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Recovery of Golden yellow and Cibacron LSG dyes from aqueous solution by bulk liquid membrane technique

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Abstract *Tri-n*-butyl phosphate (TBP) was used as carrier for the transport of Golden yellow and Cibacron LSG dyes through a hexane bulk liquid membrane. The transport efficiency of dyes by TBP was investigated under various experimental conditions such as pH of the feed phase (dyes solution), concentration of the receiving phase (NaOH solution), concentration of TBP in membrane, rate of stirring, effect of transport time, type of solvent, dye concentration in feed phase, effect of temperature.. The maximum transport dyes occurs at ratio of 1:1 TBP-hexane At pH 3.0 0.1 (feed phase) the transport dyes decreased. At high stirring speed (300 rpm) the dyes transport from the feed phase to the strip phase was completed within 60 minutes at 27ºC. Under optimum conditions: Feed phase 100 mg/L dyes solution at pH 1.0 0.1, receiving phase 0.1 mol/L NaOH solution, membrane phase 1:1 TBP-hexane , Stirring speed 300 rpm and temperature 27ºC, the proposed liquid membrane was applied to recover the textile effluent.

Keywords: bulk liquid membrane; transport; feed phase; receiving phase; stirring speed; textile effluent; recovery

1. Introduction

Dyes are used in industry such as paper, rubber, plastic and textile etc., to impart the colour to products (Malik 2003). They are classified as anionic-acid, direct and reactive, cationic-basic and non-ionic directive dyes (Masu *et al*. 2005). It is estimated that more than 100,000 commercially available dyes with over 7×10^5 tons of dyestuffs are annually produced (Lee *et al.* 2006). Cibacron LSG and Golden yellow dyes are commonly used for dyeing cotton, wool and silk materials. Though they are not hazardous it is essential to recover from textile effluent. Various methods are available to treat dye wastewater.

It consists of physical, chemical and biological methods. These include: adsorption (Shangi and Bhattarchrya 2002), nanofiltration (Koyuncu 2003), colloidal gas aphrons (Roy *et al*. 1992), ultrasonic decomposition (Ge and Qu 2003), electro coagulation (Alinsafi *et al*. 2004), coagulation and precipitation (Liu *et al.* 2003), Chemical oxidation and ozonation (Arslan 2000 Gould 1987), electrochemical oxidation (Lopez Gromau and Gutierrez 2006), photo oxidation (Carneiro *et al.* 2006), surface methodology (Lau and Ismail 2010), pre -dispersed solvent extraction (Lee etal 2000), solvent extraction (Muthuraman 2011 and Muthuraman *et al.* 2012), bulk liquid membrane (Muthuraman and Palanivelu 2008, Madaeni *et al.* 2012, Kaita Chakrabarty 2009), emulsion liquid membrane (Ng *et al.* 2009, 2010) supported liquid membrane (Muthuraman and Teng 2009,

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Muthuraman *et al.* 2010 Chiraz Zidi *et al.* 2011, Nosrati *et al.* 2011), and aerobic and anaerobic processes (Beydilli *et al.* 2000, Liakou *et al.* 2003).

The laboratory study of liquid-liquid extraction of golden yellow dye has also been studied. The dye was extracted into solvent mixture from acidic medium. The extracted dye was recovered from strip solution. (Muthuraman and Palanivelu 2004). Cibacron LSG was extracted from aqueous solution using tetra butyl ammonium bromide as a carrier. The extracted dye was stripped into salicylic acid solution (Muthuraman and Palanivelu 2005)

Liquid membrane is an alternative method over conventional treatment methods for industrial wastewater (Chimuka *et al.* 2004). This method provides low cost, simplicity, high efficiency and energy saving in comparison to classical solvent extraction processes. In the recent years a remarkable increase of the application of liquid membranes in separation processes has been observed. These membranes include bulk liquid membrane (BLM), emulsion liquid membrane (ELM) and supported liquid membrane (SLM) (Cezary *et al.* 2005, Yaamini *et al.* 2002).

In the current research, the extraction of golden yellow and Cibacron LSG from aqueous solution has been studied using bulk liquid membrane technique. Concentration of dyes, pH of source phase and strip phase, carrier concentration, solvent type, stirring speed, transport time, reuse of liquid membrane were elucidated. The proposed liquid membrane was applied to textile effluent.

