

CHAPTER 4

RESULTS AND DISCUSSION

4.1 GENERAL

Studies on removal of silk dyes from aqueous solution using solvent extraction and liquid membranes were conducted in the laboratory to optimize various experimental conditions. The possibility of reuse of solvent and liquid membrane was also examined. The kinetics of transport of dyes was studied and the mass transfer coefficient of dyes (k) was also calculated. The efficiency of these methods was tested for removal of dyes from an industrial wastewater and the results obtained are discussed here.

4.2 PRELIMINARY STUDIES

Among the dyes used for dyeing in silk two acidic dyes and two basic dyes were selected for preliminary study. The charge and nature of these silk dyes were scanned and the results are presented in Table 4.1. From the results, it was found that the acid dyes scanned were anionic in nature while the basic dyes were cationic.

The calibration graphs for these four dyes are depicted in Figure 4.1(a), 4.1 (b), 4.1 (c) and 4.1 (d). Acid Red 10 B obeyed Beer's Law up to 50 mg/L and Acid Pink BE obeyed Beer's law till 90 mg/L where as both Rhodamine B and Methyl violet obeyed Beer's law up to 20 mg/L.

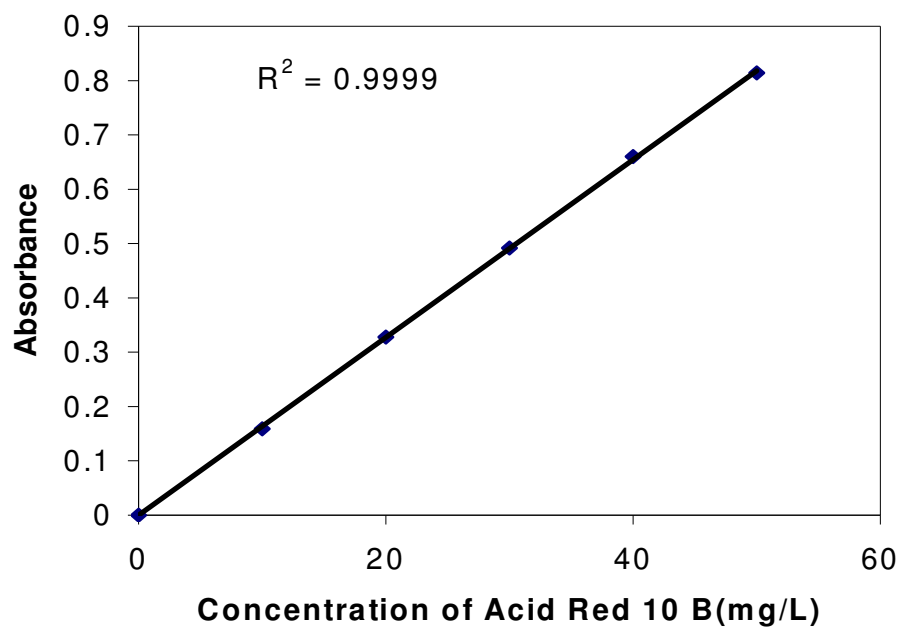


Figure 4.1(a) Calibration Graph for Acid Red 10 B

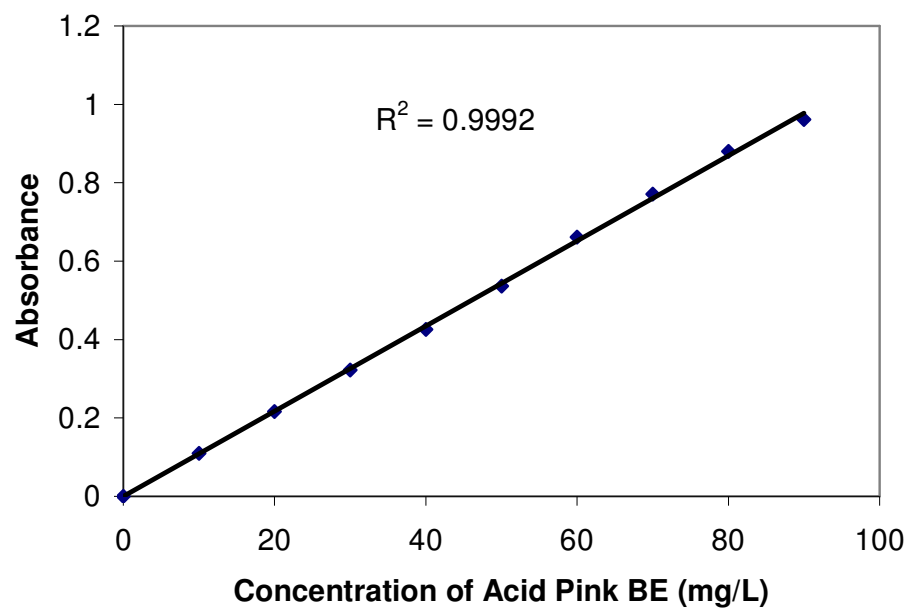


Figure 4.1(b) Calibration Graph for Acid Pink BE

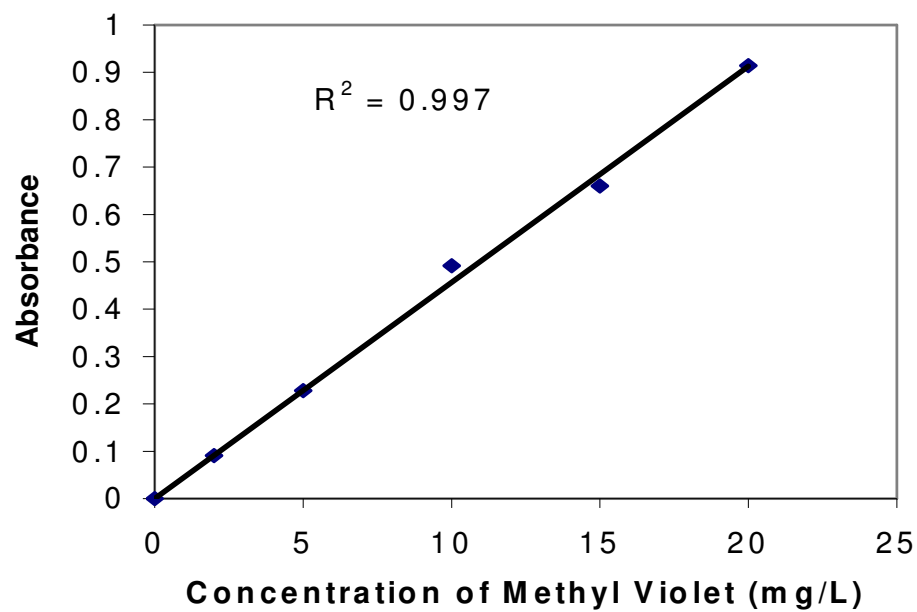


Figure 4.1(c) Calibration Graph for Methyl Violet

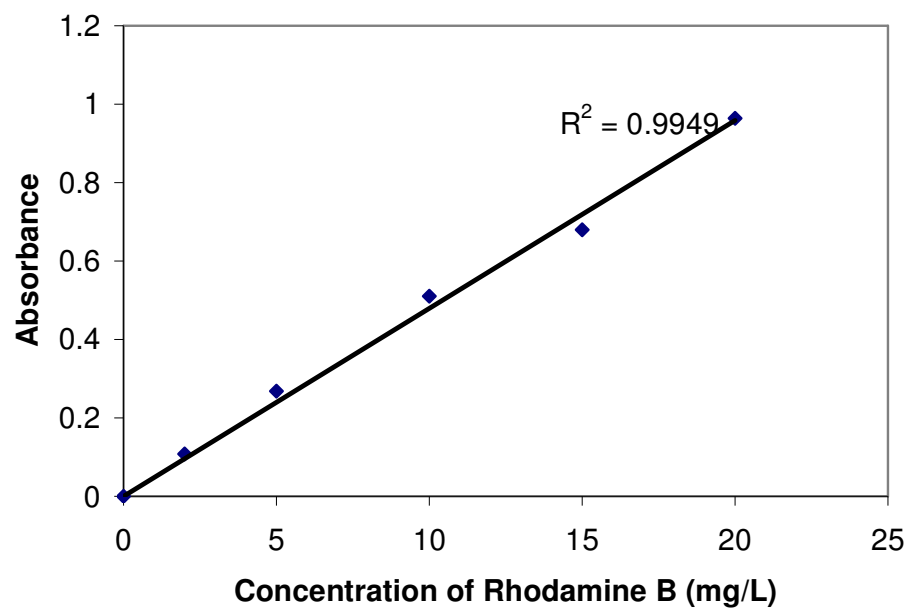


Figure 4.1(d) Calibration Graph for Rhodamine B

Table 4.1 Characteristics of Silk Dyes

Sl. No.	Name of the dye	λ_{max} (nm)	Charge	Beer's Law range (mg/L)
1.	Acid Red 10 B	566	Anionic	0-50
2.	Acid Pink BE	519	Anionic	0-90
3.	Methyl violet	584	Cationic	0-20
4.	Rhodamine B	555	Cationic	0-20

4.3 LIQUID-LIQUID EXTRACTION SYSTEM FOR ANIONIC DYES

With aim of choosing acid dyes from silk industry Acid Red 10 B and Acid Pink BE were selected for detailed studies.

4.3.1 Selection of Solvent for the Extraction of Acid Red 10 B and Acid Pink BE Anionic Dyes

Acid Red 10 B was tested using various solvents as listed in Table 4.2 at different pH conditions (pH 1-10). The equilibrium distribution coefficient obtained between aqueous phase (Acid Red 10 B) and organic phase using various solvents are given in Table 4.2. From the table, it is observed that TBP and TBP/Hexane have very higher distribution coefficient, which favour them as better extractants. Further TBP is more stable to acidic and oxidizing conditions. (Cuer et al 1974 and Shrichand and Jain 1995). Literature study reveals that the use of aliphatic solvents as a diluent are more favoured over the use of aromatic solvents (Islam and Biswas 1979 and Kondo et al 1995) and non-polar solvents have high distribution coefficient compared to polar solvents (Drapala et al 2004). Similarly high distribution coefficients were obtained for Acid Pink BE under the same extractants.

Even though both TBP and TBP/Hexane have very higher distribution coefficient, TBP/Hexane has been chosen for further studies. This is due to the fact that (i) viscosity of TBP is high compared to TBP/Hexane, which will show higher resistance for extraction (ii) the cost of TBP is also high. Various parameters such as effect of pH, stripping reagent concentration, aqueous/ solvent ratio, and carrier/diluent ratio were studied.

Table 4.2 Extraction Efficiency of Acid Red 10 B with Different Organic Solvents

(Conditions: Dye concentration 100 mg/L, pH 1.0 ± 0.1 , Volume of aqueous solution 30 mL, Volume of solvent 30 mL and equilibration time 5 min.)

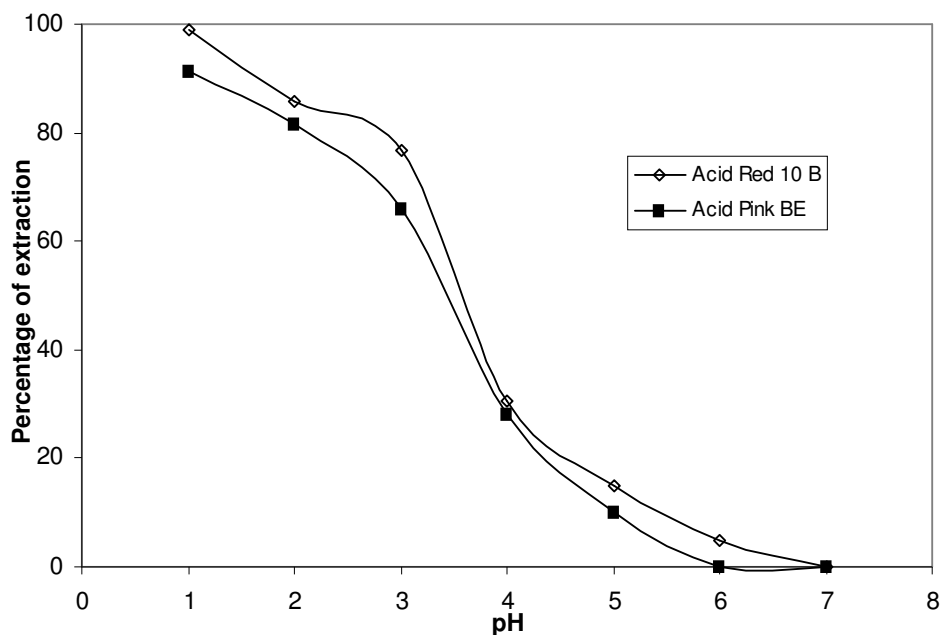
S.No.	Solvent	Percentage of extraction	Distribution coefficient (D)
1.	Hexane	3.5	0.04
2.	CCl ₄	Nil	0
3.	Toluene	Nil	0
4.	TBP	99.0	99.0
5.	CCl ₄ + TBP (1:1)	30.0	0.43
6.	Toluene + TBP (1:1)	40.0	0.67
7.	Hexane + TBP (1:1)	99.0	99.0
8.	Methyl iso butyl ketone+ TBP (1:1)	30.0	0.43

4.4 LIQUID-LIQUID EXTRACTION PROCESS FOR ACID RED 10 B AND ACID PINK BE

4.4.1 Effect of pH on Anionic Dyes Extraction

The influence of feed phase pH was studied for the extraction of the anionic dyes from aqueous solution. The pH of the feed phase was varied

from 1.0 to 7.0 and the results are shown in Figure 4.2. The extraction of dyes was maximum at lower pH. The percentage of extraction of dyes was found to decrease with increase in pH.



(Conditions: Dye concentration 100 mg/L, Volume of aqueous solution 30 mL, solvent TBP in hexane (1:1) 30 mL, equilibration time 5 min.)

Figure 4.2 Effect of pH on Extraction of Anionic Dyes

Figure 4.2 reveals that maximum extraction 99.0 % for Acid Red 10 B and 91.3 % for Acid Pink BE was achieved at $\text{pH } 1.0 \pm 0.1$, which may be due to the fact that at lower pH (1.0 ± 0.1), H^+ ion concentration is high and hence, the extractant TBP is in cationic form and the anionic dye readily forms an ion-pair complex with cationic TBP. When the pH was increased to 2, the percentage of extraction was decreased to 85.6 for Acid Red 10 B and 81.7 for Acid Pink BE respectively. Further increase in pH, the percentage of extraction was decreased. The extraction efficiency was very less at higher pH. At pH 5 the dye extracted was 14.9 % for Acid Red 10 B and 10.1 % for

Acid Pink BE. At pH 6 there was no extraction for Acid Pink BE. There was no extraction for Acid Red 10B at pH 7.0.

Cuer et al (1974) reported that at 1 mol L⁻¹ acid concentration, the distribution coefficient was 6.0 and it could be increased to 12 by doubling the acidity for chromium (VI) removal using TBP. At higher pH, TBP do not form an ion pair with dye resulting in no extraction because TBP remains neutral and not present in cationic form.

4.4.2 Effect of Carrier / Diluent Ratio

The solvent extraction was studied at different hexane / TBP ratio viz 1:1, 1.5: 1, 2:1, 3:1 and 4:1. The results are furnished in Table 4.3.

Table 4.3 Effect of Hexane-TBP Ratio on Extraction of Dyes

(Conditions: pH at 1.0 ± 0.1, Dye initial concentration 100 mg/L, Volume of aqueous solution 30 mL, Aqueous/ solvent ratio (1:1))

Sl.No.	Percentage of TBP in Hexane	Amount of dye of Extracted (mg/L)	
		Acid Red 10 B	Acid Pink BE
1.	50	99.5	91.3
2.	40	95.3	87.1
3.	33	92.1	75.8
4.	25	90.1	71.5
5.	20	89.6	67.0

The extraction of Acid Red 10 B dye was found to be maximum 99.5% when the hexane/TBP ratio was 1:1. When the hexane/TBP ratio was increased to 1.5: 1, the extraction was 95.3%. The extraction was lowered to 92.1% at 2:1, 90.1% at 3:1 and 89.6% at 4:1. For Acid Pink BE the extraction

was found to be 91.3% for the ratio of 1:1, 87.1% for 1.5:1 ratio, 75.8 % for 2:1 ratio, 71.5% for 3:1 ratio and 67.0% for 4:1 ratio.

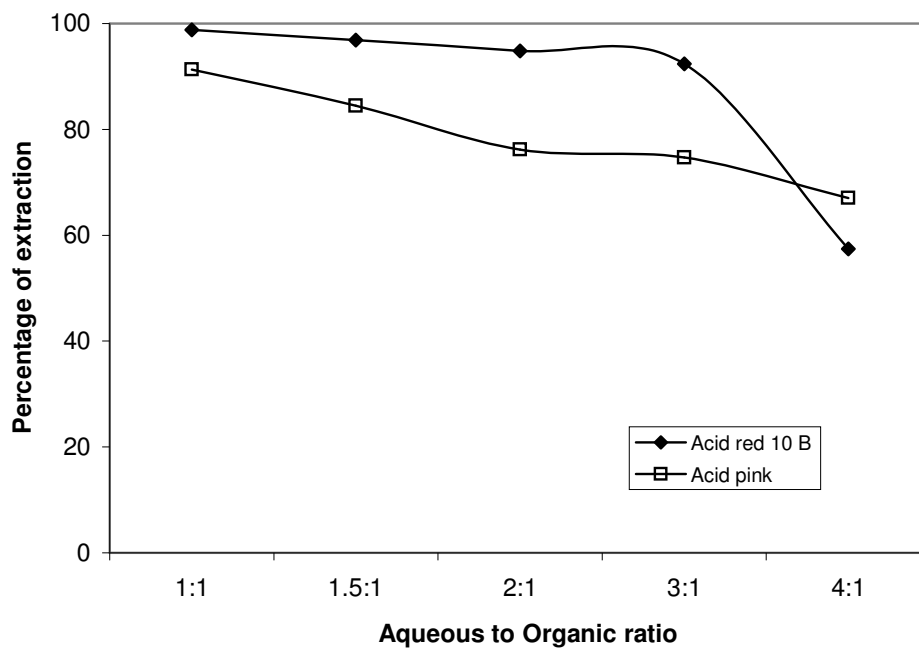
The extraction decreases with decrease in carrier concentration (Marinova 2004) because with lower carrier (TBP) volume (4:1), the interface between the aqueous and the solvent is not saturated by the carrier. Hence in all subsequent studies TBP to hexane was fixed as 1:1 ratio. A blank experiment was also performed in which the solvent contains no carrier and negligible amount of dye in the solvent was found. This has confirmed that the extraction of dye ion in solvent is facilitated by the TBP carrier only.

Srichand and Jain (1995) reported that the distribution coefficient of acetic acid is increased with increase in TBP concentration in kerosene. They also recommended that 60 Vol % TBP in kerosene could be a solvent mixture for the recovery of acetic acid.

4.4.3 Aqueous to Organic Ratio

The effect of contacting different volume ratio of aqueous to organic phase (A/O) was studied by varying from 1:1, 1.5: 1, 2:1, 3:1 and 4:1. and their efficiency are presented in Figure 4.3.

The results shown in Figure 4.3 indicate that for Acid Red 10 B, 98.8%, 96.9%, 94.8%, & 92.4% extraction was achieved at 1:1, 1.5:1, 2:1 and 3:1 respectively. At (4:1) ratio, the extraction reduced to 57.4 %. This may be due to the reduced availability of organic carrier for Acid Red 10 B dye interaction. In the case of Acid Pink BE, it is gradually decreased from 91.3 % (1:1) to 67 % (4:1), which reveals that extraction decreases with the decreased availability of organic carrier for dye interaction. Use of higher solvent ratio may not be economical since the viscosity of TBP is high to cause high energy consumption (Srichand 1995).



(Conditions: Dye concentration 100 mg/L, pH 1.0 ± 0.1 , equilibration time 5 min.)

