Transport of textile anionic dyes using cationic carrier by bulk liquid membrane

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Received 14 December 2004; revised 21 February 2005; accepted 05 May 2005

Tetrabutylammonium bromide (TBAB) has been used as carrier for the transport of dyes through methylene chloride. Using 1:1 M salicylic acid in sodium carbonate in the receiving phase, the amount of dye transported across the U-type bulk liquid membrane (BLM) after 70 min was found to be 97 ± 2 %. The percent recovery of dyes is not found to decrease in the presence of anions (Cl\(^-\) and SO\(_4\)^-\) in the feed solution.

Keywords: TBAB, Dye transport, BLM
IPC Code: B 08 B 3/00

Introduction

Large quantities of dyes are manufactured annually world wide and used in textile, paper, foodstuffs and cosmetics industries. The conventional biochemical technique is inadequate and not cost effective in removing organic dyes from water. A novel method of using colloidal gas alphorns (CGA) was proposed by Roy et al\(^1\) for the removal of organic dyes from wastewater. Cloud point separation of dyes has also been reported\(^2,3\). A number of successful researches involving the transport of metal ions\(^4,5\), rare earth elements\(^6\), drugs\(^7\), phenols\(^8-10\), lactic acids\(^11\), fructose\(^12\), and treatment of seawater and wastewater\(^13,14\) through the liquid membrane have been carried out. Liquid membrane technology has reached pilot plant stage in some cases\(^15,16\). No study is reported for recovery of dye from effluents using bulk liquid membrane (BLM), though reports on solvent extraction are available\(^17,18\).

The paper presents membrane extraction of anionic dyes using BLM technique with cationic tetrabutylammonium bromide (TBAB) carrier. The effects of TBAB in membrane, pH of source phase, concentration of salicylic acid in receiving phase and stirring rate are also reported.

Experimental Details

Reagents and Apparatus

TBAB was purchased from Merck. Analytical grade methylene chloride (Merck) was used as the organic membrane solvent. Textile anionic dyes Golden yellow LS (\(\lambda_{\text{max}} = 385 \text{ nm}\)) and Cibacron (\(\lambda_{\text{max}}=621 \text{ nm}\)) were kindly donated by Dy Star (India) and Ciba Specialty Chemicals (Switzerland) respectively. The spectrophotometer was Spekol 1200 (Analytical Jena) instrument and pH measurements were made using WTW pH meter (Germany).

Procedure

All experiments were carried out at ambient temperature (27±0.5\(^\circ\)C). The aqueous source phase (100 ml) contained 50 ppm of dye and strip phase (100 ml) contained 1:1 M salicylic acid in sodium carbonate solution. The methylene chloride solution (100 ml) contained TBAB (0.05 %), below which aqueous phases bridged the two phases. The organic layer was stirred by a teflon coated magnetic bar (2.0 cm) and both aqueous layers (feed and strip) were stirred by mechanical stirrer. In transport experiments, samples of both aqueous phases were measured by spectrophotometer. A similar experiment was carried out in the absence of the carrier.

The permeability coefficients were calculated using following expression\(^19\):

\[ \ln \left( \frac{C_t}{C_0} \right) = -\frac{Q PrV}{P} \quad \ldots \ (1) \]

where \(C_t = \text{Dye concentration in the feed at time } t\); \(C_0 = \text{Dye concentration in the feed at the beginning of the experiment}\); \(P = \text{Permeability coefficient}\); \(Q = \text{Effective membrane area in cm}^2\); \(V = \text{Volume of the feed in cm}^3\).

The cumulative percentage transport \(T\) of dye at a given time is determined by the following equation:

\[ T = \frac{\sum C_t \times V}{\sum C_0 \times V} \times 100 \]

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% $T = 100 \frac{C_t}{C_0}$ \hspace{1cm} ... (2)

**Results and Discussion**

In the preliminary experiments, the extent of TBAB mediated transport of dye to basic aqueous receiving phase was quite high. In the next step, the experimental variables (pH of source phase, salicylic acid in sodium carbonate in receiving phase and TBAB in organic phase) were optimized to achieve the highest efficiency in the transport of dye across the membrane system.