2. Experimental

2.1 Reagents

Tri-n-butyl phosphate (99.8%) was used as a carrier without any further purification. Reagent grade Hexane (99.3%), xylene (99.5%) from Merck were used as membrane organic solvent. Golden yellow (99.7%) and Cibacron LSG (99.7%) were received from Dy star India Limited Chennai. NaOH (95%) pellets, H_2SO_4 (97%) and other acids were of the highest purity available from Merck used without further purification. Stock solution was prepared from doubly distilled water.

2.2 Apparatus and procedure

The BLM apparatus namely H-type used for the study is shown in Fig. 1. The inner dimension of the transport cell was 70-mm diameter × 190-mm depth for H-type. A barrier with 45-mm height (from the bottom) divided the cell into two compartments. Both feed and stripping solutions were

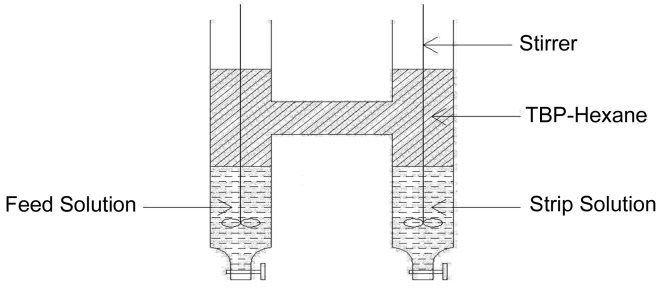

Fig. 1 Schematic experimental setup for H-type bulk liquid membrane for recovery of dyes from aqueous solution

(each 100 ml) stirred by mechanical stirrers at 300 rpm. The volume of the liquid membrane phase was 200 ml. Both interfaces (feed/membrane and membrane/stripping) were at the same level and were separated by a barrier. In transport experiments samples of both aqueous phases, dye concentration were measured by spectrophotometer

Kinetics of transport process across BLM can be described by a first order reaction with dye concentration (Cezary *et al.* 2002).

$$\ln c/c_i = -kt \tag{1}$$

Where c is the dye concentration (mg/L) in source phase at a given time, c_i is the initial dye concentration in the source phase, k is the rate constant (s^{-1}) and t is the transport time (s)

The permeability coefficient (P) was calculated as follows

$$P = -V/A\ k \tag{2}$$

Where V - Volume of aqueous in source phase (cm^3)
A - Effective area of the membrane (cm^2)
k - Rate constant

The flux (J) was calculated as follows Bukhari *et al.* (2004)

$$\text{Flux (J)} = \frac{\text{Dye conc.} \times \text{volume of solution in feed or strip } (cm^3)}{\text{Membrane area } (cm^2) \times \Delta t} \tag{3}$$

where Δt represents time interval in seconds

The percentage of dye transport was calculated as follows

$$\% = \frac{[D]_0 - [D]_t}{[D]_0} \times 100 \tag{4}$$

Where D_0 - Initial dye concentration at zero time(s)
D_t - Dye concentration at the time(mg/L)

3. Results and discussion

3.1 Effect of pH of the source phase

The effect of pH of source phase on the efficiency of dye transport was studied in the range (1.0 to 7.0) and the results are shown in Fig. 2 The results revealed that the efficiency of transport increases at pH 1.0 0.. This is because at lower pH, hydrogen ion concentration was high that the dye was transferred to organic phase very rapidly with the cationic TBP carrier. When pH was increased, hydrogen ion concentration was low and hence dye transfer to organic phase decreased due to less formation of cation $[R_3PH]^+$. From the results, a pH of 1.0 0.2 was selected for further studies in the source phase.