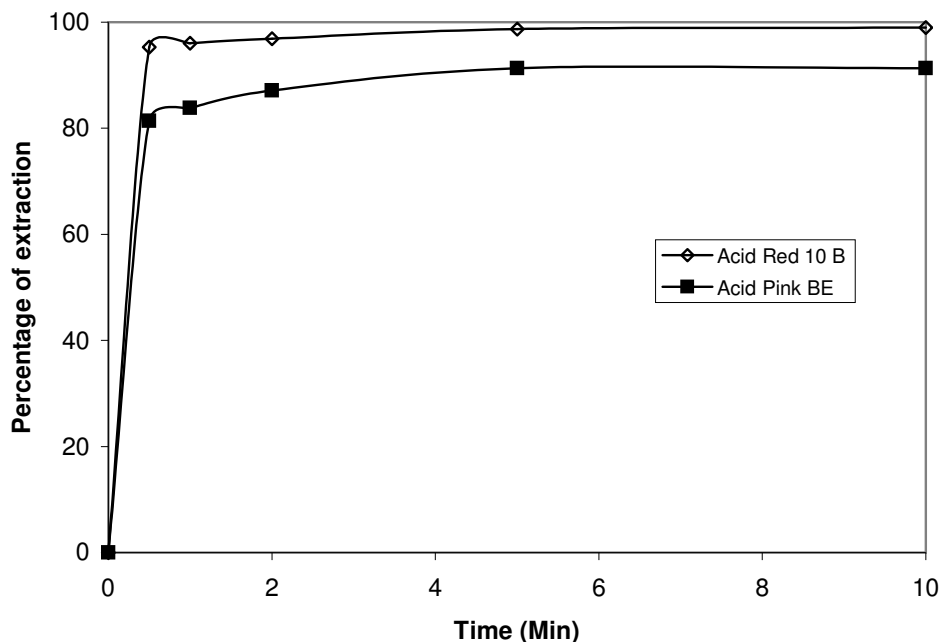
Figure 4.3 Effect of on Aqueous to Organic Ratio on Transport of Anionic Dyes

4.4.4 Effect of Equilibration Time

The two immiscible phases of aqueous dye solution and hexane - TBP solvent mixture were equilibrated for a period ranging from 30 seconds to 10 minutes and the results are depicted in Figure 4.4.

The extraction was rapid even within 2 minutes of time and the extraction obtained was 96.0 % for Acid Red 10 B and 90.0 % for Acid Pink BE. Beyond that, the rate of reaction was reduced and reached the maximum extraction of 99.0 % for Acid Red 10B and 91.3 % for Acid Pink BE respectively at 5 minutes. After that, there was no change in extraction efficiency. Based on the above results 5 minutes equilibration time was

sufficient to attain maximum efficiency of both dyes. Therefore 5 minutes equilibration time was maintained for further studies.



(Conditions: Dye concentration 100 mg/L, pH 1.0 ± 0.1 , Volume of aqueous solution 30 mL, solvent TBP in hexane (1:1) 30 mL.)

Figure 4.4 Effect of Equilibration Time on Extraction of Anionic Dyes

4.4.5 Selection of Stripping Reagent for Anionic Dyes Recovery

The amount of dye extracted at acidic pH was high and hence alkaline reagents were tried for stripping purpose. Stripping reagents like aqueous ammonia, sodium hydroxide, sodium carbonate and calcium hydroxide (each at 0.50 M) were tested for stripping the dye from hexane-TBP to identify the better stripping reagent. The results are shown in Table 4.4.

Table 4.4 Effect of Stripping of Dyes by using Different Stripping Reagent

(Conditions: Volume of aqueous solution (Sodium hydroxide) 30 mL, Dye loaded solvent TBP in hexane (1:1) 30 mL, equilibration time 5 min.)

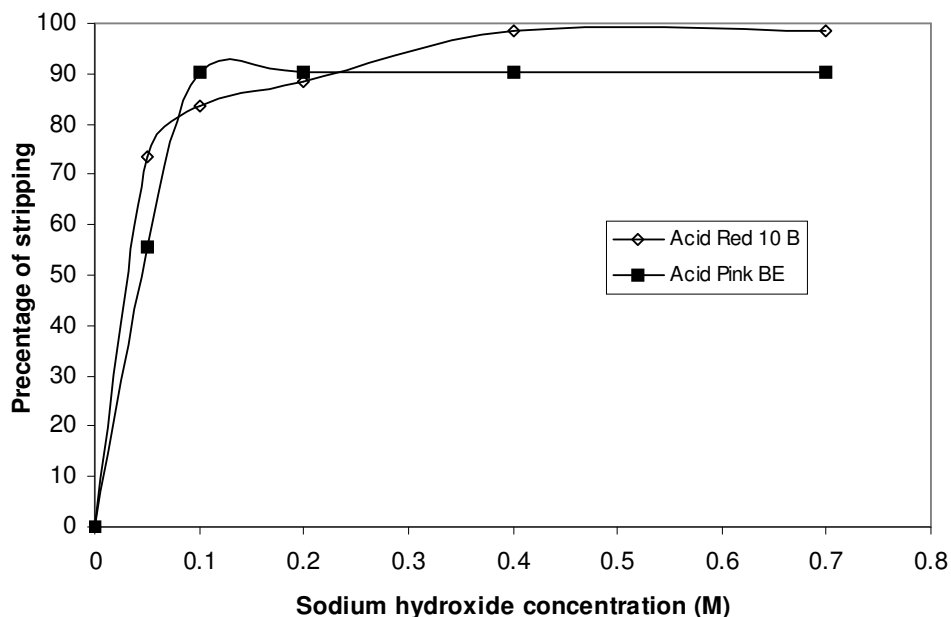
S.No.	Stripping Reagents (0.5 M)	% of Stripping	
		Acid Red 10 B	Acid Pink BE
1.	Calcium hydroxide	30	30
2.	Aqueous ammonia	35	35
3.	Sodium Carbonate	20	20
4.	Sodium hydroxide	98.5	91.4

It was found that sodium hydroxide has high stripping efficiency compared to calcium hydroxide and aqueous ammonia and hence further studies were carried out with sodium hydroxide as a stripping agent.

4.4.6 Effect of Stripping Reagent Concentration

Study on the effect of stripping reagent concentration on recovery of Acid Red 10 B and Acid Pink BE was carried out. The concentration of sodium hydroxide was varied from 0.05 to 0.70 M. The results are shown in Figure 4.5. It can be seen that the recovery of dyes increased with increase in sodium hydroxide concentration.

At 300 seconds the recovery of Acid Red 10 B dye was found to be 73.6 % at 0.05 M NaOH and 83.5 % at 0.10 M NaOH, which further increased to 88.5 % with 0.20 M NaOH. In the range of 0.40 M – 0.70 M NaOH, the stripping efficiency was found to be constant 98.5%. In the case of Acid Pink BE, the recovery was found to be 55.6 % with 0.05 M NaOH and increased to about 90.5% in the range of 0.10 M to 0.70 M NaOH. Hence 0.50 M sodium hydroxide solution was selected for subsequent studies.



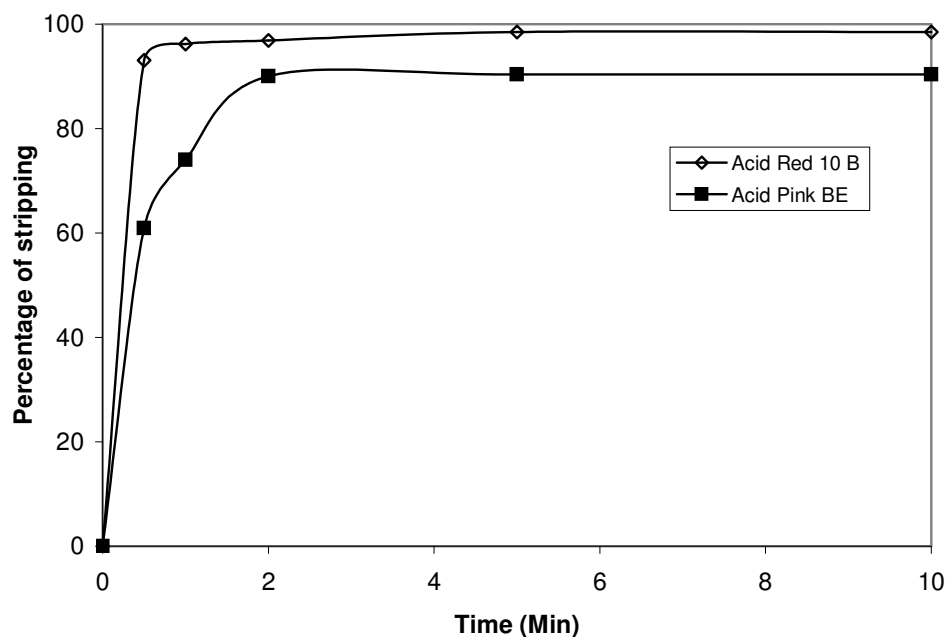
(Conditions: Volume of aqueous solution (Sodium hydroxide) 30 mL, Dye loaded solvent TBP in hexane (1:1) 30 mL, equilibration time 5 min.)

Figure 4.5 Effect of Stripping Concentration on Recovery of Anionic Dyes

Hu et al (2005) reported that stripping of acid dye intermediate from loaded organic phase was tested with NaOH and the stripping rate was increased with increase of NaOH concentration in the aqueous phase. The dye intermediates were mostly stripped with stripping rate 94.1 % when NaOH > 17.5 wt % and when NaOH < 7.5 wt %, stripping rate was only 50.6 %.

4.4.7 Effect of Stripping Time

Stripping process involves mixing of solvent phase with stripper followed by settling of phase. Proper time has to be given for mixing and phase settling (Hu et al 2005). Stripping studies with 0.50 M sodium hydroxide were also carried out from 30 seconds to 10 minutes and the results are shown in Figure 4.6.



(Conditions: Dye concentration 100 mg/L, sodium hydroxide concentration 0.5 M, Volume of aqueous solution 30 mL, solvent TBP in hexane (1:1) 30 mL.)

Figure 4.6 Effect of Equilibration Time on Stripping of Anionic Dyes

The stripping was quite rapid even within 30 seconds for Acid Red 10 B, where as for Acid Pink BE, required 2 minutes. However, the recovery amount of stripped dye from the extracted dye was 98.5 % for Acid Red 10 B and 90.5 % for Acid Pink BE, in 5 minutes, which again revealed that stripping time of 5 minutes is adequate to strip the extracted dye using 0.5 M NaOH solution.

4.4.8 Effect of Chloride and Sulphate Concentration in the Aqueous Dye Solution

In the real textile effluent, chloride and sulphate may be present along with dyes. Hence, their effect on dyes extraction was studied. The chloride and sulphate concentration in the aqueous dye solution was varied from 100 mg/L to 3000 mg/L. The results are presented in Table 4.4. There

was no appreciable effect on the dye extraction up to 1000 mg/L of salt concentration. However, the extraction efficiency was slightly lowered, when the concentration was increased from 1000 mg/L to 3000 mg/L. The amount of dye recovered for Acid Red 10 B was 97.4 mg/L and 97.1 mg/L when the concentration of chloride and sulphate was 2000 mg/L respectively. The recovery of Acid Pink BE was 90.4 mg/L and 90.2 mg/L respectively. The extraction efficiency of Acid Red 10 B was lowered to 94.6% and 94.2 % for 3000 mg/L chloride and sulphate concentration respectively. Similar effect (slight decrease) was obtained in the case of Acid Pink BE also.

Table 4.5 Effect of Chloride and Sulphate Concentration on Dye Extraction

(Conditions: Dye concentration 100 mg/L, pH at 1.0 ± 0.1 , TBP- Hexane (1:1) ratio, Aqueous/ solvent ratio (1:1, equilibration time 5 min)

S. No.	Sulphate and chloride concentration (mg/L)	Amount of dye removed in the presence of chloride		Amount of dye removed in the presence of sulphate	
		Acid Red 10 B	Acid Pink BE	Acid Red 10 B	Acid Pink BE
1.	100	99.0	91.3	99.0	91.3
2.	500	99.0	91.3	99.0	91.2
3.	1000	98.9	91.0	98.5	91.0
4.	2000	97.4	90.4	97.1	90.2
5.	2500	95.8	89.0	95.4	88.5
6.	3000	94.6	88.5	94.2	88.2

4.4.9 Initial Dye Concentration Variation in Aqueous Solution

The effect of varying the initial concentration of dye from 50-1000 mg/L in 30 mL of aqueous phase was tried with 30 mL of

TBP-Hexane (1:1 ratio) at pH 1.0 ± 0.1 . The extracted dyes in liquid-liquid extraction were stripped with 0.5 M NaOH. The results are furnished in Table 4.5.

Table 4.6 Effect of Dye Initial Concentration on Recovery of Anionic Dyes

(Conditions: pH at 1.0 ± 0.1 , TBP- Hexane (1:1) ratio, Aqueous/ solvent ratio (1:1), equilibration time 5 min.)

Sl.No.	Dye initial Concentration (mg/L)	Amount of dye recovered (mg/L)		Percentage of Extraction	
		Acid Red 10 B	Acid Pink BE	Acid Red 10 B	Acid Pink BE
1.	50	49.5	45.3	99.0	90.6
2.	100	98.9	90.5	98.9	90.5
3.	250	246.8	226.2	99.0	90.4
4.	500	494.2	452.4	98.8	90.4
5.	800	784.4	715.4	98.1	89.4
6.	1000	923.4	891.2	92.3	89.1

It was observed that for Acid Red 10 B, 99.0 % of efficiency was achieved up to 500 mg/L using 1:1 TBP-hexane ratio. Further increase in initial dye concentration, the percentage of extraction was decreased. For 800 mg/L initial dye concentration, the percentage of recovery was 98.0 %. Then it was reduced to 92.8 % at 1000 mg/L. For Acid Pink BE the percentage of recovery was 90.4 % up to 500 mg /L. When the concentration was increased to 800 mg/L, the percentage of recovery was 89.4 %. Further increase in initial dye concentration the percentage of recovery was reduced to 89.1 %.

When the initial dye concentration is high, more and more dye molecules are expected to be extracted and availability of organic carrier is reduced for extraction. Hence an increase of dye concentration, the extraction efficiency is decreased. However, the absolute amount of dye extracted was increased from 49.7 mg/L to 923.4 mg/L for Acid Red 10 B and from 45.3 to 891.2 mg/L for Acid Pink BE respectively with initial dye concentration of 50 to 1000 mg/L.

4.4.10 Reuse of the Solvent

When the dye stripped solvent mixture was reused for dye extraction under the optimized conditions, it was found that 99.0 % of Acid Red 10 B was extracted in the solvent which was the same as in the case of the virgin solvent mixture. After five extraction cycles, Hexane + TBP mixture showed no loss in efficiency of extraction and retained the same extraction ability. From the dye loaded solvent 98.5 % of Acid Red 10 B was stripped with 0.5 M NaOH. Similarly for Acid Pink BE, 91.3 % of extraction and 90.5 % of stripping efficiency was obtained. From these results it is inferred that the process developed has good economy in terms of reuse.

4.4.11 Extraction Mechanism

The plots of log D versus log TBP concentration for Acid Red 10 B and Acid Pink BE are given in Figures 4.7a and 4.7b respectively. The plots are linear. The slopes obtained are 2.37 and 2.17 for Acid Red 10B and Acid Pink BE respectively, which indicates that one mole of dye forms a complex with two moles of TBP. The dye to reagent mole ratio is 1:2. This may be due to the presence of two $(\text{SO}_3)^- \text{Na}^+$ group in both dyes.

The acidic dyes are anionic in nature. In acidic pH, the extractant TBP is in protonated form with H^+ ion. The extraction is due to the formation

of ion- pair complex $[(RO_3P^+O H)_2 Dye^{2-}]_{org}$ by cationic TBP with anionic dye.

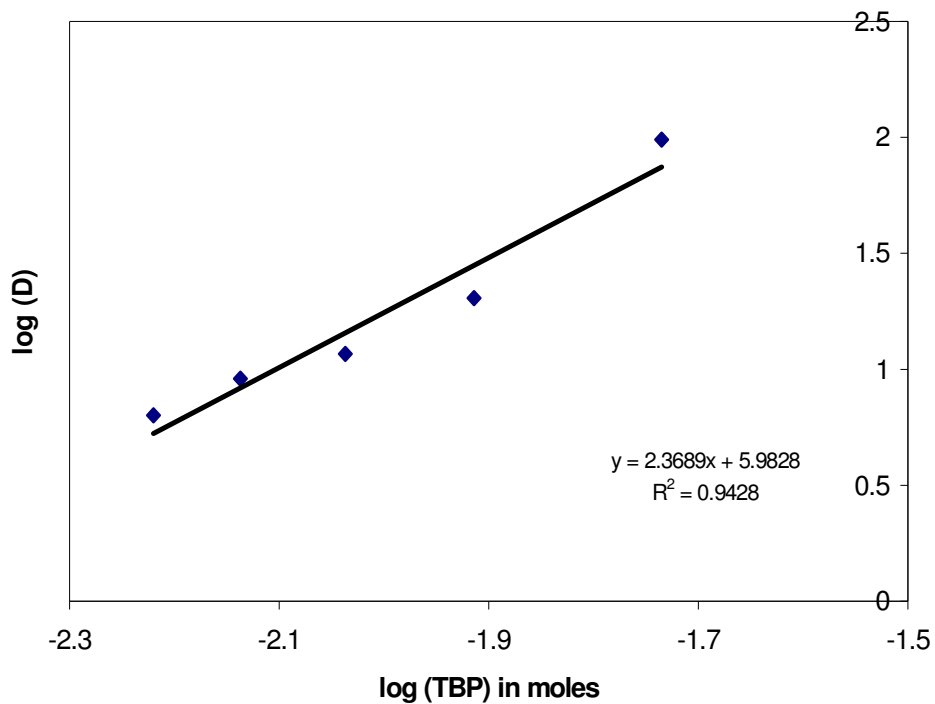
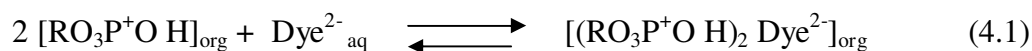
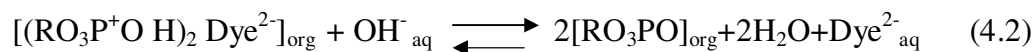


Figure 4.7(a) Relationship between log D and log (TBP) for Acid Red 10B



The stripping reaction with OH^- is as follows. The hydroxyl ion reacted with ion-pair complex $[R_3PO H^+ Dye^-]_{org}$ and releasing neutral TBP and dye.



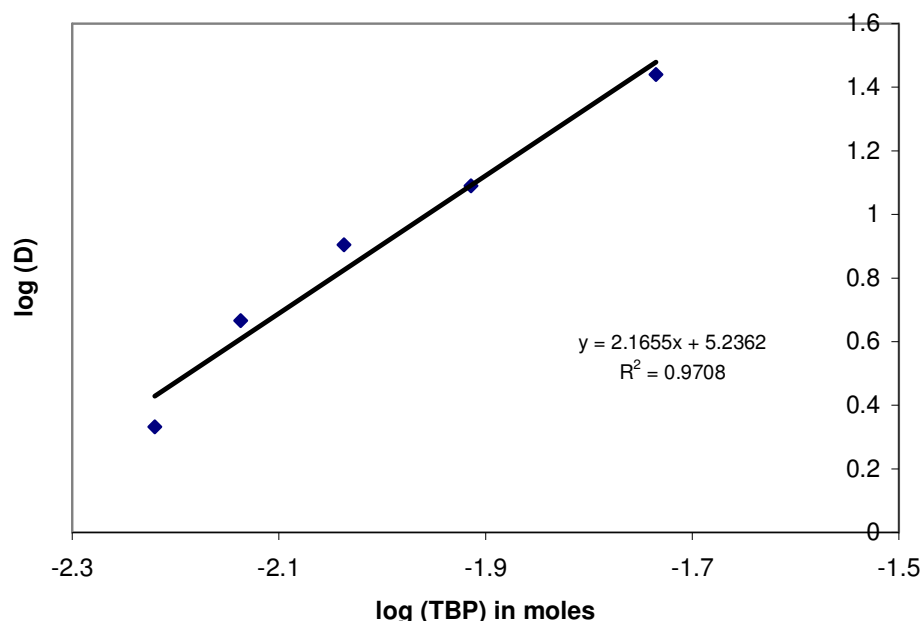


Figure 4.7(b) Relationship between log D and log (TBP) for Acid Pink BE

4.5 BULK LIQUID MEMBRANE PROCESS FOR ACID RED 10 B AND ACID PINK BE

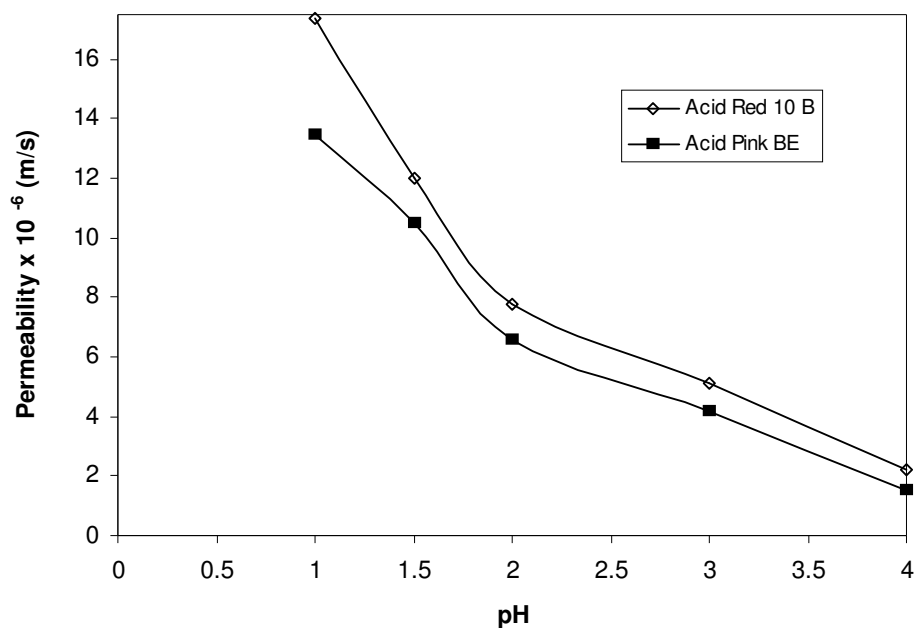
The preliminary experiments were carried out by liquid-liquid extraction method. The liquid-liquid extraction process, which involves extraction and stripping steps, is not economical for dilute solutions. This method usually involves the handling of large quantities of organic solvents. Hence based on the results obtained, by liquid-liquid extraction method, the experiments were conducted by bulk liquid membrane process to recover Acid Red 10 B and Acid Pink BE.