**Effect of pH of the Source Phase**

The effect of pH (1-9) of the source phase on the efficiency of golden yellow dye transport was studied (Fig 1). The results revealed that the efficiency of transport was marginally increased up to pH 5 and was maximum (97%) at pH 5 to 7.5. At higher pH (pH >8) transport of the dye was decreased. pH 7±0.2 was selected for further studies.

**Effect of TBAB Concentration in Organic Phase**

The influence of TBAB (0.0125-0.2 %) in organic phase on the transport efficiency of dye was studied (Table 1). The percentage transport of dye was found to increase with an increase in TBAB concentration with a maximum transport at about 0.05 percent. At higher concentration of the carrier, the extraction of dye into membrane phase was very high. But at the higher carrier concentration, the dye in strip was low, as higher carrier concentration does not favour the release of dye. It was only partially released into receiving phase. Hence, in all further experiments, the carrier concentration was maintained at 0.05 percent in organic phase.

**Effect of Stripping Reagent**

Stripping agents for recovery of the extracted dye by solvent extraction has been studied earlier. Stripping agent in receiving phase. During stripping, emulsion was formed in the organic and aqueous phase where benzoic acid dissolved in potassium hydrogen phosphate and sodium hydrogen phosphate was used as a stripping agent. No emulsion formation was found when salicylic acid (dissolved in sodium carbonate) was used as stripping agent. 1:1 $M$ Salicylic acid in sodium carbonate has been found the best-stripping agent to recover dye from source phase (Table 2).

![Fig 1](image.png)

**Table 1** — Effect of TBAB concentration in organic phase

<table>
<thead>
<tr>
<th>TBAB in CH$_2$Cl$_2$</th>
<th>Dye in source phase</th>
<th>Dye in receiving phase</th>
<th>Dye in organic phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>%</td>
<td>%</td>
<td>%</td>
</tr>
<tr>
<td>0.0125</td>
<td>7.0</td>
<td>72.0</td>
<td>18.0</td>
</tr>
<tr>
<td>0.0250</td>
<td>6.5</td>
<td>85.0</td>
<td>6.2</td>
</tr>
<tr>
<td>0.0500</td>
<td>3.0</td>
<td>97.1</td>
<td>1.0</td>
</tr>
<tr>
<td>0.1000</td>
<td>2.0</td>
<td>95.0</td>
<td>3.0</td>
</tr>
<tr>
<td>0.2000</td>
<td>2.0</td>
<td>93.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Experimental conditions: Source phase, 100 ml of 50 mg dye at pH 7; Liquid membrane phase, 100 ml of 0.05 % TBAB; Receiving phase, 100 ml of different stripping agent; Rate of stirring, 250 rpm; Time of transport, 70 min.

**Table 2** — Effect of stripping reagent

<table>
<thead>
<tr>
<th>Stripping agent</th>
<th>pH</th>
<th>Dye transported %</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 % KHP</td>
<td>4</td>
<td>97</td>
<td>Nil</td>
</tr>
<tr>
<td>C$_6$H$_5$COOH + K$_2$HPO$_4$</td>
<td>10</td>
<td>50</td>
<td>Emulsion was formed in organic phase</td>
</tr>
<tr>
<td>C$_6$H$_5$COOH + Na$_2$HPO$_4$</td>
<td>12</td>
<td>55</td>
<td>Emulsion was formed in both phases</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + Na$_2$HPO$_4$</td>
<td>12</td>
<td>65</td>
<td>No emulsion</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + K$_2$HPO$_4$</td>
<td>12</td>
<td>65</td>
<td>No emulsion</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + NaOH</td>
<td>12</td>
<td>55</td>
<td>No emulsion</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + Na$_2$CO$_3$ (1:1 M)</td>
<td>11</td>
<td>97</td>
<td>No emulsion</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + Na$_2$CO$_3$ (2:1 M)</td>
<td>11</td>
<td>95</td>
<td>No emulsion</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + NaHCO$_3$ (1:1 M)</td>
<td>7.5</td>
<td>90</td>
<td>No emulsion</td>
</tr>
<tr>
<td>C$_6$H$_5$OHCOOH + NaHCO$_3$ (2:1 M)</td>
<td>7.5</td>
<td>87</td>
<td>No emulsion</td>
</tr>
</tbody>
</table>