3.2 Effect of carrier concentration

The influence of the concentration of TBP in the organic phase on the transport efficiency of dye

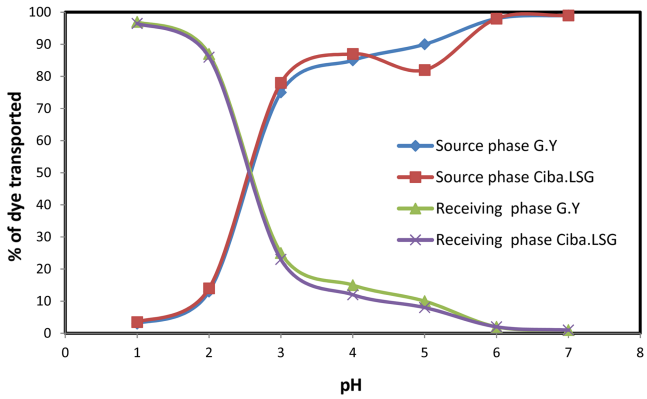

Fig. 2 Effect of source and receiving phase

Table 1 Effect of carrier composition on extraction of dye

TBP – hexane ratio	Dye remained in feed side (%)		Dye transported in receiving phase (%)	
	G.Y	Cib. LSG	G.Y	Cib. LSG
1 : 1	3.1	2.9	97.2	97.1
1 : 2	19.2	20.1	80.1	80.0
1 : 4	25.8	26.2	75.2	74.0
1 : 6	33.1	35.2	33.0	64.8
1 : 8	46.4	48.2	54.8	51.6

was also studied. The results are presented in Table 1. As it is evident, the percentage transport of dye decreases with decreasing concentration of TBP in hexane. Maximum transport of dye occurs at a ratio of 1:1 (TBP-hexane). A further excess of TBP has no significant effect on the transport efficiency.

Sarkar and Dhadke (1999) also found that increasing carrier (> 5×10^{-2} m of Cyanex 301) concentration had no considerable effect on the transport of bismuth. This is most probably due to the fixed stoichiometry of the resultant 1:1 carrier bismuth complex as well as the more or less constant viscosity of the membrane phase at this concentration range. Thus, concentration ratio of TBP-hexane (1:1) was adopted for further studies.

3.3 Effect of receiving phase concentration

In LLE, NaOH was used as stripping agent and thus sodium hydroxide (0.05 -1.5 M) was used to recover the dyes. Table 2 shows that an increase in NaOH concentration from 0.025M to 0.1 M increased the efficiency of dye transport and then remained constant. For further studies, 0.1 M NaOH concentrations was used as the receiving phase.

3.4 Influence of stirring speed

The influence of the stirring speed (100 – 350 rpm) of the aqueous phase was studied for mixing of both aqueous phase and to minimize the thickness of the aqueous boundary layer in the feed and

Table 2 Effect of receiving phase concentration

Receiving agent concentration	Dye remained in organic phase (%)		Dye transported into receiving phase (%)	
	G.Y.	Ciba. LSG	G.Y.	Ciba. LSG
0.025 M NaOH	10.0	12.0	89.0	87.0
0.05 M NaOH	6.5	6.3	93.1	93.6
0.1 M NaOH	3.1	2.8	97.2	97.2
0.5 M NaOH	2.9	2.8	97.1	96.8
1 M NaOH	3.1	3.0	97.1	97.0
1.5 M NaOH	3.1	3.0	97.1	97.0

strip solutions. The transport of dye is plotted vs stirring speed in Fig. 3. It can be seen that under higher stirring speed the transport increased rapidly. At a stirring speed 300 rpm, the dye transport from the feed to strip was completed with 60 min whereas it needs about 2 h at 150 rpm. This is mainly attributed to the increase in contact between the aqueous and membrane phase. It should be noted that the stirring speed could not exceeded 300 rpm because intermixing of feed and strip solutions at higher stirring speed was observed and transport of dye was decreased due to intermixing. Yang and Fane (1999) also observed similar effects at high mixing speed.

3.5 Effect of time on dye recovery

Fig. 4 shows the time dependence (0.25 to 1 h) of dye transport through the liquid membrane under the optimum experimental conditions. It is obvious that the increase in time increased the percentage transport of dye to the receiving phase and decreased the percentage of dye remaining in the source phase up to 55 min. The transport was nearly complete (97%) in 60 min.