4.5.1 Effect of Feed Phase pH

The influence of pH of feed phase on the transport efficiency of dye molecules was studied in the pH range from 1.0 – 4.0 in BLM process. The Figure 4.8 provides experimental results in the form of plot of permeability of dyes with feed phase pH.

It was observed that permeability was high (17.37×10^{-6} m/s for Acid Red 10 B and 13.43×10^{-6} m/s for Acid Pink BE) at lower pH (1.0 ± 0.1) and then it was decreased with increase of pH. At lower pH, H^+ ion concentration is high and hence the anionic dye readily forms an ion-pair complex with cationic TBP. At higher pH, TBP does not form an ion pair complex with dye resulting in poor transport because TBP remains neutral and not present in cationic form.

It was found that maximum dye transport occurs at pH 1.0 ± 0.1 . The maximum dye transported within 120 minutes was 96.2 % for Acid Red 10 B and 90.3 % for Acid Pink BE respectively.

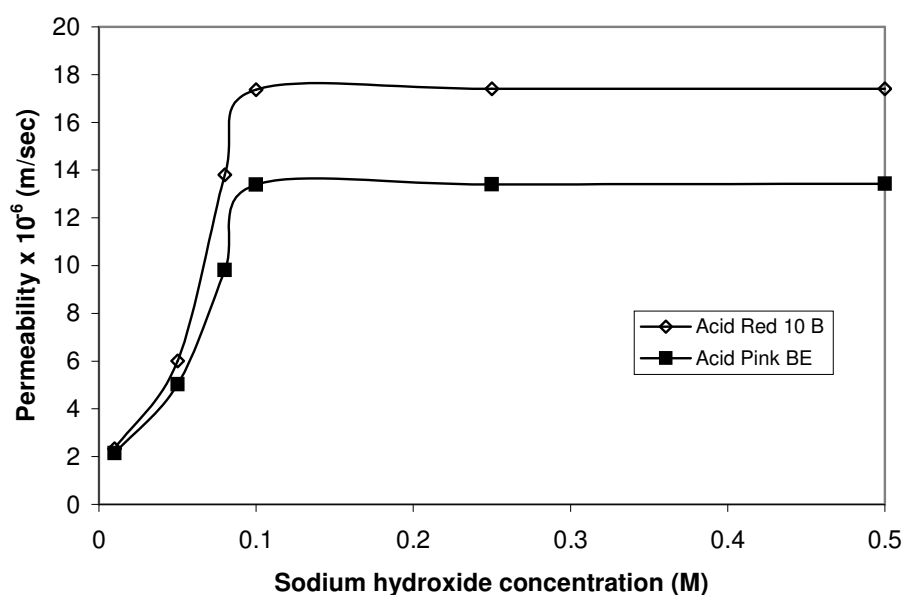


(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 . Liquid membrane phase 200 mL of TBP-Hexane (1:1) receiving phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm, time of transport 120 min.)

Figure 4.8 Effect of pH on Permeability of Anionic Dyes

4.5.2 Effect of Stripping Reagent Concentration

Preliminary study reveals that sodium hydroxide showed good stripping efficiency among the various alkaline chemicals. In order to optimise the effect of stripping reagent concentration, the concentration of receiving phase (sodium hydroxide) was varied in the range of 0.01 M to 0.50 M. The plot of permeability with various concentration of sodium hydroxide is shown in Figure 4.9.



(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 . Liquid membrane phase 200 mL of TBP-Hexane (1:1) rate of stirring 220 rpm, time of transport 120 min.)

Figure 4.9 Effect of NaOH Concentration in the Receiving Phase

The permeability value was found to increase with increase of sodium hydroxide concentration up to 0.1 M. After that it was plateau. At 0.01 M NaOH, the permeability was 2.33×10^{-6} m/s and 2.14×10^{-6} m/s for Acid Red 10 B and Acid Pink BE respectively. At 0.05 M NaOH, it was slightly increased to 6.01×10^{-6} m/s and 5.03×10^{-6} m/s for Acid Red 10 B

and Acid Pink BE respectively. When it reaches 0.1 M concentration, the permeability was 17.38×10^{-6} m/s and 13.4×10^{-6} m/s respectively.

At 0.01 M, the percentage of recovery was 67.5 for Acid Red 10 B and 59.5 for Acid Pink BE. Then it was increased to 72.4 % for Acid Red 10 B and 65.3 % for Acid Pink BE at 0.05 M sodium hydroxide concentration. It was observed that, the percentage of dye removal and recovery was increased with increase of sodium hydroxide concentration. The maximum recovery of dye in 120 minutes was 96.2 % for Acid Red 10 B and 90.1 % for Acid Pink BE from dye loaded Hexane + TBP mixture for the concentration range 0.1 to 0.5 M sodium hydroxide respectively. Hence for further studies 0.1 M NaOH was chosen.

4.5.3 Effect of Hexane / TBP Ratio

The experiments were accomplished at different TBP percentage viz., 25 %, 33 %, 40 % and 50 %, and the results are tabulated in Table 4.7.

Table 4.7 Effect of TBP Concentration

(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 Liquid membrane phase 200 mL of TBP-Hexane, receiving phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm, time of transport 120 min.).

Sl.No.	Percentage of TBP in Hexane	Permeability \times (10^{-6} m/s)		Amount of dye recovery (mg/L)	
		Acid Red 10 B	Acid Pink BE	Acid Red 10 B	Acid Pink BE
1.	50.0	17.41	13.40	48.1	45.2
2.	40.0	14.01	10.32	46.1	43.3
3.	33.0	8.02	6.62	39.9	38.5
4.	25.0	3.28	2.87	32.4	30.0

The amount of dye recovered was found to be 32.4 mg/L, 39.9 mg/L, 46.1 mg/L and 48.1 mg/L for Acid Red 10 B and the permeability was found to be 3.28×10^{-6} m/s, 8.02×10^{-6} m/s, 14.01×10^{-6} m/s and 17.41×10^{-6} m/s. In the case of Acid Pink BE, the dye recovered was 30.0 mg/L, 38.5 mg/L, 43.3 mg/L, 45.2 mg/L and the permeability was 2.87×10^{-6} m/s, 6.62×10^{-6} m/s, 10.32×10^{-6} m/s and 13.40×10^{-6} m/s respectively. When 100 % TBP was used, emulsion was noticed during the process.

In lower carrier concentration, the interface between the aqueous phase and the solvent is not saturated by the carrier. Therefore the extraction decreases with decrease in carrier concentration. Hence in all further BLM studies, the carrier TBP and solvent hexane was fixed as 1:1 ratio. A blank experiment was also performed in which the LM (hexane) contains no carrier in BLM method. Negligible amount of dye in the LM and no recovery of dye in the stripping phase were found. This was found to confirm to the transport of dye ions by LM as fulfilled by the TBP carrier only.

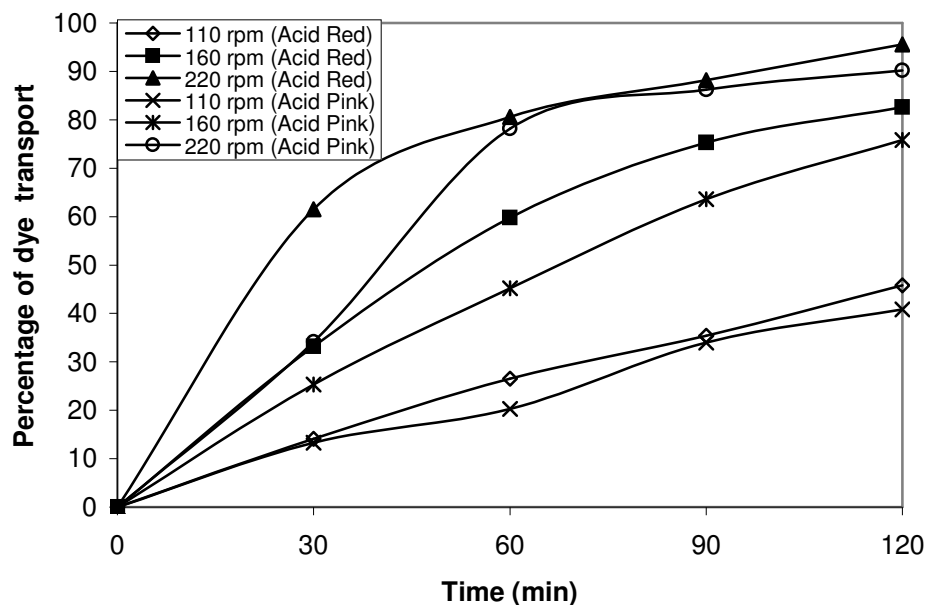
The maximum percentage of extraction under 50% TBP was found to be 95.6 % for Acid Red 10B and 90.3 % for Acid Pink BE respectively.

4.5.4 Effect of Mixing Speed

The experiments were accomplished at different mixing speeds from 110 ± 10 rpm, 160 ± 10 rpm, 220 ± 10 rpm, 330 ± 10 rpm and 440 ± 10 rpm. The results are shown in Figure 4.10.

The results show that when the speed was decreased to 110 ± 10 rpm, the percentage of transport was reduced to 45.8 % for Acid Red 10 B and 40.8 % for Acid Pink BE respectively. When the speed is increased to 160 ± 10 rpm, the percentage of transport is increased to 82.6 %

for Acid Red 10 B and 75.8 % for Acid Pink BE respectively. The permeability was also found to be increased in the same manner. It is presented in Table 4.7.



(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 , Liquid membrane phase 200 mL of TBP-Hexane (1:1), rate of stirring 220 rpm, time of transport 120 min.)

Figure 4.10 Effect of Mixing Speed on Transport of Dyes

The maximum transport of dyes was obtained at 220 ± 10 rpm. When the mixing speed was further increased (above 220 ± 10 rpm), intermixing of source phase and receiving phase was found to take place. This type of observation had been already reported by Yamini et al (1994) during the recovery of Bismuth. They reported that in higher rates, mixing of source phase and receiving phase would occur.

Table 4.8 Effect of Mixing Speed on Permeability of Dyes

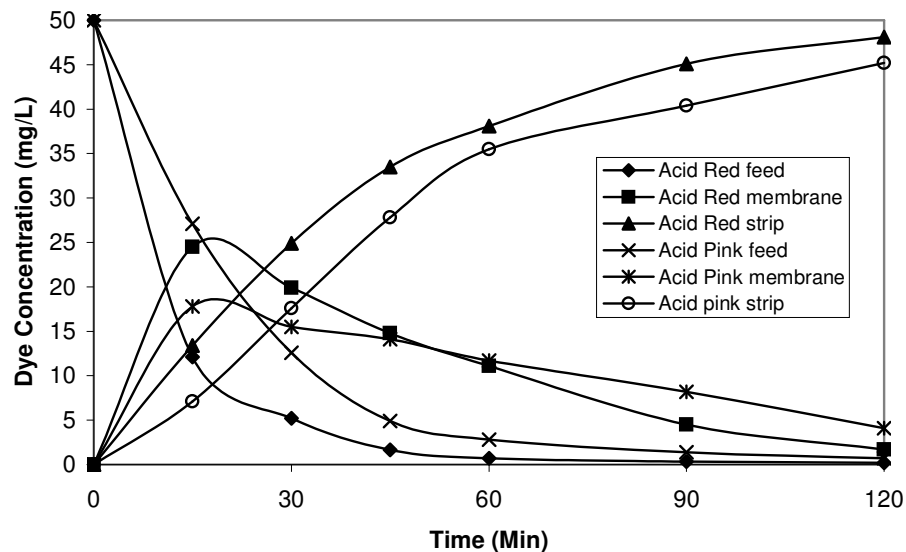
(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 , Liquid membrane phase 200 mL of TBP-Hexane (1:1), rate of stirring 220 rpm, time of transport 120 min.)

Sl.No.	Mixing speed (rpm)	Permeability $\times 10^{-6}$ m/s	
		Acid Red 10 B	Acid Pink BE
1.	110 ± 10	5.93	5.18
2.	160 ± 10	11.50	9.46
3.	220 ± 10	17.38	13.37
4.	330 ± 10	No Transport	No Transport
5.	440 ± 10	No Transport	No Transport

4.5.5 Effect of Time

The time dependence of dye transport through the liquid membrane was investigated and the results are shown in Figure 4.11. It is obvious that the extraction of dyes from the source phase into the organic membrane is found to occur at a faster rate than release of dyes from the membrane phase in to receiving phase.

It was observed that after 60 minutes, the amount of dye in the source phase was 0.74 mg, in the membrane 8.96 mg and in the receiving phase 40.3 mg for Acid Red 10 B. For Acid Pink BE, the amount of dye in the source phase was 10.3 mg, in the membrane 5.8 mg and in the receiving phase 34.1 mg respectively. However, the maximum dye recovered at 120 minutes was 48.1mg and 45.2 mg respectively.



(Conditions: Feed phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 . Liquid membrane phase 200 mL of TBP-Hexane (1:1), strip phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm, time of transport 120 min).

Figure 4.11 Effect of Time on Transport of Dyes

4.5.6 Effect of Initial Concentration on Transport of Dyes

The initial concentration of the dye was varied from 50 mg/L to 1000 mg/L at pH 1.0 ± 0.1 . Table 4.8 presents the amount of dye transported for different dye concentration. It is observed that for Acid Red 10 B, 96.2 ± 1 % of efficiency was achieved up to 500 mg/L using 1:1 TBP-hexane ratio. Then it was reduced to 92.2 % at 1000 mg/lit. The effect was similar for Acid Pink BE also.

Table 4.9 Effect of Dye Initial Concentration on Dyes Transport

(Conditions: Source phase 100 mL of dye solution at pH 1.0 ± 0.1 , Liquid membrane phase 200 mL of TBP-Hexane (1:1), receiving phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm, time of transport 120 min.)

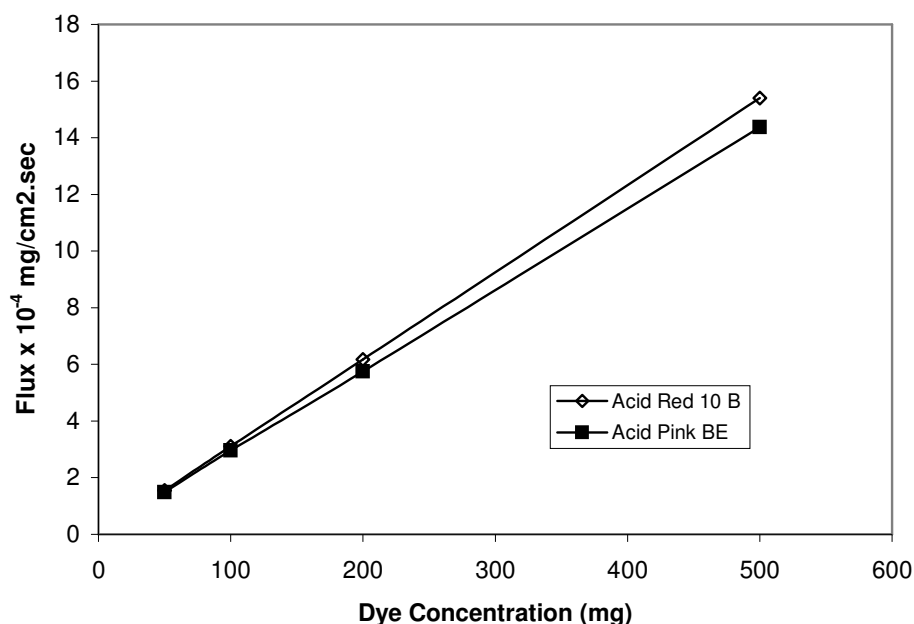
Sl. No.	Dye initial Concentration (mg/L)	Acid Red 10B		Acid Pink BE	
		Amount of dye recovered (mg/L)	Percentage of Transport	Amount of dye recovered (mg/L)	Percentage of Transport
1.	50	48.1	96.2	45.2	90.4
2.	100	95.9	95.9	90.1	90.1
3.	200	192.1	96.2	180.6	90.3
4.	500	478.6	95.7	450.7	90.1
5.	1000	921.8	92.1	803.1	80.3

When the initial dye concentration is high, more and more dye molecules are expected to be extracted and availability of organic carrier is reduced for extraction. Hence an increase of dye concentration, the transport efficiency was slightly decreased, but the absolute amount of dye transported was increased from 48.1 mg/L to 921.8 mg/L for Acid Red 10 B and from 45.2 mg/L to 803.1 mg/L for Acid Pink BE respectively. When compared with LLE, the efficiencies were almost same for both Acid Red 10 B and Acid Pink BE.

The plot of flux with various concentrations of dye solutions varying from 50 mg/L to 500 mg/L is shown in Figure 4.12. The results revealed that at lower concentrations the initial flux depends on the initial dye concentration in the feed phase that was in accordance with the expected trend, since the flux varies with the pollutant concentration (Wodzki et al

1999) as per equation (3). Hence, there should be an increase in flux with increase of dye concentration.

$$J = P [\text{dye}] \quad (4.3)$$



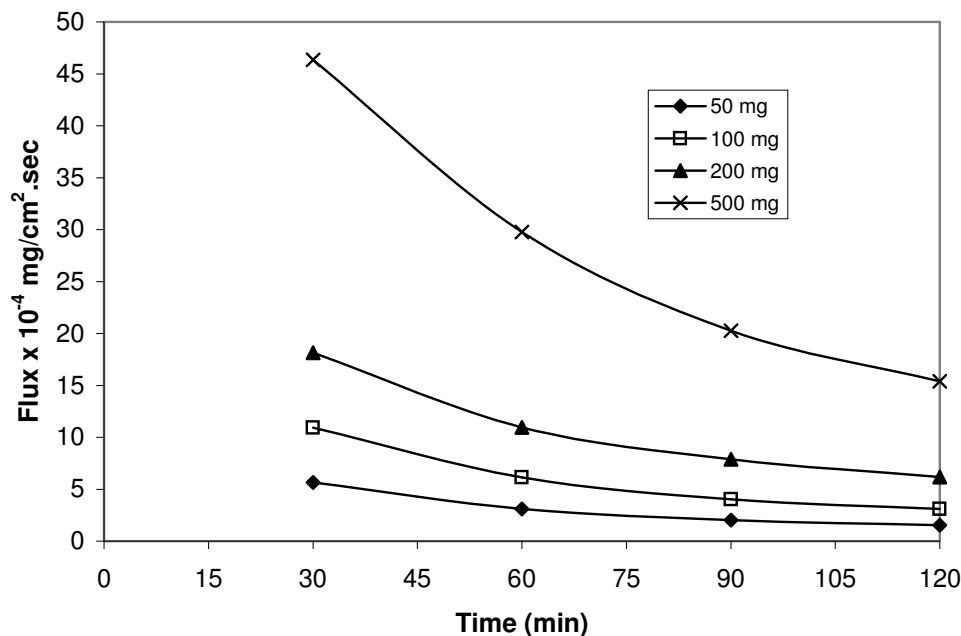
(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1, Liquid membrane phase 200 mL of TBP-Hexane (1:1), receiving phase 100 mL of 0.1M NaOH, rate of stirring 220 rpm, time of transport 120 min s).

