) through the aqueous diffusion layer. Secondly, at the feed-membrane interface, metal ions react with the extractant (TODGA) in organic phase in the membrane pores to form metal-ligand complexes. Thirdly, metal-ligand complex diffuses from the feed-membrane interface to the outside wall of fiber through the filled membrane pores, while the free ligand diffuses in the opposite direction from the shell side boundary wall to the inner boundary wall. Finally, the metal-extractant complex diffused from the outside fiber wall to the bulk organic phase. Based on this mechanism, the overall mass transfer coefficient $K_m$ were calculated from the following equation reported earlier [4],

\[
\frac{1}{K} = \frac{1}{k_a} + \frac{1}{D k_m} + \frac{1}{D k_o} \quad \cdots \cdots \quad (1)
\]

where $k_a$, $k_m$ and $k_o$ are the individual aqueous, membrane and organic mass transfer coefficients, respectively; and D is the distribution ratio. The membrane mass transfer coefficients ($k_m$) and aqueous mass transfer coefficient ($k_a$) were calculated for an identical system involving hollow fiber supported liquid membrane as $3.25 \times 10^{-5}$ and $1.04 \times 10^{-4}$ cm/s, respectively [2]. From the overall mass transfer coefficients calculated in the present study, and the D value for

**Table 1: Specifications of hollow fiber membrane contactor**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
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<tbody>
<tr>
<td>Fibre type</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>Number of fibers</td>
<td>9950</td>
</tr>
<tr>
<td>Fibre internal diameter (μm)</td>
<td>240</td>
</tr>
<tr>
<td>Fibre outer diameter (μm)</td>
<td>300</td>
</tr>
<tr>
<td>Fibre wall thickness (μm)</td>
<td>30</td>
</tr>
<tr>
<td>Effective pore size (μm)</td>
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</tr>
<tr>
<td>Porosity (%)</td>
<td>40</td>
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<tr>
<td>Tortuosity</td>
<td>2.5</td>
</tr>
<tr>
<td>Effective fiber length (cm)</td>
<td>15</td>
</tr>
<tr>
<td>Effective surface area (m²)</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Figs.1a & b: Schematic representation of the NDSX process in hollow fibre liquid membrane; (a) hollow fibre assembly; (b) hollow fiber module
Nd(III) reported in literature, the organic mass transfer coefficient was calculated as \(1.57 \times 10^{-5}\) cm/s.

Table 2 shows the overall mass transfer coefficients for different aqueous feed flow rates while keeping all other conditions same. A decrease in the \(k_m\) value was observed with increasing the flow rate which almost stabilized at higher flow rates. This was explained on the basis of higher mass transfer rates at the feed – membrane interface in the lumen side tending towards attainment of steady state. On the other hand, increasing the flow rate beyond a certain value makes this improbable.

In general, increasing the time of contact also increases the mass transfer coefficient. However, optimization of contact time as well as flow rate is required for getting favourable mass transfer. Fig. 2 shows a three dimensional plot of variation of \(K_m\) with contact time and flow rate. The overall mass transfer coefficient also decreases with metal ion concentration [4]. Fig. 3 shows the straight line plot of \(K\) with increasing Nd content in the feed. In these studies, the feed volume was changed while keeping Nd concentration constant at 1 g/L. The trends are similar to those reported by Yang and Cussler for the extraction of Cu(II) using HD2EHP [4].

References