3.6 Effect of salt concentration

In the actual textile dye bath effluent, the dye is along with salts like NaCl and Na_2SO_4. To

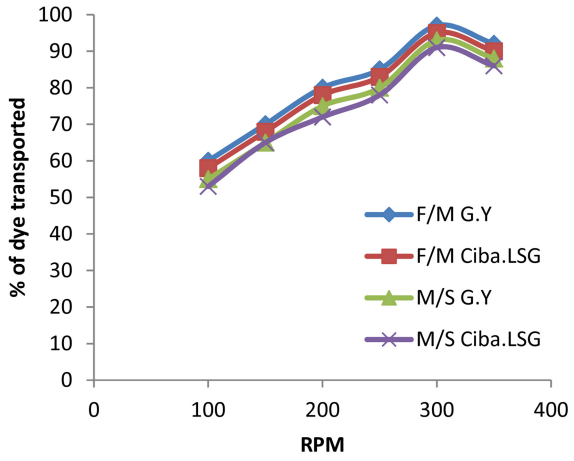

Fig. 3 Effect of stirring speed

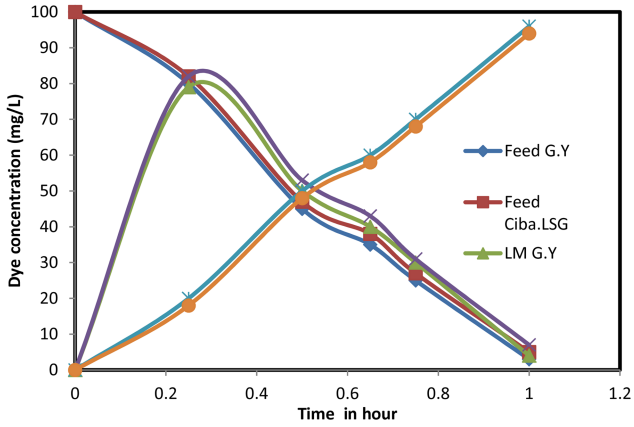

Fig. 4 Effect of time of varies phases (Feed, Membrane and Receiving)

Table 3 Effect of salt concentration

Anion Concentration (mg/L)	Dye remained in source phase (%)		Dye transported into receiving phase (%)	
	G.Y.	Ciba. LSG	G.Y.	Ciba. LSG
Sulphate				
1000	3.2	3.5	97.3	97.1
2000	3.3	3.7	97.1	96.5
3000	3.4	3.5	97.3	97.0
5000	3.6	3.4	97.2	97.0
Chloride				
1000	3.9	4.0	97.3	96.1
2000	3.8	4.1	75.0	73.0
3000	3.6	3.9	72.0	70.0
5000	3.8	4.0	69.0	67.0

understand the influence of sulphate and chloride concentration on dye extraction, dye solutions with different concentration of sodium chloride and sodium sulphate were prepared and tested at pH. 1.0 ± 0.2. In TBP-LLE system, the extraction efficiency of dye decreased with increasing chloride concentration (> 1000 mg/L). Similar results were obtained also in the present case. Table 3 shows the effect of NaCl and Na_2SO_4 on the percentage removal of dyes from aqueous solution in the presence of TBP as a carrier at pH 1.0 ± 0.2. The percentage removal of dye decreased beyond 1000 mgL^{-1} chloride concentration. However, the percentage removal of dye was not affected up to 5000 mgL^{-1} sulphate concentration.

3.7 Suggested mechanism

Based on the results obtained, the anionic dye transported across the TBP-BLM system can be explained as follows. The schematic diagram is shown in Fig. 4.

i. The extraction of dye from feed solution into organic membrane is accompanied by the presence

of TBP carrier as ion pair complex $[Dye]^-[R_3P^+H]$, the resulting neutral ion paired complex being preferentially distributed into the organic membrane.

ii. The ion-pair thus formed diffuses across the membrane

iii. At the membrane-strip solution interface i.e., in alkaline condition, the cationic carrier is converted into neutral TBP.

iv. The neutral carrier (TBP) diffuses back across the membrane to the feed solution membrane interface where the cycle starts again.

3.8 Reusability of liquid membrane

The reusability of bulk liquid membranes is shown in Fig. 5. When the stripped solvent was reused for dye transport, the transport efficiency did not decrease up to five cycles. After five cycles, decrease in efficiency of extraction was noticed

3.9 Reproducibility and kinetic study of BLM technique

The reproducibility of the above system was studied by performing five replicate transport experiments and was found to be 98.0 ± 1.0%. Using the above optimized parameters, the rate constant, permeability coefficient and flux were calculated. As it can be seen from Table 4 the rate constant, permeability coefficient and flux are decreasing with increasing dye concentration. This may be due to lowering of the dye transport. Cezary *et al.* (2002) also reported about decreasing rate constant, permeability coefficient and flux with increasing chromium concentration in the source phase of polymer inclusion membrane system.