Figure 4.12 Flux Vs Initial Dye Concentration on Transport of Dyes

Yahaya et al (2005) reported that in the concentration range of 0-30,000 ppm, the flux was linearly proportional to the feed concentration. They also concluded that as the flux increased linearly through out the range of the feed concentration examined in this particular investigation, the membranes did not probably reach saturation.

The plot of flux with time for various concentrations of dye solutions varying from 50 mg/L to 500 mg/L is shown in Figure 4.13. The

flux was decreased with increase of time because the availability of dye molecules decreased with increase of time.



(Conditions: As in Figure 4.12, except dye concentration.)

Figure 4.13 Flux Vs Time on Transport of Acid Red 10 B

4.5.7 Influence of Salt

The effect of various concentrations of chloride and sulphate from 1000 mg/L to 5000 mg/L was also studied in BLM. The results are presented in Table 4.9. There was no effect of salt up to 3000 mg/L. For Acid Red 10 B, when the salt concentrations were increased beyond 3000 mg/L, the percentage of recovery was reduced to 85.2 % (42.6 mg/L) for sodium chloride and 80.4 % (40.2 mg/L) for sodium sulphate at 5000 mg/L. For Acid Pink BE 89 % was recovered up to 3000 mg/L. Then it was decreased to 80.2 % (40.1 mg/L) for sodium chloride and 80.1% (40.1 mg/L) for sodium sulphate at 5000 mg/L.

Table 4.10 Effect of Chloride and Sulphate Concentration in BLM

(Conditions: Source phase 100 mL of 50 mg/L dye solution at pH 1.0 ± 0.1 , Liquid membrane phase 200 mL of TBP-Hexane (1:1), receiving phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm, time of transport 120 min.).

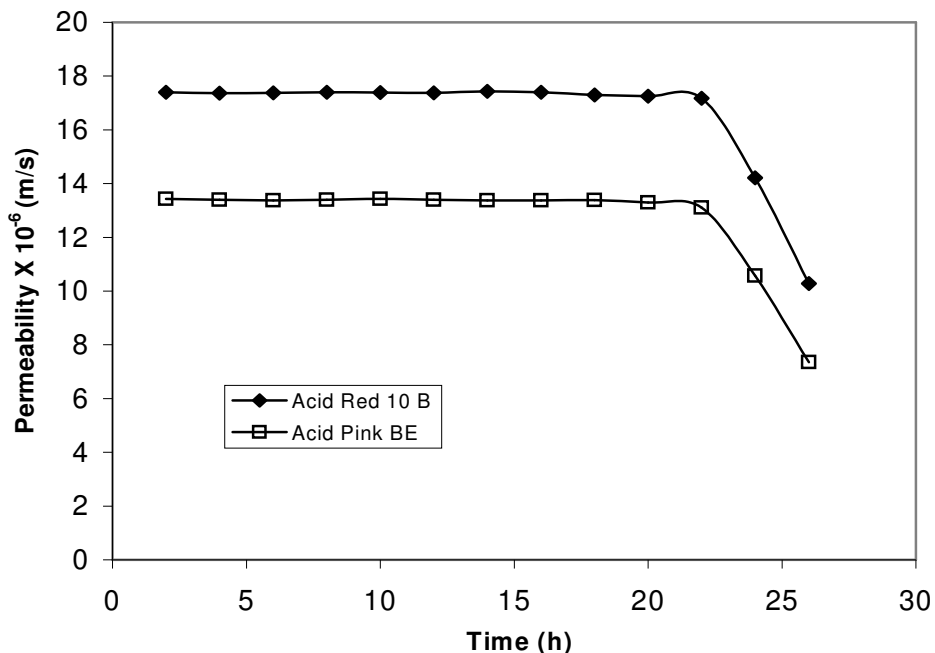
Sl. No.	Sulphate and chloride concentration (mg/L)	Amount of dye recovered in the presence of chloride		Amount of dye recovered in the presence of sulphate	
		Acid Red 10 B	Acid Pink BE	Acid Red 10 B	Acid Pink BE
1.	1000	48.1	45.2	48.4	45.1
2.	2000	48.0	45.1	47.1	45.0
3.	3000	47.0	44.2	47.1	44.2
4.	4000	45.2	43.3	44.1	43.2
5.	5000	42.6	40.1	40.2	40.1

The BLM transport efficiency was almost similar for LLE in the presence of salt. The percentage of recovery at 3000 mg/L of salt concentration was 94.2 % in BLM and 94.6 % in LLE for Acid Red 10 B and 88.4 % in BLM and 88.5 % in LLE for Acid Pink BE.

4.5.8 Reuse of the Solvent

The spent LM (TBP-Hexane) was reused for dye transport under the optimized conditions. The results are shown in Figure 4.14. It was found that from the dye loaded LM 96.2 % of Acid Red 10 B and 90.5 % Acid Pink BE dye was transported respectively. The used liquid membrane (TBP and hexane) after extraction and stripping was first treated with 0.1 M NaOH and then with water to remove the unstripped dye if present. The regenerated liquid membrane was used for further removal of dye. Ten cycles (2 hours for each cycle) were carried out using the same LM mixture without loss of

efficiency. From these results, it is inferred that the process developed has good economy in terms of LM reuse.



(Conditions: Source phase 100 mL of 50 mg/L dye at pH 1.0 ± 0.1 . Liquid membrane phase 200 mL of TBP-Hexane (1:1), receiving phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm, time of transport 120 min.)

Figure 4.14 Reusability of the Membrane

4.5.9 Transport Mechanism

As explained in LLE section 4.4.11, in acidic condition, H^+ ion concentration is high and hence TBP is in cationic form. It readily combines with the anionic dye in the feed side and forms an ion-pair complex.

At the source phase - membrane interface, $[(RO_3POH)_2^+Dye^{2-}]_{org}$ ion pair complex is formed. At the membrane-receiving phase interface, OH^- with high affinity for $[Dye]^-$ ions completes the transport process by removing dye⁻ ions from its ion pair complex. Finally, the free carrier RO_3PO diffuses across the membrane to the source phase–membrane interface, where the cycle starts

again. The mechanism for dye removal is similar to anionic chromium (VI) transport (Palanivelu et al 1998).

4.5.10 Kinetics of Dyes Transport in BLM

The kinetics of transport process across BLM can be described by a first order reaction with respect to dye concentration (Alguacil et al 2002), and after 2 hours, its concentration in the stripping phase was found to become higher than in the donor phase.

First order rate equation

$$\frac{dC}{dt} = -kC \quad (4.4)$$

where C is the concentration, t is time and k is the first orders rate constant of the feed side reaction.

$$\ln_e C_t = -kt + \ln_e C_0 \quad (4.5)$$

On rearranging the above equation

$$\ln_e C_t - \ln_e C_0 = -kt \quad (4.6)$$

Consider $Y = \ln C_t - \ln C_0$, $X = t$

Hence $Y = -kX$ (4.7)

Normal equation (4.7) is given by

$$\sum Y = -k \sum X$$

$$k = \frac{-\sum Y}{\sum X} \quad (4.8)$$

In BLM experiments, a plot of the of $-\ln C_t/C_o$ against the time was fitted against experimentally obtained values. The kinetic parameters of the transport dye through the BLM containing TBP were determined and the fitted values were plotted against experimental values.

Following the work of Danesi et al (1984) a mass balance to the feed compartment can be written as follows

$$-V dc/dt = (PA) C \quad (4.9)$$

where A = Area of the membrane, V = Volume of the feed phase

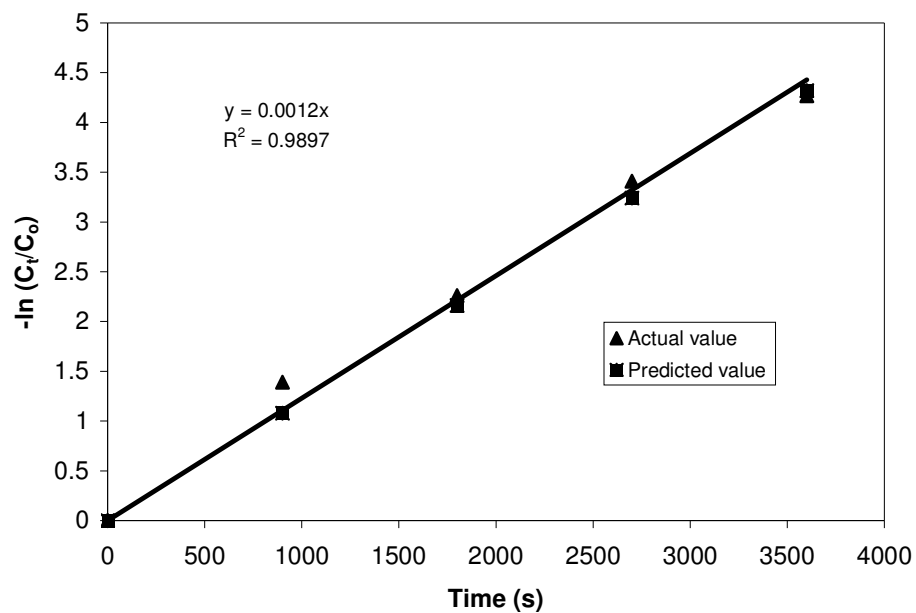
When $t = 0$, $C=C_o$

where P is the mass transfer coefficient. Integration of the above equation give rise to

$$\ln C_t/C_o = -kt ,$$

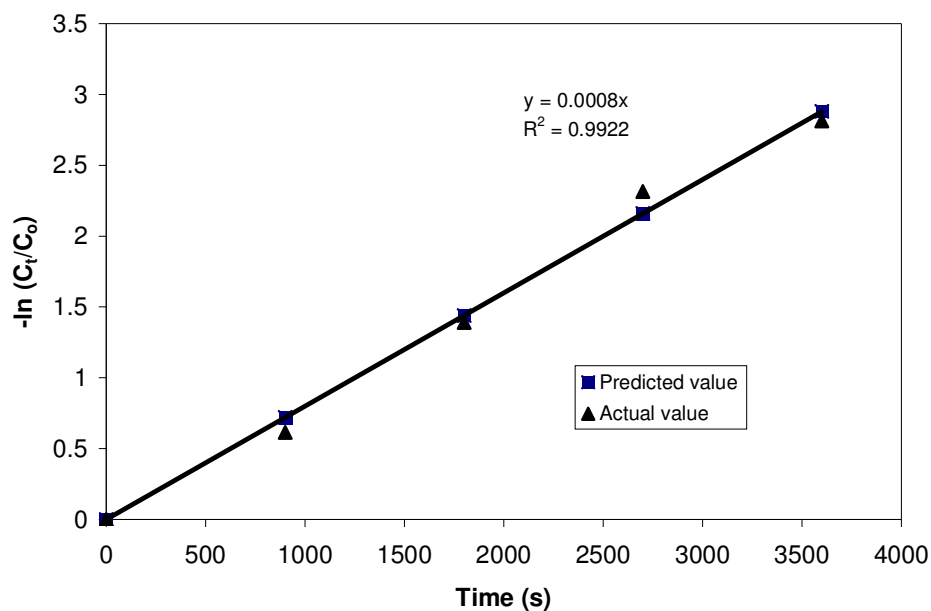
where $k=(PA/V)$. Based on the value of k , the mass transfer coefficient (P) was calculated (Uritaga et al 2000).

The Figures 4.15 and 4.16 shows the linear relationship of $-\ln C_t/C_o$ Vs time for Acid Red 10 B and Acid Pink BE respectively and confirmed by high values of correlation coefficient (r^2). The k value calculated was $1.29 \times 10^{-3} \text{ s}^{-1}$ for Acid Red 10 B where as for Acid Pink BE; it was $7.92 \times 10^{-4} \text{ s}^{-1}$. The mass transfer coefficient calculated was $2.72 \times 10^{-5} \text{ m/s}$ for Acid Red 10 B and $1.81 \times 10^{-5} \text{ m/s}$ for Acid Pink BE.



(Conditions: Source phase 100 mL of 50 mg/L dye solution at $\text{pH } 1.0 \pm 0.1$, Liquid membrane phase 200 mL of TBP-Hexane (1:1), receiving phase 100 mL of 0.1 M NaOH, rate of stirring 220 rpm.)

Figure 4.15 Kinetics of Acid Red 10 B Transport in BLM

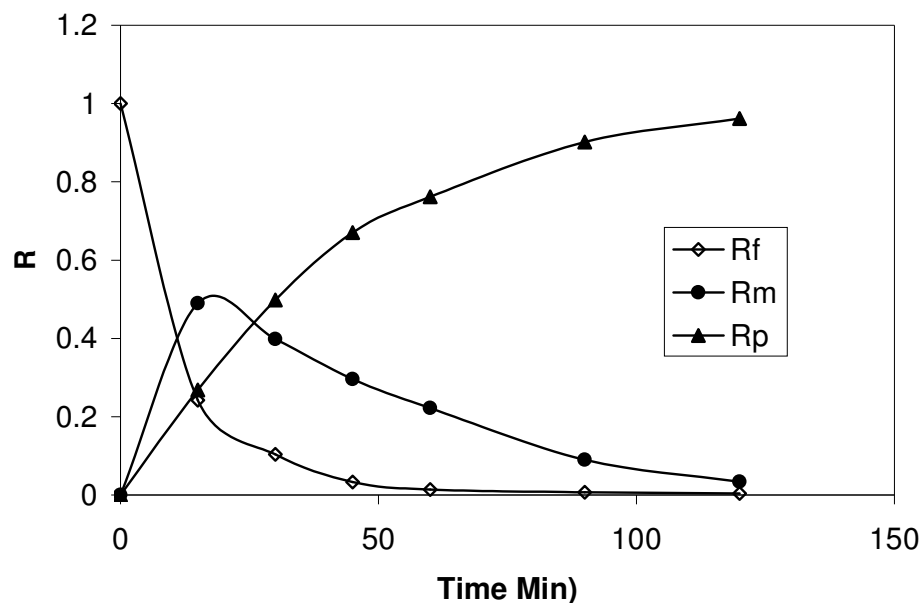


(Conditions: As given in 4.15.)

Figure 4.16 Kinetics of Acid Pink BE Dye Transport in BLM

For practical reasons, dimensionless reduced concentrations of dye in the feed (R_f), membrane (R_m), and strip phases (R_p) were used ($R_f = C_f/C_o$, $R_m = C_m/C_o$ and $R_p = C_p/C_o$, the sum of $R_f + R_m + R_p = 1$).

Variation with time of the reduced dye concentration (R) in the feed, membrane and product phases are shown in Figures 4.17a and 4.17b. It can be evaluated that R_f decreases monoexponentially with time, while R_p follows an increasing sigmoid type curve and R_m presents a maximum.

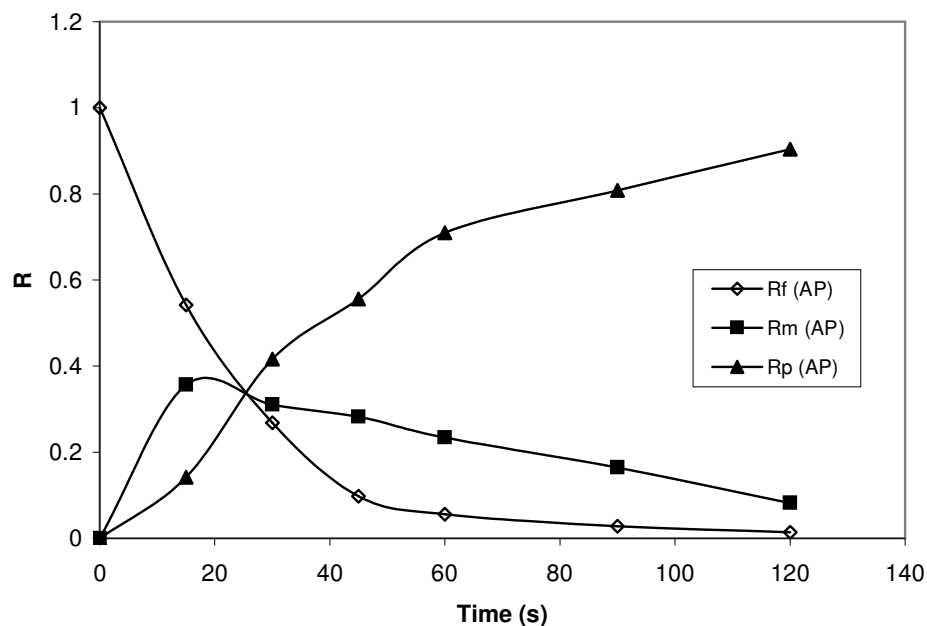


(Conditions: Time dependence of R_f in the feed phase, R_m in the membrane phase, R_p in the product phase. TBP concentration in membrane phase 50 %, NaOH concentration in product phase 0.1 M, Points, experimental values; line, model values)

Figure 4.17a Reduced Dye Concentration (R) Vs Time for Acid Red 10 B

These results suggest that dye transport obeys the kinetic laws of two consecutive irreversible first order reactions, the extraction (rate constant, k_1) and the stripping (rate constant k_2) reactions. This mechanism has been used to describe the transport of dye through bulk liquid membranes (Leon

and Guzman (2004). The irreversibility is to be expected because R_f tends to Zero. The kinetic irreversibility of the whole transport process is expected to derive from the high gradient across the membrane.



(Conditions : As given in Figure 4.17a)

Figure 4.17b Reduced Dye Concentration (R) Vs Time for Acid Pink BE

The kinetic behaviour can be described according to the following equations:

$$dR_f/dt = -k_1 R_f \quad (4.10)$$

$$dR_m/dt = k_1 R_f - k_2 R_m \quad (4.11)$$

$$dR_p/dt = k_2 R_m \quad (4.12)$$

Integration of these differential equations gives

$$R_f = \exp(-k_1 t) \quad (4.13)$$

$$R_m = k_1 [\exp(-k_1 t) - \exp(-k_2 t)] / k_2 - k_1 \quad (4.14)$$

$$R_p = 1 - [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] / (k_2 - k_1) \quad (4.15)$$

These equations show that the time dependence of R_f is monoexponential and the time dependence of both R_m and R_p is biexponential.

As mentioned above R_m has a maximum, the time at which it occurs being obtained from $dR_m/dt = 0$.

$$t_{\max} = \ln(k_1/k_2) / k_1 - k_2 \quad (4.16)$$

The value of R_m at that time being.

$$R_m^{\max} = (k_1/k_2)^{k_2/k_1 - k_2} \quad (4.17)$$

Combining Equations (4.16) and (4.17) the following relationship can be obtained.

$$K_2 = \ln(1/R_m^{\max}) / t_{\max} \quad (4.18)$$

Numerical analysis by non-linear curve fitting permits the rate constants to be determined. The value k_1 is obtained from equation (4.13). This value is introduced as a constant value in equations (4.14) and (4.15). An initial value of k_2 is obtained from equation (4.18) and introduced in equations (4.14) and (4.15) and iterated. Two values of rate constant k_2 are obtained, one derived from equation (4.14), k_{2m} , and the other derived from equation (4.15), k_{2p} . Excellent agreement between k_{2m} and k_{2p} constants was observed.

Rate constants of the reactions of extraction (k_1) and stripping (k_2). [k_{2m} derived from equation (4.14)., k_{2p} derived from equation (4.15) and the results are tabulated in Table 4.11.