Experimental conditions: Source phase 100 ml 50 mg dye at pH 7; Liquid membrane phase, 100 ml of 0.05 % TBAB; Receiving phase, 100 ml of different stripping agent; Rate of stirring, 250 rpm; Time of transport, 70 min.
Effect of Diluents

Extraction efficiency of dye from aqueous solution (50 mg) was studied using TBAB (0.05 %) in various diluents (Fig 2). Diluents (CCl₄, CHCl₃) show lower extraction efficiency of dye, whereas good extraction of dye was from CH₂Cl₂, which was used as diluent in this study.

Effect of Time

The time profiles (Fig 3) of dye transport in the various phases (source, organic, receiving) show a rapid rise in dye concentration in the receiving phase and a sharp decrease in the source phase during the first 50 min of transport. After 50 min, dye transport was as follows: receiving phase, 90; source phase, 2; and organic phase, 8 %. After 65 min, almost all dye in source phase transported, but residual dye in the membrane slowly transported to receiving phase. After this, no transport of dye occurred. Hence, transport studies were carried for 70 min.

Effect of Stirring Speed

At a stirring speed of 250 rpm, 97 percent dye transported from the feed to strip with in 70 min, whereas for stirring speed of 150 rpm, 76 percent of the dye transported (Fig 4). The stirring speed could not exceed 300 rpm because intermixing of feed solution to strip solution was noticed at higher stirring speed.

Effect of Initial Dye Concentration in the Source Phase

The effect of dye concentration (50-100 mg) in the source phase was investigated at 0.05 % TBAB in methylene chloride. The percentage removal of dye decreases with increase in dye concentration (Table 3). At the dye concentration of 50 mg, 97 percent extraction was observed. With further increase in dye concentration, percent of dye extraction decreased. However, the absolute amount of dye extracted increased with increasing dye concentration.

Effect of Anion Concentration

In the actual textile dye bath effluent, the dye will present along with salts like NaCl and Na₂SO₄. The percentage removal of dye from aqueous solution in the presence of TBAB as a carrier at neutral pH is not affected with the increase in NaCl and Na₂SO₄ up to 5000 ppm (Table 4). This shows the selectivity of the

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Table 3—Effect of source phase concentration of dye

<table>
<thead>
<tr>
<th>Concentration of dye</th>
<th>Dye remaining in source phase</th>
<th>Dye transport to receiving phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mg in 100 ml</td>
<td>5.1</td>
<td>97.0</td>
</tr>
<tr>
<td>70 mg in 100 ml</td>
<td>9.8</td>
<td>90.1</td>
</tr>
<tr>
<td>90 mg in 100 ml</td>
<td>12.2</td>
<td>88.1</td>
</tr>
<tr>
<td>100 mg in 100 ml</td>
<td>15.2</td>
<td>84.8</td>
</tr>
</tbody>
</table>

Experimental conditions: Source phase, pH 7; Liquid membrane phase, 100 ml of 0.05 % TBAB; Receiving phase, 100 ml of (1:1 M) salicylic acid in sodium carbonate; Rate of stirring, 250 rpm; Time of transport, 70 min.
transport of anionic dyes. The efficiency of transport of dyes depends on the concentration of receiving phase. Therefore, the above system, which is specific for anionic dyes, can be a potential candidate for practical use of dye separation with advantages of high efficiency, selectivity, simplicity and speed.

Acknowledgement
The authors thank Dy Star Ltd for providing the dyes.

References
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