3.10 Application

The developed BLM was tested for its applicability to real textile wastewater obtained from a dyehouse in Tiruppur, India. The general characteristics of the textile wastewater are given in Table 5.

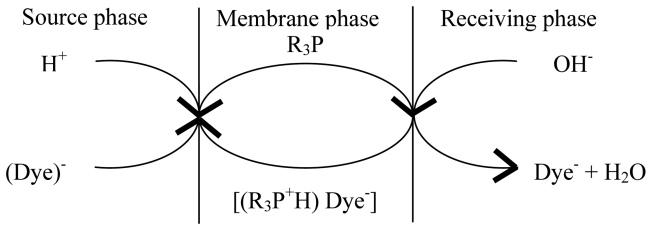

Fig. 5 Schematic diagram of transport mechanism of anionic dyes with TBP

Table 4 Kinetic parameters for transport of dyes through BLM by TBP as carrier

Conc in the source phase (mg/L)	Rate constant, k (h^{-1})	Permeability coefficient (cm/h)	Flux ($mg/cm^2/s$) $\times 10^{-5}$
100	2.9958	7.7893	7.0780
150	1.9476	5.0639	6.8613
200	1.4270	3.7103	6.5002

Table 5 Characteristics of textile effluent

Parameters	Dye bath	Wash bath
pH	10.8	10.6
λ_{max} (nm)	385 (Golden yellow)	385 (Golden yellow)
	621 (Cibacron LSG)	621 (Cibacron LSG)
Conductivity (mS/cm)	20.1	7.71
Nature of dye	Anionic	Anionic
Chloride (mg $CaCO_3$/L)	158.1	85.2
Carbonate (mg $CaCO_3$/L)	6500	32
Bicarbonate (mg/L)	750	100
Sulphate (mg/L)	3681	945
COD (mg/L)	640	340
TOC (mg/L)	275	150
TDS (mg/L)	11550	4090
Conc. of dye (mg/L)	125	10

Table 6 Comparative results of synthetic and textile effluent

Dye sample	Recovery (%)
Synthetic dye (50 mg/L)	
a. Golden yellow	97.8
b. Cibacron LSC	97.5
Dye bath (125 mg/L)	
a. Golden yellow	96.4
b. Cibacron LSC	96.1
Wash bath (10 mg/L)	
a. Golden yellow	97.5
b. Cibacron LSC	97.3

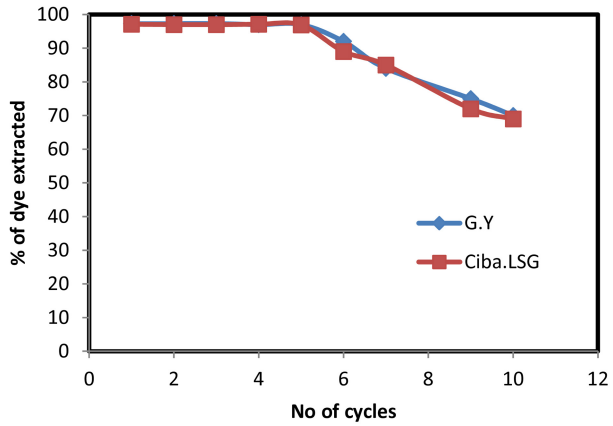

Fig. 6 Reusability of liquid membrane

The pH of the textile effluent was adjusted to 1.0 ± 0.2 and the optimum conditions already obtained for LM were used to find out the percentage recovery of dyes. The results, presented in Table 6, show that the recovery efficiency is almost same for synthetic solution and textile effluent.

4. Conclusions

Golden yellow and Cibacron LSG have been effectively transported by means of a liquid membrane containing TBP-hexane. The efficiency of the method depends on various parameters such as the pH of the donor and acceptor phase, effect of dye and carrier concentration, type of solvent, stirring speed and temperature. At low pH there was a increase in the transport of dye (donor phase) and the flux rate increased (acceptor phase) with increase in stirring speed. In optimized conditions the transport efficiency of dye for the 5 replicate measurements after 60 minutes was $98.1 \pm 1.1\%$. The proposed method was applied to textile wastewater. The transport efficiency after 60 minutes was 97 %.

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