Table 4.11 Rate Constants for BLM Transport of Anionic Dyes

Sl.No.	Name of the Dye	K_1 (min^{-1})	k_{2m} (min^{-1})	k_{2p} (min^{-1})
1.	Acid Red 10 B	0.076	0.071	0.075
2.	Acid Pink BE	0.047	0.048	0.047

4.6 SUPPORTED LIQUID MEMBRANE PROCESS FOR ANIONIC DYES

Based on the results obtained from LLE and bulk liquid membrane processes (BLM), experiments were conducted in supported liquid membrane process. In particular, a significant advantage of using SLM over conventional LLE and BLM is that only a trace amount of organic carrier (liquid membrane) is required for transferring solute from the source phase into the receiving phase (Rhlalou et al 2000). Yang et al (2001) reported that the application of SLM using PTFE and PVDF membranes appear to be more stable than that of poly propylene membranes. When TBP-hexane was used in SLM, there was a drawback in stability of the system. When attempts were made with TBP in hexane, the pH of the feed solution changed from acidic to alkaline. This may be due to the evaporation of hexane. When TBP was used, there was no such effect. This may be due to the nature of carrier that provided stability to SLM system. Hence TBP alone was chosen for further studies without hexane as diluent.

4.6.1 Selection of Support Material for SLM

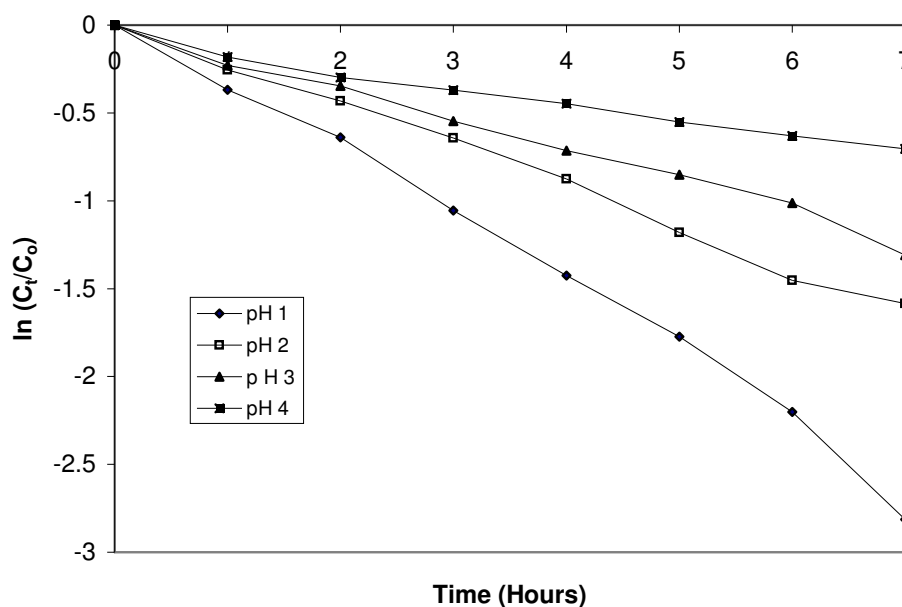
Teflon (PTFE) possesses extreme toughness, high softening point (about 350 c), exceptionally high chemical resistance towards all chemicals, high density ($2.1\text{--}2.3 \text{ g cm}^{-3}$) and very low coefficient of friction. Hence PTFE plain membrane of pore size 0.5 and 1.0 μm were screened for the dye transport studies. The transport studies revealed that the membrane of 1.0 μm pore size was found to have more transport efficiency with a permeability $7.3 \times 10^{-6} \text{ m/s}$ for Acid Red 10 B and $5.9 \times 10^{-6} \text{ m/s}$ for Acid Pink BE respectively, where as the membrane of 0.5 μm pore size had the permeability of $5.28 \times 10^{-6} \text{ m/s}$ for Acid Red10 B and $4.41 \times 10^{-6} \text{ m/s}$ for Acid Pink BE respectively for four hours. The smaller pore size gives the slowest mass transfer rate through the membrane. Zha et al also reported similar results for gallium transport using Celgard 2400 (0.05 μm). Further experimental studies were carried out using 1.0 μm pore size teflon membrane.

4.6.2 Effect of Source Phase pH

In the TBP-SLM system, the pH gradient between the feed and the receiving phases is the main driving forces for the permeation of dyes. In order to assess the role of feed phase pH, pH variation studies in the range of 1-4 were carried out. The receiving phase consisted of 0.1 M NaOH, where as the membrane carrier was TBP. The Figures 4.18 & 4.19 present the experimental results in the form of a plot of $\ln (C_t/C_0)$ with time for Acid Red10 B and Acid Pink BE respectively.

It was found that maximum dye transport occurred at $\text{pH } 1.0 \pm 0.1$ as expected. From the results, it is clear that at lower pH, H^+ ion concentration is high and form cationic species with TBP carrier in liquid membrane. So the anionic dye readily forms an ion-pair complex with cationic TBP. At higher

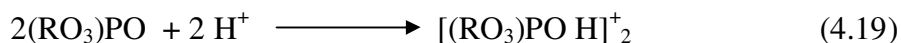
pH, decrease in hydrogen ion concentration causes decrease in rate of formation of an ion-pair complex with TBP, resulting in poor extraction because TBP remains neutral and is not present in cationic form. The maximum dye transported within 7 hours was 94.2 % for Acid Red10 B and 85.7 % for Acid Pink BE respectively at pH 1.0 ± 0.1 .



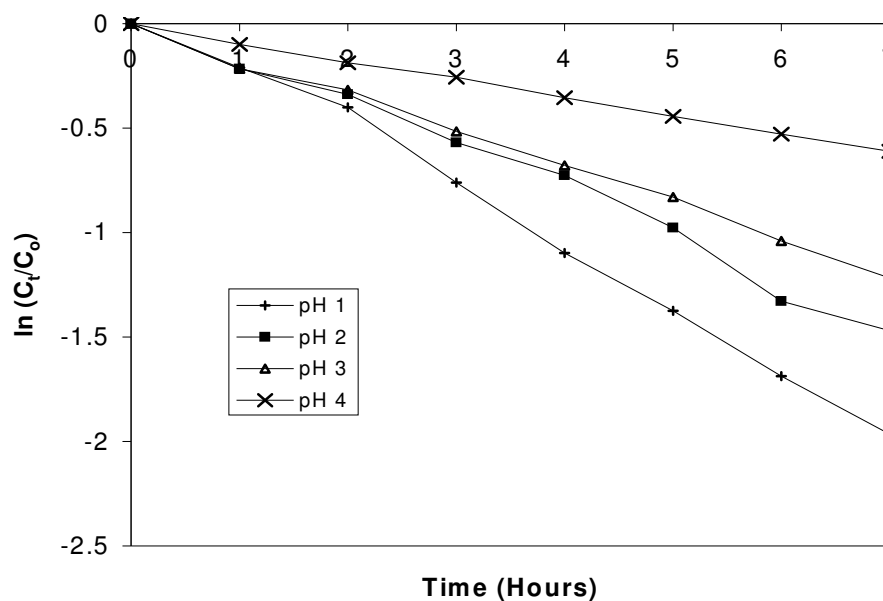
(Conditions: Source phase 150 mL of 10 mg/L dye solution at pH 1.0 ± 0.1 , receiving phase 150 mL of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours.)

Figure 4.18 Effect of Feed Phase pH on Permeability of Acid Red 10 B Dye

It was found that the permeability was high (11.0×10^{-6} m/s for Acid Red 10 B and 7.7×10^{-6} m/s for Acid Pink BE) at the lower pH 1.0 ± 0.1 and then it decreased with the increase of pH. The decrease in permeability with the decrease in proton concentration of cationic species $(RO_3)PO$ decreases due to the less availability of protons for the cation formation reaction.



$[(\text{RO}_3)\text{PO H}]_2^+$ is not formed and hence permeability decrease at high pH. From the above results, a pH of 1.0 ± 0.1 was selected for further studies in the feed solution. Similar type of observation was reported for metals (Chaudry et al 1998, Venkateswaran and Palanivelu 2005) using TBP.



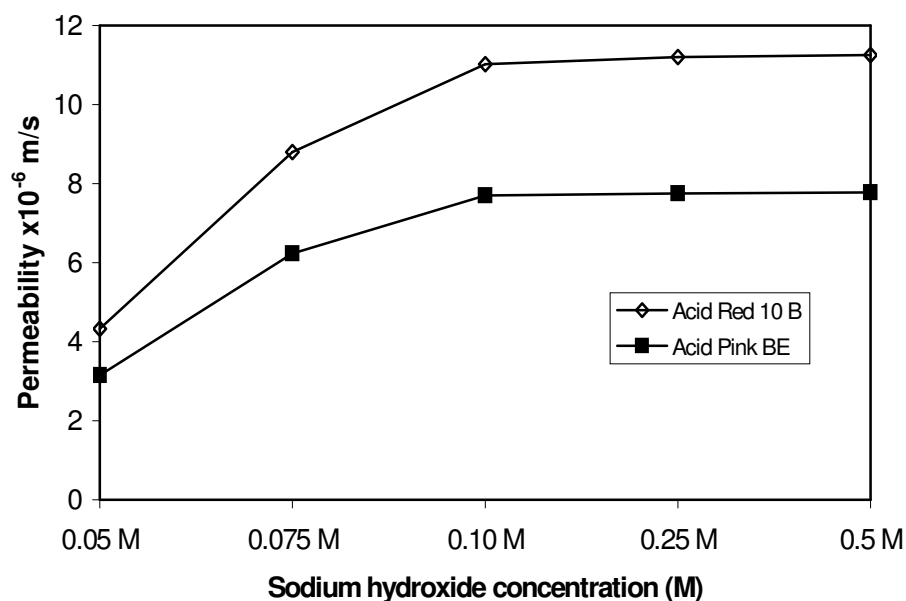
(Conditions : Source phase 150 mL of 10 mg/L dye solution at pH 1.0 ± 0.1 , receiving phase 150 mL of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours.)

Figure 4.19 Effect of Feed Phase pH on Permeability of Acid Pink BE dye

4.6.3 Effect of Stripping Reagent Concentration on the Permeability of Dyes

The transport of anionic dyes from aqueous feed across TBP is dependent upon the concentration of the sodium hydroxide and hence the concentration of receiving phase (sodium hydroxide) was varied in the range

of 0.05 M to 0.50 M. The result of dyes permeation using various concentrations of sodium hydroxide is thus shown in Figure 4.20.



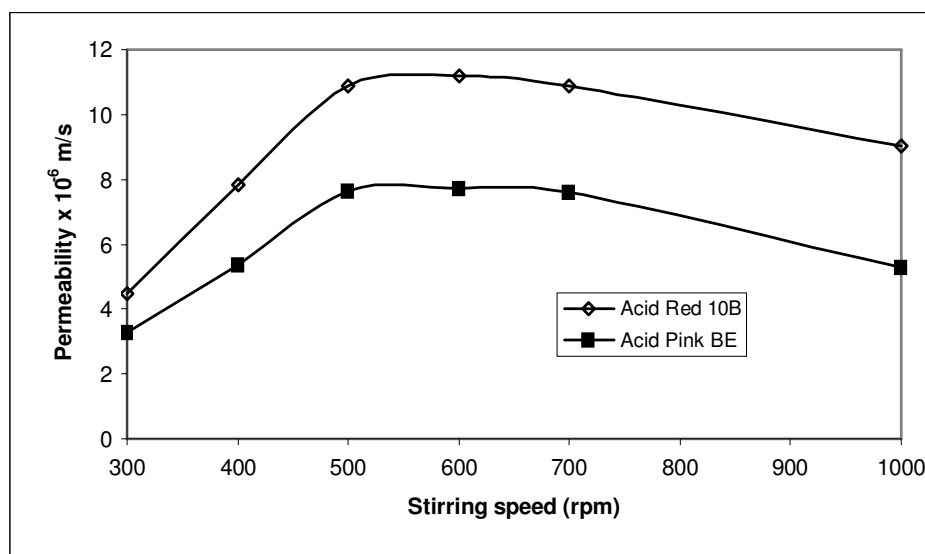
(Conditions: Source phase 150 mL of 10 mg/L dye solution at pH 1.0 ± 0.1 , receiving phase 150 mL of NaOH, rate of stirring 600 rpm, time of transport 7 hours).

Figure 4.20 Effect of NaOH Concentration on Permeability of Dyes

The permeability value increased with the increase of sodium hydroxide concentration up to 0.1 M and it remains constant up to 0.5 M. There was no effect on permeability of dyes after 7 hours. This might be due to the saturation of driving force for diffusion through the SLM owing to an increase of an ion pair complex concentration at the membrane-strip interface. The maximum recovery of dye in 7 hours was 94.2 % for Acid Red10 B and 85.7 % for Acid Pink BE respectively with 0.1 to 0.5 M sodium hydroxide. Hence for further studies 0.1 M NaOH was chosen.

4.6.4 Effect of Stirring Speed

In order to achieve effective permeation of dye in a SLM system, it is necessary to explore the effect of the stirring speed on the permeability coefficient. Diffusional resistances encountered during the transport of dye ion across a SLM are of two types (i) the resistance due to liquid boundary layer and (ii) the resistance due to the membrane. Sometimes the magnitude of the boundary layer resistance is comparable to or even greater than the membrane resistance. In the present work, the experiments were accomplished at different mixing speeds in the range of 300-1000 rpm. The plot of permeability with various stirring speeds is shown in Figure 4.21.



(Conditions: Source phase 150 mL of 10 mg/L dye solution at pH 1.0 ± 0.1, receiving phase 150 mL of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours.)

Figure 4.21 Effect of Stirring Speed on Transport of Dyes

The results reveal that when the speed was increased from 300 rpm, the percentage of transport was also increased. When the speed was increased beyond 700 rpm, the percentage of transport was decreased. The maximum permeability was obtained in the range of 500-700 rpm. This indicates that the

aqueous boundary thickness diminished continuously with the increasing stirring speed and that the boundary layer is minimum in the range of 500-700 rpm.

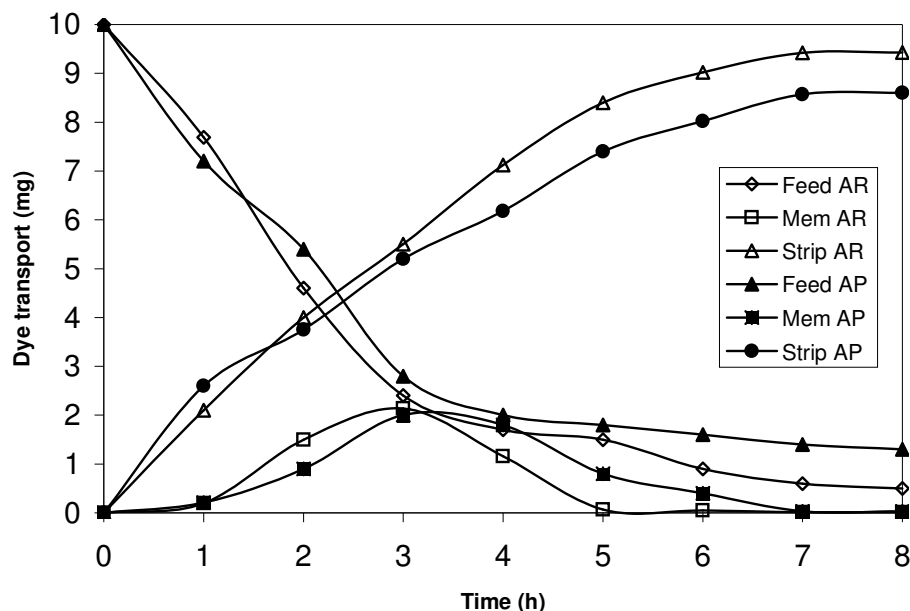
The appearance of the plateau region does not necessary mean the elimination of aqueous diffusion layer, but the resistance due to it is minimized. When the mixing speed was increased above 700 rpm, the permeability was decreased. This could be due to the high turbulence caused by stirring, resulting in the displacement of carrier from the membrane pore. Hence for further studies 600 rpm was chosen.

Alguacil et al (2002) reported for copper separation from nitrate/nitric acid media, a decrease in permeability from the stirring speed 1400 min^{-1} could be due to the high turbulence caused by stirring, resulting in displacement of carrier from the membrane pore.

4.6.5 Effect of Time

The amount of dye transport through the supported liquid membrane as a function of time was studied with 10 mg/L under the optimum conditions. The result is shown in Figure 4.22. It shows a constant increase in dye concentration in the receiving phase and a decrease in source phase.

It was observed that after 4 hours the amount of dye in the source phase was 1.7 mg, in the membrane 1.16 mg and the amount of dye in the receiving phase was 7.12 mg for Acid Red10 B. The amount of dye in the source phase was 2.0 mg, in the membrane 1.8 mg and in the receiving phase 6.2 mg for Acid Pink BE. However, the maximum dye recovered at 7 hours was 9.42 mg and 8.57 mg respectively for Acid Red10 B and Acid Pink BE. After this time, there was no change in the concentration of dye in the aqueous phases.



(Conditions: Source phase 150 mL of 10 mg/L dye solution at pH 1.0 ± 0.1 , receiving phase 150 mL of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours.)

Figure 4.22 Effect of Time on Dyes Transport.

4.6.6 Effect of Initial Concentration of Dyes

In order to study the influence of the initial concentration of dyes in the feed solution, the dye initial concentration was varied from 10 mg/L to 200 mg/L. Table 4.12 presents the permeability of dyes for different dye concentrations.

It is clear from the table that the permeation of dyes decrease with increase of initial dye concentration. This decrease should be explained as being due to the saturation of the membrane when higher concentrations are used. The initial flux (J) was dependent on the initial concentration of dye in the source phase (Wodzki et al 1999) and it is given by the Equation (4.20).

$$J = P [\text{dye}] \quad \text{or} \quad J/P = [\text{dye}] \quad \text{or} \quad 1/P \propto [\text{dye}] \quad (4.20)$$

Hence, there should be a decrease in permeability with an increase in dye concentration. The efficiency ($94.0 \pm 0.5 \%$) of Acid Red10 B of was achieved up to 50 mg/L using TBP as carrier. Then it was reduced to 85.5 % at 100 mg/L and 78.5 % at 200 mg/L. The effect was similar for Acid Pink BE also, but the absolute amount of dye transported was increased from 9.4 mg/L to 156 mg/L for Acid Red10 B and from 8.6 mg/L to 143.2 mg/L for Acid Pink BE.

Table 4.12 Effect of Dye Initial Concentration on Dyes Transport

(Conditions: Source phase 150 mL of different concentration dye solution at pH 1.0 ± 0.1 , receiving phase 150 mL of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours.)

Sl. No.	Dye initial Concentration (mg/L)	Permeability of dyes $\times (10^{-6} \text{ m/s})$	
		Acid Red 10 B	Acid Pink BE
1.	10	11.02	7.7
2.	20	11.01	7.7
3.	50	11.00	7.69
4.	100	9.91	7.21
5.	150	8.52	6.65
6.	200	7.72	6.11

Similar findings were observed by Calzado et al (2001) for amino acid transport. They found that the permeability of amino acid decreased from $11 \pm 3 \times 10^{-3} \text{ cm/min}$ for 0.05 mM concentration to $3 \pm 1 \times 10^{-3} \text{ cm/min}$ for 1.00 mM concentration. They also observed that at high initial amino acid concentrations, the amount of amino acid that crossed the membrane was found to be relatively high and do not represent bigger permeabilities or faster transport.

Jaber et al (2005) reported on phenol permeation through supported liquid membranes that the concentration of phenol permeation through SLM increased with time up to about 100 min, after which either a steady state concentration was reached for the case of relatively low feed concentrations (< 10,000 g/L) or a maximum followed by a decrease in concentration until a plateau was reached were observed for the case of relatively high feed concentration (40,000 g/L).

4.6.7 Influence of Salt

The effect of various concentrations of sodium chloride and sodium sulphate salts in the feed phase varying from 500 mg/L to 2000 mg/L was studied because dye effluent contains chloride and sulphate. The results are presented in Table 4.13. There was no effect of salt up to 1000 mg/L. For Acid Red 10 B when the salt concentrations were increased beyond 1000 mg/L, the percentage of recovery was reduced to 88.3 % for sodium chloride and 85.1 % for sodium sulphate at 2000 mg/L. The percentage of Acid Pink BE recovered was 83.3 % up to 1500 mg/L. Then it was decreased to 78.7 % for sodium chloride and 78.4 % for sodium sulphate at 2000 mg/L.

4.6.8 Reuse of Supported Liquid Membrane

The stability of PTFE-TBP system was studied by using one disc for different runs without further impregnation of the carrier. The stability of the SLM was quite remarkable when seven consecutive experiments were performed without reimpregnation of the TBP carrier. This shows that the TBP has formed a stable SLM system in PTFE membrane and the results are furnished in Table 4.14.

Table 4.13 Effect of Salt Concentration (Sodium Chloride and Sodium sulphate) On Recovery of Dyes

(Conditions: Source phase (SP) 150 mL of dye solution (10 mg/L) at pH 1.0 ± 0.1 , receiving phase (RP) 150 mL of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours.)

Concentration BE dye of salt (mg/L)	Salt used	Amount of Acid Red 10B dye (mg/L)		Amount of Acid Pink BE (mg/L)	
		SP	RP	SP	RP
500	NaCl	0.60	9.42	1.40	8.56
	Na ₂ SO ₄	0.59	9.41	1.41	8.57
1000	NaCl	0.54	9.43	1.39	8.52
	Na ₂ SO ₄	0.58	9.40	1.40	8.50
1500	NaCl	0.73	9.15	1.65	8.33
	Na ₂ SO ₄	0.64	9.06	1.61	8.32
2000	NaCl	0.90	8.83	1.92	7.87
	Na ₂ SO ₄	1.20	8.51	2.01	7.84

This may be due to high viscosity of TBP (3.8 m pa/s at 25°C, Perry and Dongreen 1984). No water transport through the SLM was observed during the experiment because there was no change of pH during the process. This may be due to the stability SLM system containing TBP as carrier. Thus the developed SLM system containing TBP as carrier possesses good stability with uphill transport for anionic silk dyes.

Table 4.14 Reusability of the Membrane

(Conditions: Source phase (SP) 150 mL of dye solution (10 mg/L) at pH 1.0 ± 0.1 , receiving phase (RP) 150 mL of 0.1 M NaOH, rate of stirring 600 rpm.)

Run	Membrane usage (h)	Permeability $\times 10^{-6}$ m/s	
		Acid Red10 B	Acid Pink BE
1	0	11.02	7.70
2	7	11.01	7.65
3	14	11.02	7.64
4	21	10.80	7.67
5	28	10.90	7.61
6	35	10.90	7.64
7.	42	10.70	7.55
8.	Re-impregnation	11.02	7.70

4.6.9 Feed to Strip Ratio

In the above optimised conditions, the obtained results showed that the stripping of dye was achievable with a concentration factor equal to 1. To increase the concentration factor, the same strip solution was used with series of feed solution. On continuous repetition of procedure up to four runs without change of strip solution, the average permeability rate was found to be 10.8×10^{-6} m/s for Acid Red10 B and 7.4×10^{-6} m/s for Acid Pink BE by achieving the concentration factor of four easily.

In another experiment, the volume of the reactor was increased to 500 mL. All the studies were carried out without increasing the membrane area of 15.19 cm^2 . The permeability was found to be 7.2×10^{-6} m/s for Acid Red10 B and 5.1×10^{-6} m/s for Acid Pink BE respectively. The results showed that with increase in the volume of the aqueous phase,

the permeability decreased from 10.8×10^{-6} m/s for Acid Red10 B and 7.40×10^{-6} m/s for Acid Pink BE (150 mL). This might be due to the less membrane area and maximizing the contact area between the aqueous phase and the organic membrane phase could enhance the separation efficiency. Guha et al (1994) suggested that increasing the membrane area could increase the transfer rate.

4.6.10 Transport Mechanism

The Figure 4.23 depicts schematically the dye transport processes in the SLM process. Based on the results obtained, the dye⁻ anion transport across the developed SLM system containing TBP as carrier [C] can be explained as follows.

1. The anionic dye⁻ diffuses from the bulk of the source phase to the source / membrane interface through aqueous boundary layer.
2. At the source phase–membrane interface, $[(\text{RO}_3\text{POH})_2^+\text{Dye}^{2-}]_{\text{org}}$ an ion pair complex is formed with cationic TBP as a result of concentration gradient.
3. The complexes diffuse through the liquid membrane to the receiving phase.
4. At the membrane- receiving phase interface, the OH⁻ ions complete the transport process by removing dye⁻ ions from its ion pair complex and cationic carrier is converted into $[\text{RO}_3\text{PO}]$.
5. This is confirmed by the presence of dye ion in the receiving phase and also there is no change in pH of receiving phase.
6. Finally, the free carrier $[\text{RO}_3\text{PO}]$ diffuses across the membrane to the source phase –membrane interface, where the cycle starts again.

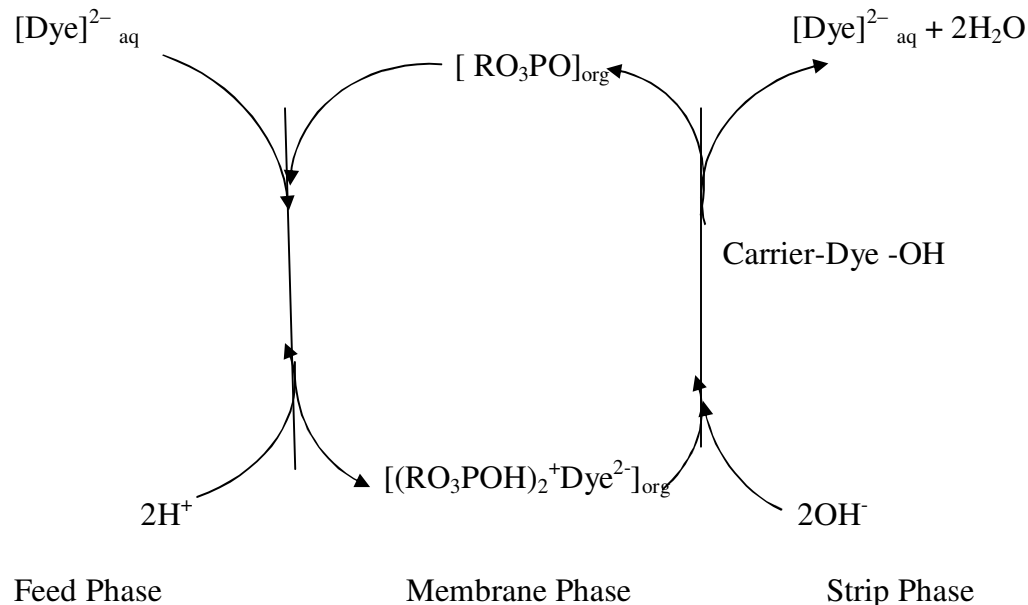


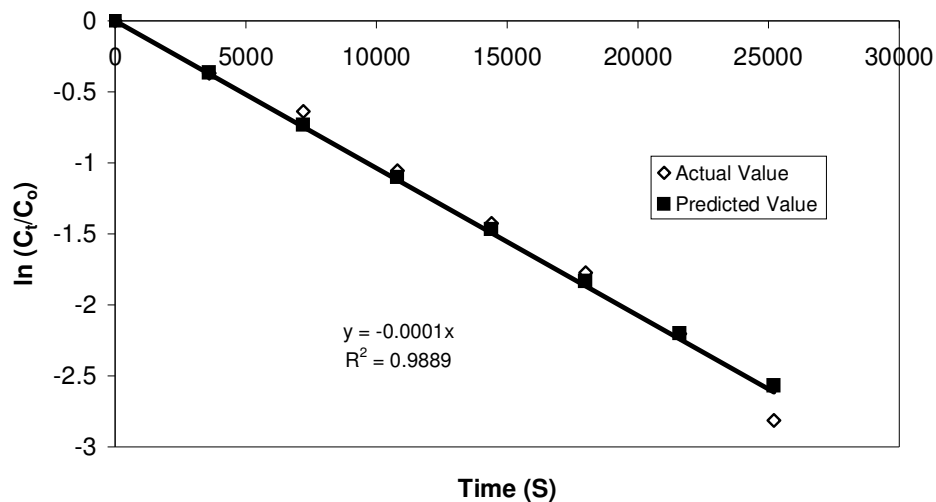
Figure 4.23 Schematic Representation for Transport of Anionic Dyes by Supported Liquid Membrane

4.6.11 Kinetic Transport of Dyes in SLM

The kinetics of transport process across SLM can be described by a first order reaction with respect to dye concentration (Alguacil et al 2002), mass transfer coefficient k can be calculated from

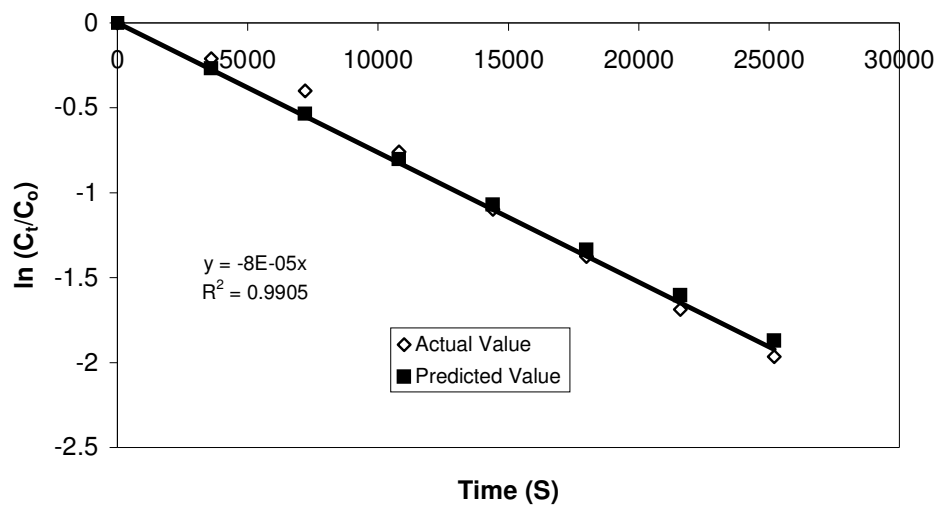
$$\ln C_t / C_o = -kt \quad (4.21)$$

To calculate the k value, a plot of $\ln C_t / C_o$ Vs time was made. The Figures 4.24 and 4.25 show the linear relationship of $\ln C_t / C_o$ Vs time confirmed by high values of determination coefficient (r^2). The rate constant k value calculated was 1.04×10^{-4} m/s, 7.43×10^{-5} for Acid Red 10 B and Acid Pink BE respectively. The mass transfer co-efficient (P) calculated was 10.24×10^{-6} m/s for Acid Red 10B and 7.34×10^{-6} m/s for Acid Pink BE.



(Conditions: Source phase (SP) 150 ml of dye solution (10 mg/L) at pH 1.0 ± 0.1 , receiving phase (RP) 150 ml of 0.1 M NaOH, rate of stirring 600 rpm, time of transport 7 hours).

Figure 4.24 Kinetics of Acid Red 10 B Transport in SLM



(Conditions: As in Figure 4.24)

Figure 4.25 Kinetics of Acid Pink BE Transport in SLM

4.7 APPLICATION TO ANIONIC SILK DYES EFFLUENT

The untreated dye effluent was collected from Uma silk dyeing works, Kancheepuram, India to test the applicability of the developed method. The characteristics of the effluent are furnished in Table 4.15. The dyeing effluents contain high concentration of dye, chloride and sulphate and in high alkaline conditions. Hence, it was neutralized to acidic pH and the further treatments were carried out in LLE, BLM and SLM processes. The efficiency of dye recovery for all process is summarized in Table 4.16.

Table 4.15 Characteristics of Silk Dyeing Effluent

Sl. No.	Parameter	Dye effluent	
		(Acid Red 10B)	(Acid Pink BE)
1.	pH	8.30	8.65
2.	Conductivity m S/cm	2.47	2.46
3.	Total dissolved solids (mg/L)	2400	2350
4.	Total suspended solids (mg/L)	38.0	39.5
5.	Dye Concentration (mg/L)	550	500
6.	Chloride (mg/L)	925	750
7.	Colour	Red	Pink
8.	λ_{\max}	564	519

4.7.1 Liquid-Liquid Extraction Method

Studies were conducted in separating funnel by liquid-liquid extraction (LLE) to determine the efficiency of the recovery of dyes from textile silk dyeing wastewater. The pH of the silk dyeing effluent was adjusted to 1.0 ± 0.1 . The optimum conditions already obtained for LLE were used to find out the % of recovery of dyes. Under optimised conditions the actual dye effluent was tested and $97.7 \pm 0.5\%$ of extraction and stripping was

obtained for Acid Red 10 B in solvent extraction method. For Acid Pink BE, the maximum extraction and stripping was found to be $89.2 \pm 0.5 \%$. The small decrease in efficiency may be due to other impurities present in the effluent.

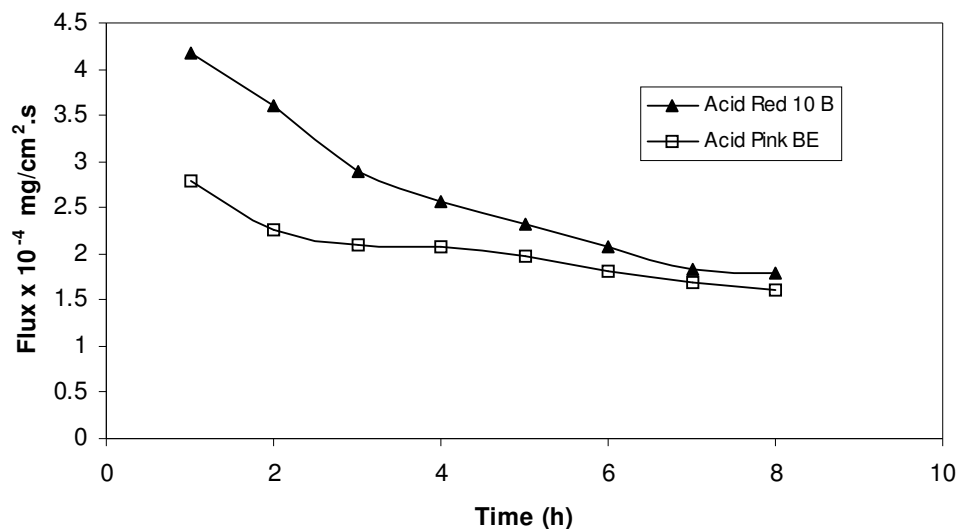
4.7.2 Bulk Liquid Membrane Method

To determine the efficiency of the recovery of dyes from textile silk dyeing wastewater, pH was adjusted to 1.0 ± 0.1 and studies were carried out in BLM reactor. Under optimised conditions obtained from bulk liquid membrane method, the actual dye effluent was tested. $95.0 \pm 0.5 \%$ of Acid Red 10 B was recovered. For Acid Pink BE the maximum dye recovered was found to be $89.0 \pm 0.5 \%$.

4.7.3 By Supported Liquid Membrane Method

Under optimised conditions obtained from supported liquid membrane method, the actual dye effluent was tested. It was found that $74.0 \pm 0.5 \%$ of Acid Red 10 B was recovered. For Acid Pink BE, the maximum dye recovered was found to be $70.0 \pm 0.5 \%$. During the initial concentration variation, it was observed that up to 50 mg/L of dye concentration, there was no change in permeability and with maximum recovery. Hence the effluent was diluted to 10 times and subjected to SLM transport. The maximum dye recovered was 94.0 % for Acid Red 10 B and 85.0 % was Acid Pink BE. The plot of flux for dyeing effluents (feed solution) with time was shown in Figure 4.26. From the results it was also realised that the flux decreased, as the concentration of dye decreased in feed phase. Hence, higher dye concentration in the feed phase led to higher flux. A large membrane area was required to treat high volume of wastewater. This large membrane cost in industrial application may be compensated by higher flux rate of dye transport, which reduces the operating cost and time. The

results show that the SLM developed works satisfactorily for the recovery of anionic dyes.



(Conditions: Source phase 150 mL of 50 mg/L dye effluent at pH 1.0 ± 0.1 , receiving phase 150 mL of 0.1 M NaOH, rate of stirring 500 rpm, time of transport 7 hours.)

Figure 4.26 Flux of Dye Effluents Vs Time

Table 4.16 Removal Efficiency of Silk Dyeing Effluent

Sl. No.	Process	Aqueous dye solution	% of recovery	
			Acid Red 10B	Acid Pink BE
1.	LLE	Synthetic	99.0	91.5
		Real effluent	97.7±0.5	89.2±0.5
2.	BLM	Synthetic	96.2±0.5	90.3±0.5
		Real effluent	95.0±0.5	89.0±0.5
3.	SLM	Synthetic	94.2	85.7
		Real effluent	74.0±0.5	70.0±0.5
		Diluted (10 times)	94.0	85.0

4.8 RECOVERY OF CATIONIC DYES

4.8.1 Liquid-Liquid Extraction Process for Cationic Dyes

Preliminary studies were carried out for the basic dyes (Rhodamine B and Methyl Violet) through liquid-liquid extraction method by using separating funnel using D2EHPA carrier and kerosene as a diluent. Drapola et al (2004) reported that more polar solvents namely tri-2-(ethyl hexyl) phosphate (TEHP) gave significantly lower extraction efficiencies compared to hydrophobic liquids like dihexyl ether and kerosene. Many researchers reported using kerosene as a diluent (Ulewicz 2003, Ma 2004). Hence, further studies were carried out by using kerosene as a diluent.

4.8.2 Influence of pH on Cationic Dyes Extraction

In order to assess the role of the pH of the dye solution during the extraction of cationic dyes, pH variation studies in the range 2.0-7.0 were carried out using a feed solution of 50 mg/L and the results are presented in Table 4.17.

Table 4.17 Effect of Feed Phase pH on Extraction of Cationic Dyes

(Conditions: (Feed phase 10 mL of 50 mg/L dye solution, 20 % D2EHPA in kerosene, equilibration time 10 minutes.)

Sl. No.	pH	Percentage of extraction	
		Rhodamine B	Methyl Violet
1.	2.0	48.3	34.5
2.	3.0	86.4	85.5
3.	3.5	89.2	91.5
4.	4.0	92.6	95.7
5.	4.5	88.4	90.1
6.	5.0	85.3	83.2
7.	6.0	72.5	55.8
8.	7.0	34.5	10.0

The maximum extraction was obtained at $\text{pH } 4.0 \pm 0.1$. With further increasing or decreasing pH in the feed phase lowered extraction efficiency.

4.8.3 Stripping of Cationic Dyes from Loaded Organic Phase

Various acid solutions such as hydrochloric, sulphuric and nitric acids were used as strip phase in ELM and SLM processes for extracting amino acids with D2EHPA as a carrier (Ma et al 2002). Hence the influence of several acids such as sulphuric acid, nitric acid, hydrochloric acid and acetic acid were tested as strip phase in liquid-liquid extraction method. The results are tabulated in Table 4.18. Since acetic acid is used as a one of the ingredients for the dyeing process, acetic acid was used as a stripping reagent and analyzed along with other acids. Among several acids used, only acetic acid showed highest stripping efficiency in liquid-liquid extraction method. Hence, for further studies acetic acid was chosen.

Table 4.18 Effect of Stripping Reagent on Dyes Extraction

(Conditions: Strip phase 10 mL of 0.5 M strip phase, dye loaded D2EHPA in kerosene 10 mL, equilibration time 10 minutes.)

Stripping reagent (1 M)	Recovery of Rhodamine B (%)	Recovery of Methyl Violet (%)
Sulphuric acid	No stripping	No stripping
Nitric acid	No stripping	No stripping
Hydrochloric acid (HCl)	No stripping	No stripping
Sulphuric acid + AcOH (1:1)	53.3	53.1
Nitric acid + AcOH (1:1)	56.3	54.5
HCl + AcOH (1:1)	52.5	51.3
Acetic acid (AcOH)	97.5	95.3
Sodium hydroxide	No stripping	No stripping

4.9 SUPPORTED LIQUID MEMBRANE PROCESS FOR CATIONIC DYES RECOVERY

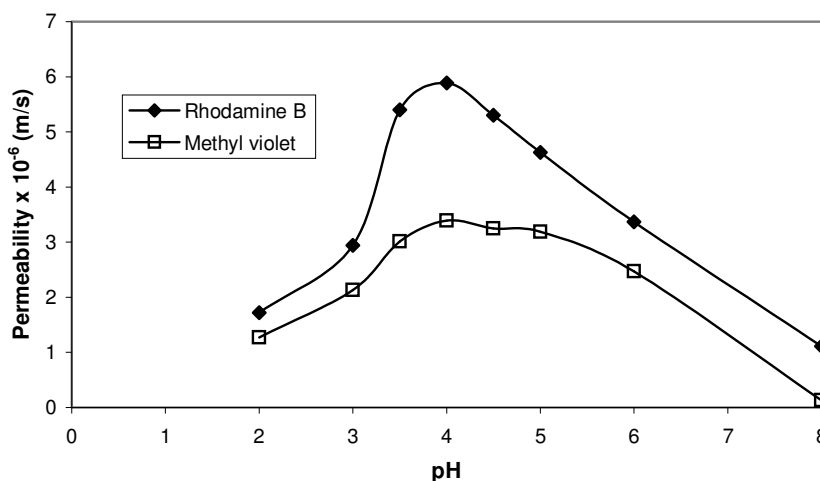
Since the liquid-liquid extraction method usually involves the handling of large quantities of organic solvents, the effect of other parameters such as carrier diluent ratio, equilibration time was not carried out in LLE and straight away carried out in SLM. The experiments were carried out in 100 mL capacity of the reactor.

4.9.1 Effect of Organic Diluent in SLM

In this study carrier D2EHPA (20 %) dissolved in kerosene was tried by liquid-liquid extraction method and better results were obtained in liquid-liquid extraction method. However when it was applied in SLM, there was a drawback in stability. The change in pH of the feed phase was observed during the course of the reaction. Pannu et al (2004) reported that the solvents used, for example, alkanes, alcohols, ketones and alkyl amines are typically flammable, volatile and toxic and their use involves significant safety and environmental risks and application of stringent costly measures to minimize those risks (Gherrou et al 2002). A search for less hazardous solvents for use in extraction of hydrophobic contaminants led us to consider vegetable oil, a natural non-toxic, cost effective and biodegradable extractant for this application. When coconut oil was used, the permeability was found to be 5.9×10^{-6} for Rhodamine B and 3.4×10^{-6} for Methyl Violet at pH 4 after 7 hours and there was no change in the pH during the process. Hence, coconut oil was selected as a diluent and better SLM stability was observed and hence, for further studies coconut oil was used as a diluent instead of Kerosene.

4.9.2 Effect of pH in the Feed Phase

The presence of carrier D2EHPA in the liquid membrane enables the dye transport from feed to the strip phase. The plot of permeability with pH is shown in Figure 4.27.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at $\text{pH } 4.0 \pm 0.1$, strip phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 500 rpm, time of transport 7 hours.)

Figure 4.27 Effect of Feed Phase pH on Permeability of Dyes

The results show that the permeability of dyes increased with increase of pH up to 4. The permeability was found to be 5.9×10^{-6} for Rhodamine B and 3.4×10^{-6} for Methyl Violet at pH 4. Further increase in pH of the feed solution, permeability of both dyes were gradually decreased and at pH 8, the permeability was 1.11×10^{-6} for Rhodamine B and 1.31×10^{-6} for Methyl Violet. The transport of both dyes was maximum at pH 4. Further increasing or decreasing pH in the feed phase lowered extraction efficiency due to the decreasing fraction of dye molecules in the cationic form present in the feed solution. The observed low mass transfer of dyes at $\text{pH} < 4$ is caused by decreasing the driving force of the process. The

result showed that only cationic forms of dyes are extracted across the hydrophobic membrane with high values of the extraction efficiency. The analyses of the feed and strip phases after 7 h of transport did not reveal any pH change implying no effect on membrane stability due to oil diluent used during this study of pH effect.

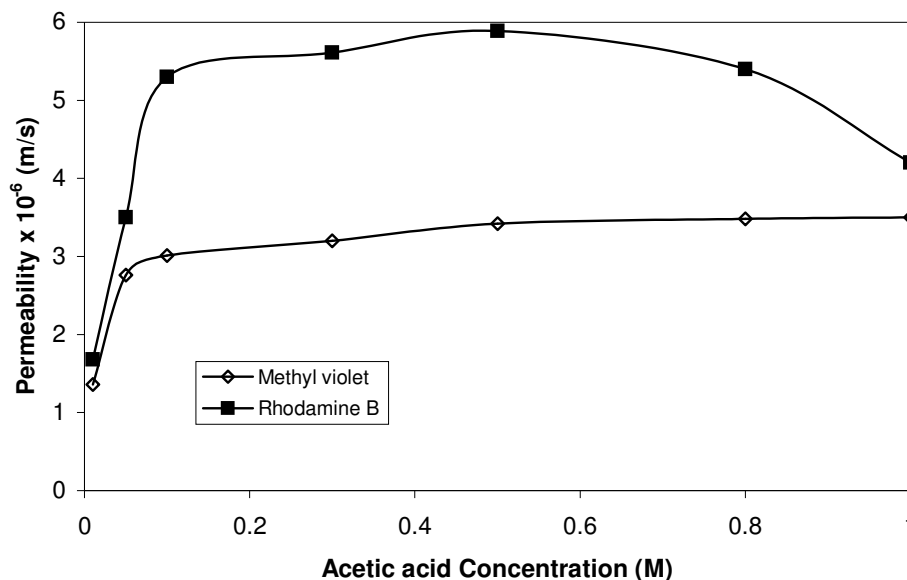
Similar results were reported for peptide extraction by Drapala et al (2004). They concluded that only cationic forms of peptides are extracted across the hydrophobic liquid membrane with high values of the extraction efficiencies and the observed low mass transfer of peptides at $\text{pH} < 3$ is caused by decreasing the driving force of the process. The cationic dye forms a neutral ion pair complex with the anionic carrier equation (4.21).



Ma et al (2002) observed that the extraction rate of L-isoleucine increases with increasing pH at lower pH values, and then decreases with increasing pH at higher pH values. The maximum values of the extraction rate are achieved at lower pH values and a higher extraction rate was obtained at pH 3.5. They also reported that D2EHPA is a weak organic acid, and its capacity for extraction decreases as the acidity in the aqueous solution increases.

4.9.3 Effect of Stripping Reagent Concentration

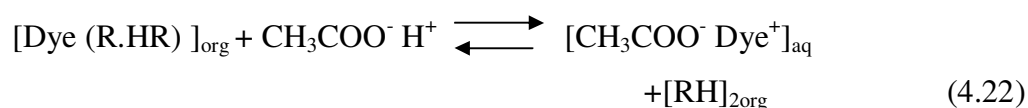
In order to achieve effective permeation of dye in a SLM system, it is necessary to explore the effect of stripping concentration on the permeability. Based on the results obtained in liquid-liquid extraction method, acetic acid was chosen for further studies in SLM. The plot of permeability with strip phase concentration is shown in Figure 4.28.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at $\text{pH } 4.0 \pm 0.1$, strip phase 100 mL acetic acid, rate of stirring 500 rpm, time of transport 7 hours.)

Figure 4.28 Effect of Acetic Acid Concentration in the Strip Phase on Permeability of Dyes

The permeability of dyes increased with increase in the concentration of acetic acid in strip phase. To obtain a high mass transfer, the presence of a proton gradient (driving force) between the strip and feed phase is essential. However the highest permeability was obtained for acetic acid concentration 0.5 M. Further increase in acetic acid concentration in strip phase, permeability was increased for Methyl Violet and decreased for Rhodamine B. This might be due to the fact that the presence of electron withdrawing group (COO^-) in Rhodamine B. From the results obtained for SLM extraction of dyes by using acetic acid, the following reaction equation can be proposed for stripping of dyes across supported liquid membrane containing D2EHPA as a carrier. The dye ion in ion pair complex of cationic dye and anionic carrier is exchanged with a proton and released into the acceptor phase.

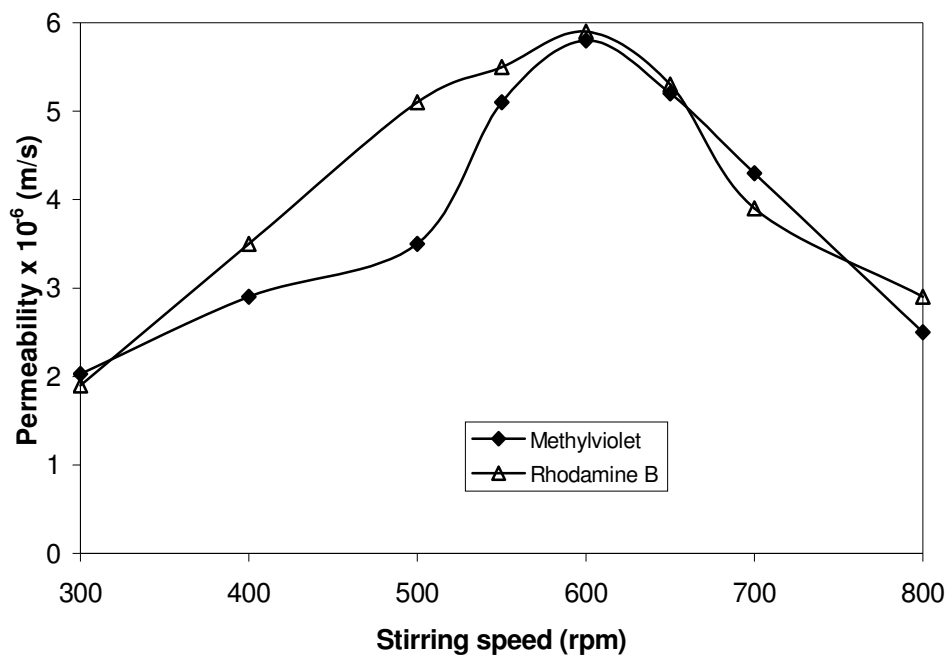


Wieczorek et al (1997) reported that the extraction efficiency depends on the type of acid used in the acceptor phase and as the proton concentration in the acceptor increases, the extraction efficiency of all amino acids investigated increases strongly. Drapola et al (2004) concluded that to obtain a high mass transfer the presence of a proton gradient between the acceptor and donor phase is essential. However, the highest extraction efficiencies were obtained for 1.0 M hydrochloric acid solution. Ming Ma et al (2002) also reported that the stripping rate of L-isoleucine increases with the increase of H^+ concentration.

4.9.4 Effect of Stirring Speed

To study the influence of stirring speed, the experiments were accomplished at different mixing speeds in the range of 300-800 rpm. The plot of permeability with various stirring speed is shown in Figure 4.29. The results revealed that when the speed is increased from 300 rpm, the permeability of dyes is also increased. The maximum permeability was obtained at 600 rpm. When the mixing speed was increased above 600 rpm, the permeability was found to decreased.

This indicates that the aqueous boundary thickness diminishes continuously with increasing stirring speed and that the boundary layer is minimum at 600 rpm. Further decrease in permeability from 600 rpm could be due to the high turbulence caused by stirring, resulting in the displacement of carrier from the membrane pore. This type of observation has been already reported by Alguacil et al (2002). Hence for further studies 600 ± 10 rpm was chosen.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at pH 4.0 ± 0.1 , strip phase 100 mL of acetic acid concentration 0.5 M, time of transport 7 hours.)

Figure 4.29 Effect of Stirring Speed on Permeability of Dyes

The percentage of recovery increases with increase of stirring speed. The Maximum percentage of recovery for Methyl Violet was 85.8 % and for Rhodamine B was 89.5 % at 600 rpm for 7 hours. It was observed that further increase on stirring speed to 800 rpm, decreased the value to 60.5% and 65.4 % after 7 hours respectively.

4.9.5 Effect of D2EHPA Concentration in the Organic Phase

The teflon membrane support was soaked in D2EHPA solutions of different concentrations viz 0 %, 10%, 20 %, 33 %, 50 %, and 66%. The results of effect of different carrier concentrations on permeability of dyes are tabulated in Table 4.19.

Table 4.19 Effect of D2EHPA Concentration on Dyes Transport

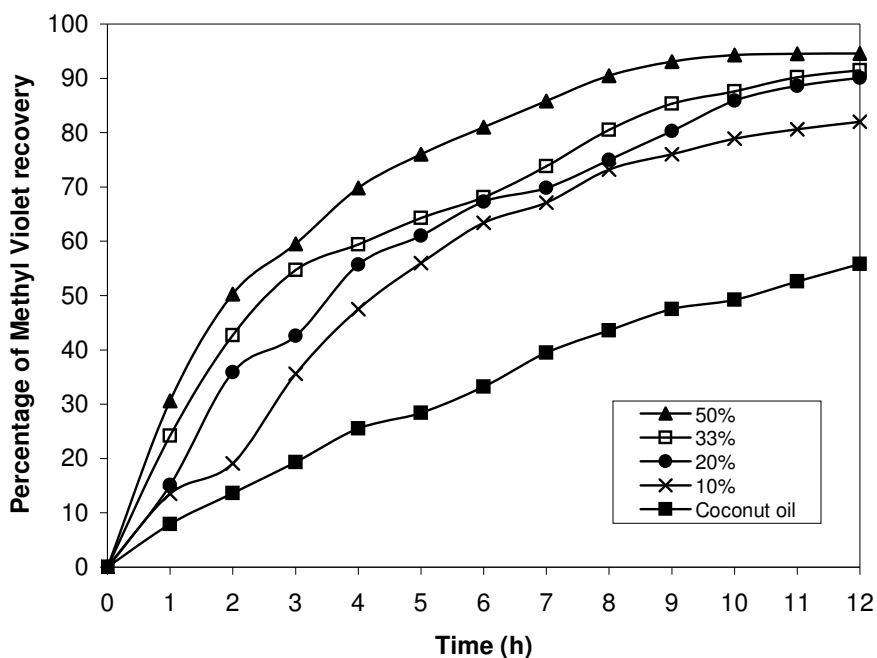
(Conditions: Feed phase 100 mL of 10 mg/L dye solution at pH 4.0 ± 0.1 , receiving phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm, time of transport 7 hours.)

D2EHPA concentration in Coconut Oil (in %)	Permeability for Rhodamine B (10^{-6} m/s)	Permeability for Methyl Violet (10^{-6} m/s)
60	3.61	3.54
55	4.95	4.15
50	5.91	5.10
45	4.80	4.32
40	3.92	3.90
33	3.23	3.51
20	2.05	2.41
10	1.21	1.89
0	0.92	1.01

The permeability was increased with increase of carrier concentration up to 50 %. Further increase in D2EHPA concentration, i.e. above 50 %, the permeability was decreased. At higher carrier concentrations the decrease of permeability can be explained in terms of the increase in solution viscosity that increases membrane resistance (Alguacil 2004).

Chaudry et al (1992) reported that in the transport of Ti (IV), permeability increases to 8.02×10^{-12} at $2.04 \text{ mol. dm}^{-3}$ D2EHPA and then decrease and this may be attributed to the increasing viscosity with the increase in carrier concentration in the membrane liquid. They also reported that increase in viscosity increases the resistance to the movement of the complex species under transport.

The plots of recovery of dyes by using different concentrations of the carrier are shown in Figures 4.30 and 4.31 for Rhodamine B and Methyl Violet respectively.

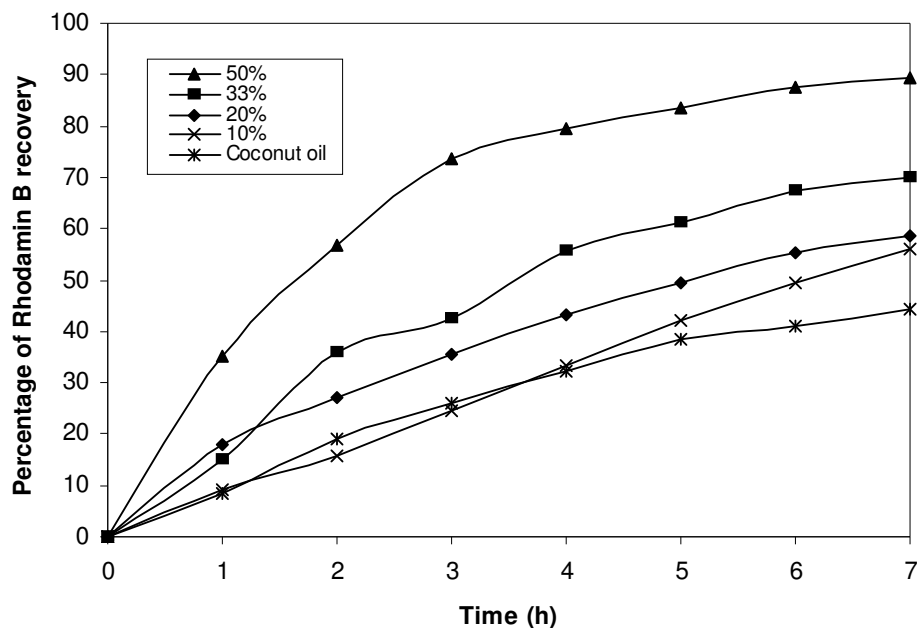


(Conditions: Feed phase 100 mL of 10 mg/L Methyl Violet solution at pH 4.0 ± 0.1 , receiving phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm, time of transport 12 hours.)

Figure 4.30 Effect of D2EHPA Concentration on Recovery of Methyl Violet

Ma et al (2002) reported that for higher concentration of D2EHPA, the maximum values of the extraction rate are achieved. The stability of the membrane was tested by measuring pH on both sides. No change in the pH confirmed the stability. A similar transport experiment was carried out in the absence of D2EHPA (100 % of coconut oil) for reference. In the absence of carrier, the percentage of transport was 39.5 % for Methyl Violet and 44.0 % for Rhodamine B for 7 hours. This might be due to the diffusion of the unionised dye taken place into the oil phase due to the hydrophobic nature of

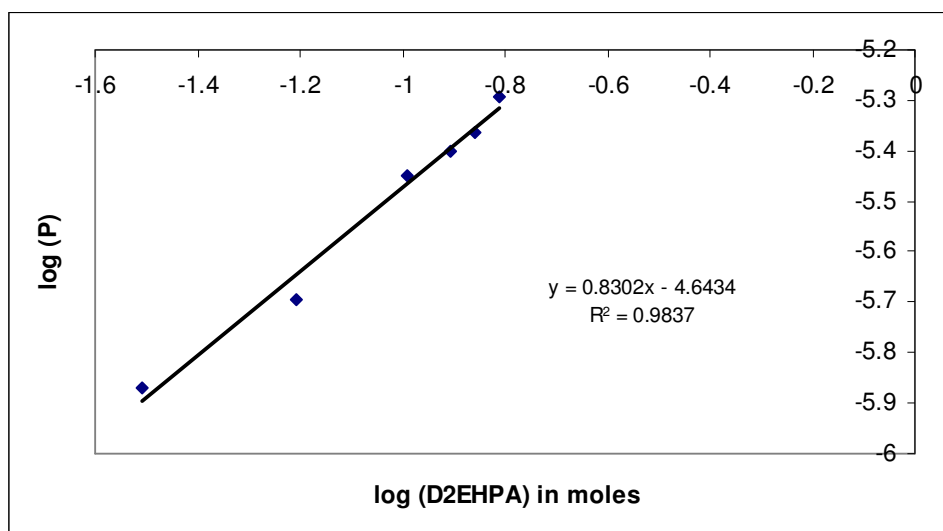
dye and oil. Hence for further studies 50 % D2EHPA carrier concentration was chosen.



(Conditions: Feed phase 100 mL of 10 mg/L Rhodamine B solution at pH 4.0 ± 0.1 , receiving phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm, time of transport 7 hours.)

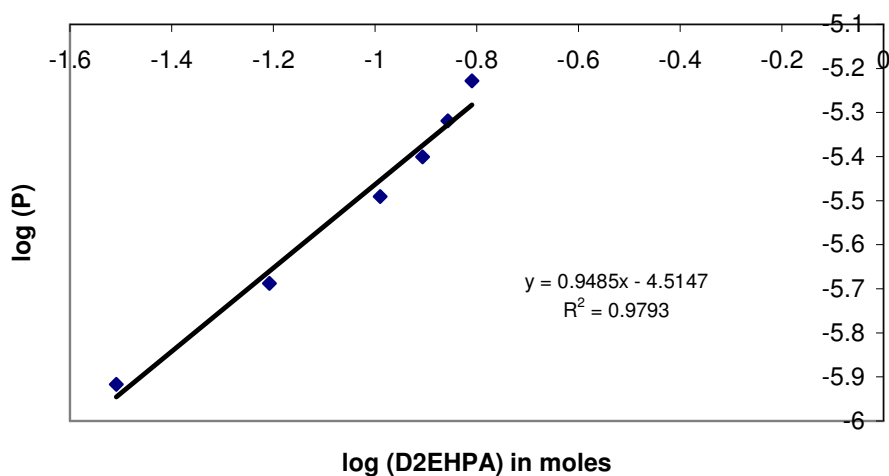
Figure 4.31 Effect of D2EHPA Concentration on Recovery of Rhodamine B

The plots of \log D2EHPA concentration versus \log P for Rhodamine B and Methyl Violet are given in Figures 4.32a and 4.32b respectively. The plots are linear found to be slopes with values of 0.95 and 0.83 for Rhodamine B and Methyl Violet respectively, which indicates that one mole of dye forms a complex with one mole of D2EHPA. The dye to reagent mole ratio is 1:1. This may be due to the presence of $=N^+$ group in both dyes.



(Conditions: Feed phase 100 mL of 10 mg/L Rhodamine B solution at pH 4.0 ± 0.1 , receiving phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm, time of transport 7 hours.)

Figure 4.32a Plot of log D2EHPA Vs log P for Methyl Violet

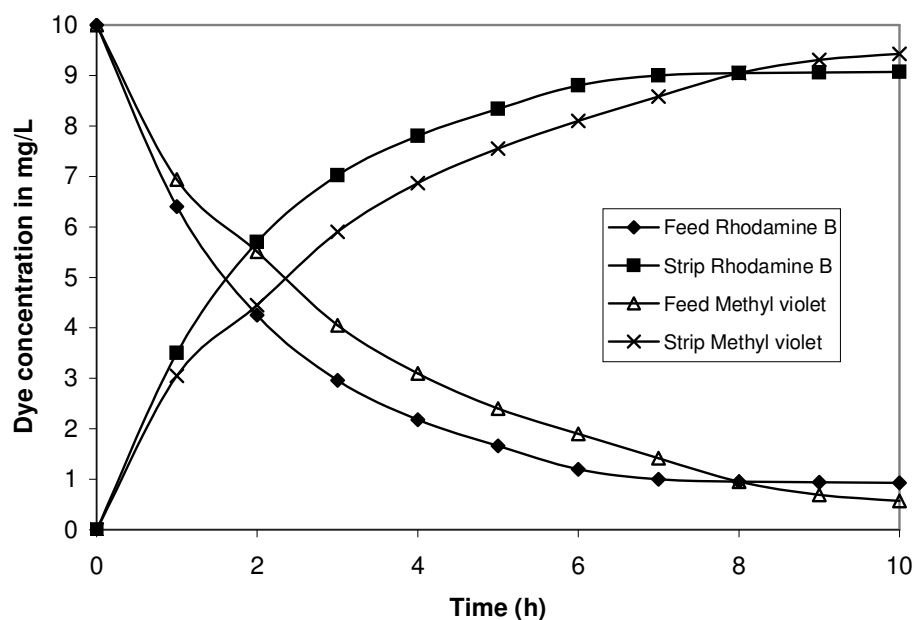


(Conditions: As given in Figure 4.32 a)

Figure 4.32b Plot of log D2EHPA Vs log P for Rhodamine B

4.9.6 Effect of Time

The amount of dye transport through the supported liquid membrane as a function of time was studied under the optimum conditions. The results are shown in Figure 4.33. It shows a constant increase in dye concentration in the strip phase and decrease in feed phase for both dyes. It was observed that after 4 hours the amount of dye in the feed phase was 2.18 mg and in the strip phase 7.8 mg for Rhodamine B respectively. For Methyl Violet, the amount of dye in the feed phase was 2.4 mg and in the strip phase 7.55 mg respectively. However, the maximum Rhodamine B dye recovered at 7 hours was 9.02 mg and Methyl Violet at 9 hours was 9.57 mg respectively. After this time, there was no appreciable change in the concentration of dye in the aqueous phases.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at pH 4.0 ± 0.1 , strip phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm.)

Figure 4.33 Effect of Time on Dyes Transport

4.9.7 Effect of Initial Dye Concentration on Dyes Transport

To study the effect of the initial dye concentration in the feed solution, the dye initial concentration was varied from 10 mg/L to 200 mg/L. Table 4.20 presents the permeability of dyes for different dye concentration.

Table 4.20 Effect of Dye Initial Concentration on Dyes Transport

(Conditions: Feed phase 100 mL of dye solution at pH 4.0 ± 0.1 , receiving phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm, time of transport 7 hours)

Sl.No.	Initial dye concentration (mg/L)	Permeability for Methyl Violet (10^{-6} m/s)	Permeability for Rhodamine B (10^{-6} m/s)
1.	10	5.14	5.89
2.	20	5.12	5.86
3.	30	5.12	5.86
4.	50	5.03	5.60
5.	100	4.90	4.80
6.	150	4.70	4.60
7.	200	4.40	4.20

From the results it was observed that the permeability of dyes decreased with increase of initial dye concentration. The maximum permeability achieved was 5.89×10^{-6} m/s for Rhodamine B and 5.14×10^{-6} m/s for Methyl Violet up to 30 mg/L using D2EHPA carrier. Then it was reduced to 4.4×10^{-6} m/s for Rhodamine B and 4.2×10^{-6} m/s for Methyl Violet at 200 mg/L. Calzado et al (2005) found that the permeability of amino acid decreased from 11 ± 3 cm/s for 0.05 mM amino acid concentration to 3 ± 1 cm/s for 1.00 mM amino acid concentration.

This decrease might be attributed to two reasons (Alguacil et al 2004): membrane saturation and lower effective membrane area and maximization due to saturation of the membrane pores with dye-carrier species and in addition, the build up of a carrier layer on the membrane interface which assists the retention of the separating constituent on the entry side. The percentage of recovery was decreased from 89.5 % (10 mg/L) to 85.5 % (200 mg/L) for Rhodamine B. Similar results were obtained for Methyl Violet also. Wieczorek (1997) also reported that the percentage of extraction decreased with increase of aminoacid concentration. When the concentration of tryptophan was 0.01 mM, the % of extraction was 34.2 and it was 4.9 % for 10 mM.

4.9.8 Feed to Strip Volume

Based on the results obtained for previous SLM system for anionic dyes, in the initial experimental studies, a volume of 100 mL in both feed and strip solutions were taken. The maximum permeability obtained was 5.9×10^{-6} m/s for Rhodamine B and 5.1×10^{-6} m/s for Methyl Violet. In another experiment, the volume of feed and strip solution was increased to 150 mL and the studies were carried out without increasing membrane area. The permeability was slightly decreased to 5.5×10^{-6} m/s for Rhodamine B and 4.9×10^{-6} m/s for Methyl Violet. The results showed that with increase in volume of the aqueous phase, the permeability was decreased. This may be due to the less membrane contact area. By maximising the contact area between the aqueous phase and organic phase, the separation efficiency could be enhanced.

The obtained results showed that the stripping of dyes were achievable with a concentration factor equal to 1. Another way of increasing the concentration factor in strip is by reusing the same strip solution. On

continuous repetition of the procedure up to three runs without change of strip solution, the average permeability was 5.6×10^{-6} m/s for Rhodamine B and 5.01×10^{-6} m/s for Methyl Violet. A concentration factor of three can be achieved easily. It shows that the D2EHPA in coconut oil has an efficiency of uphill transport and achieve a concentration factor > 3 .

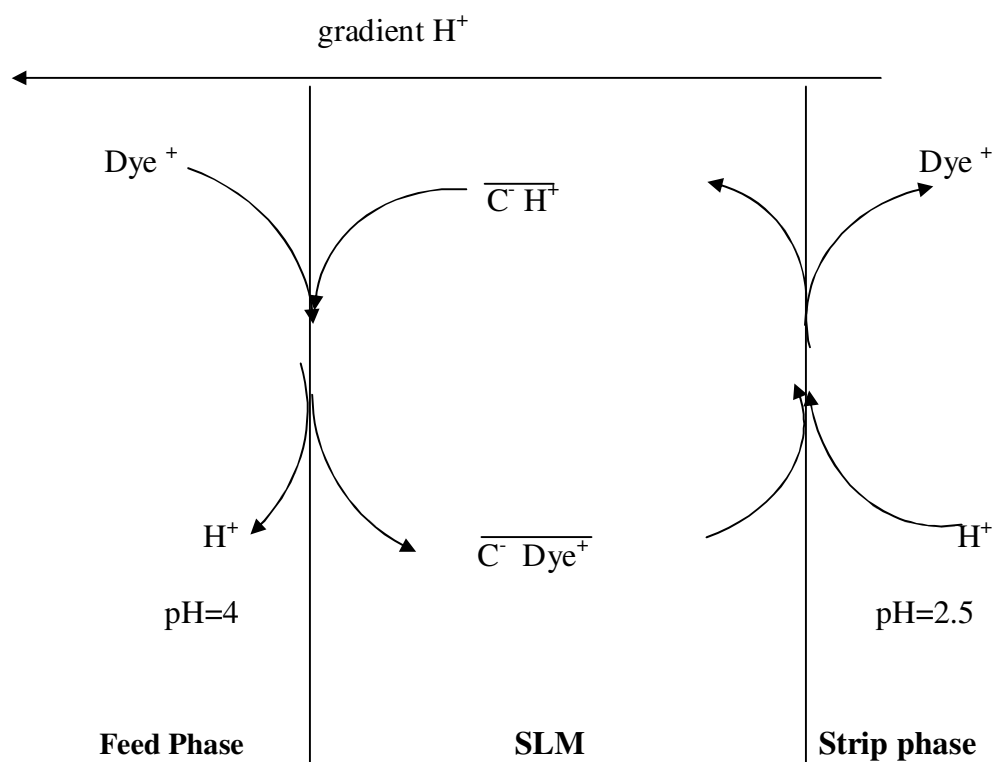
4.9.9 Transport Mechanism

The dyes used were cationic in nature. Based on the results obtained, the facilitated transport of cationic dye transport across the developed SLM system containing D2EHPA as carrier can be explained as follows. Figure 4.34 depicts schematically the dye transport processes in the SLM process as counter-coupled transport of dyes using D2EHPA as carrier.

1. The cationic dye diffuses from the bulk of the source phase to the source / membrane interface through aqueous boundary layer.
2. At the feed phase–membrane interface, the cationic form of dye forms a neutral ion pair complex with the carrier.
3. The complex diffuses through the liquid membrane to the strip phase due to the potential gradient between feed and strip phases.
4. Then on the strip membrane interface, the dye ion is exchanged with a proton and released into the strip phase.
5. This is confirmed by the presence of dye ion in the strip phase and also there is no change in pH of strip phase.
6. Finally, the free D2EHPA acid is diffused back to the feed phase and the cycle is repeated.

In peptide extraction Drapola et al (2004) proposed the mechanism such that, in the donor phase, the cationic form of peptide forms a

neutral complex, which diffuses across the membrane. Then the peptide ion is exchanged with a proton in the acceptor membrane interface and released into the acceptor phase. The proton carrier complex is diffused back to the donor side and the cycle is repeated.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at $pH\ 4.0 \pm 0.1$, strip phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm, time of transport 7 hours.)

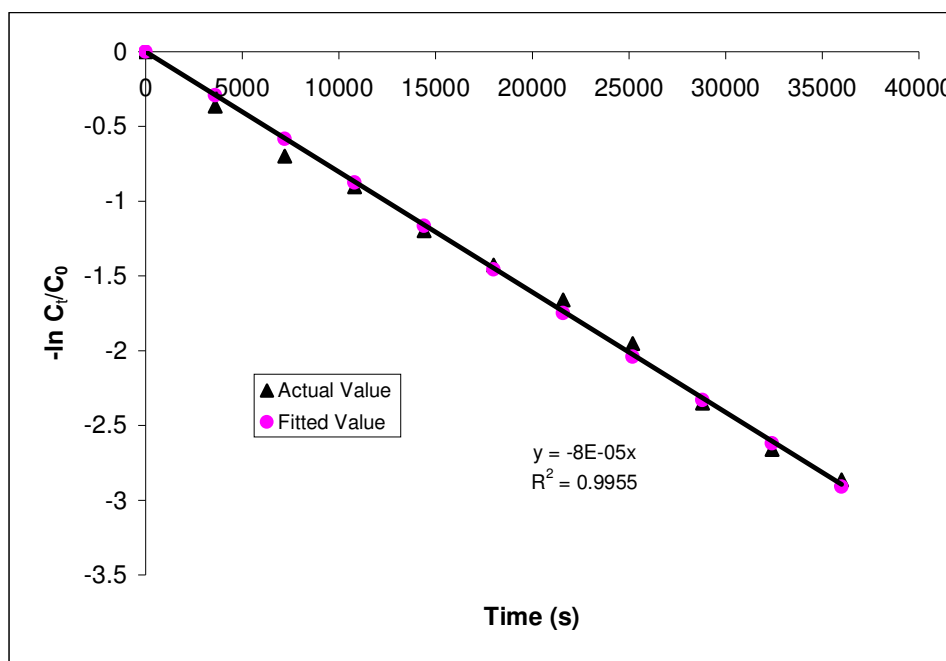
Figure 4.34 The Mechanism of Cationic Dye Transport with SLM using the Anionic Carrier D2EHPA

4.9.10 Kinetics of Cationic Dye Transport in SLM

The kinetics of transport process across SLM can be described by a first order reaction with respect to dye concentration (Yang et al 2003), the mass transfer coefficient k can be calculated by the equation

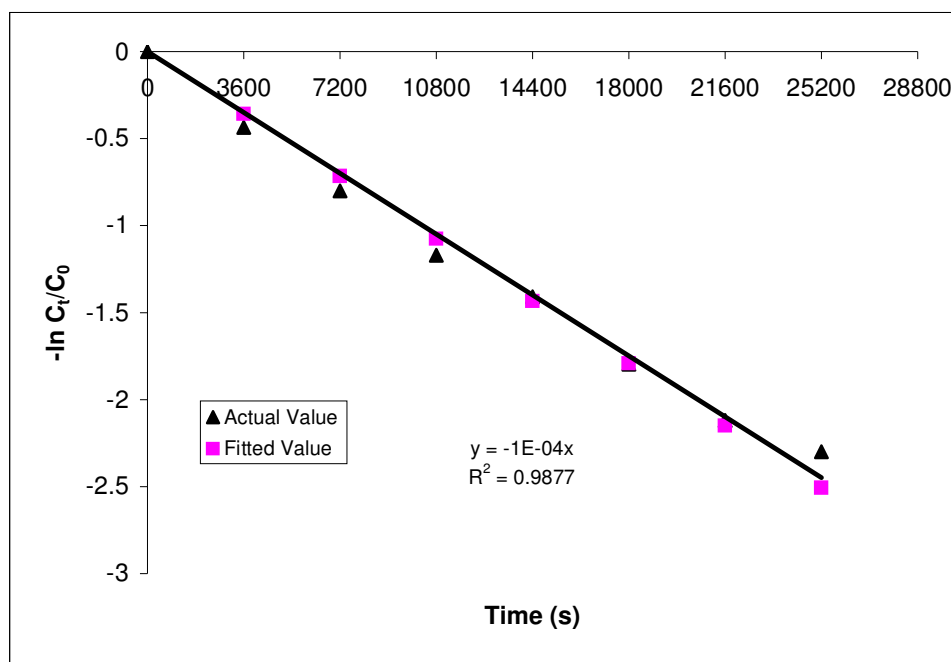
$$\ln C_t / C_o = -k t$$

To calculate the k value, a plot of $\ln c_t/c_o$ Vs time was made. The mass transfer coefficient is obtained from the graph by determining the slope of the corresponding linear relationship for the experimental data. Figures 4.35 and 4.36 show the linear relationship of $\ln C_t/C_o$ Vs time confirmed by high values of correlation coefficient (r^2). The rate constant k value calculated was $9.95 \times 10^{-5} \text{ s}^{-1}$, $8.10 \times 10^{-5} \text{ s}^{-1}$ for Rhodamine B and Methyl Violet respectively. From the K value, the mass transfer coefficient P calculated was $6.55 \times 10^{-6} \text{ m/s}$ for Rhodamine B and $5.30 \times 10^{-6} \text{ m/s}$ for Methylviolet.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at pH 4.0 ± 0.1 , strip phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm.)

Figure 4.35 Kinetics of Methyl Violet Dye Transport in SLM



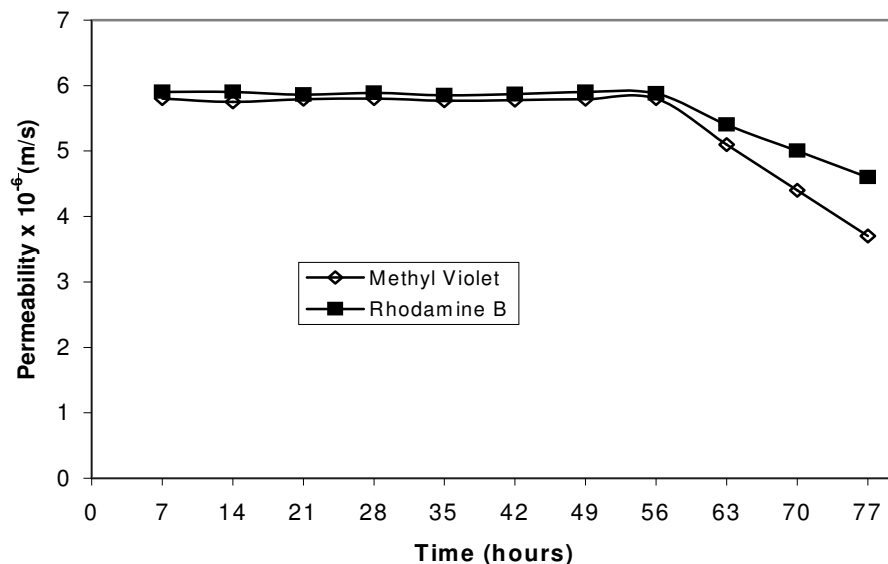
(Conditions: Feed phase 100 mL of 10 mg/L dye solution at pH 4.0 ± 0.1 , strip phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm.)

Figure 4.36 Kinetics of Rhodamine B Dye Transport in SLM

4.9.11 Reuse of Supported Liquid Membrane

Stability of PTFE-D2EHPA in coconut oil system was studied by using one disc for different runs without further impregnation of carrier. The results are shown in Figure 4.37. Stability of the SLM was quite remarkable when eight consecutive experiments for 7 hours were performed without re-impregnation of the D2EHPA carrier. This showed that the D2EHPA performed a stable SLM system in PTFE membrane. This may be due to high viscosity of D2EHPA and coconut oil. No water transport through the SLM was observed during the experiment because there was no change of pH during the process. This may be due to the stability SLM system containing D2EHPA as carrier in coconut oil. After 56 hours there was a decrease in

permeability. Thus it was observed that the developed SLM system containing D2EHPA as carrier possessed good stability with uphill transport for cationic silk dyes.



(Conditions: Feed phase 100 mL of 10 mg/L dye solution at pH 4.0 ± 0.1 , strip phase 100 mL of acetic acid concentration 0.5 M, rate of stirring 600 rpm time of transport 7 hours for each run.)

Figure 4.37 Reusability of Cationic Dyes Transport in SLM

Alguacil (2004) reported that the lifetime of the membrane was evaluated by using the same support in several runs of 3 h duration and after three consecutive experiments, the zinc extraction only suffered a slight variation, but the membrane efficiency was achieved by re-impregnating the support. In this experiment also, the same membrane efficiency (89.5 % for Rhodamine B and 89.3% for Methyl Violet) was achieved by re-impregnation after 56 hours.

4.10 APPLICATION TO CATIONIC SILK DYES EFFLUENT

The untreated dye effluent was collected from Uma silk dyeing works, Kancheepuram to test the applicability of the developed method. Characteristics of effluents generated in terms of pH, TDS and TSS were characterized using standard methods for analysis of wastewater. The characteristics of the effluent are given in Table 4.21. The dyeing effluents were found to contain high concentration of dye, chloride and sulphate and in high alkaline conditions. Hence, it was neutralized to acidic pH 4

Table 4.21 Characteristics of Cationic Silk Dyeing Effluent

Sl. No.	Parameter	Dye effluent	
		Rhodamine B	(Methyl Violet)
1.	pH	8.80	8.70
2.	Conductivity m S/cm	5.71	4.46
3.	Total dissolved solids (mg/L)	3500	2350
4.	Total suspended solids (mg/L)	48.0	59.5
5.	Dye Concentration (mg/L)	300	250
6.	Chloride (mg/L)	1825	1382
7.	Colour	Pink	Violet
8.	λ_{\max}	554	582

4.10.1 Effluent Treatment by Supported Liquid Membrane Method

To determine the efficiency of the recovery of dyes from textile silk dyeing wastewater, pH was adjusted to $\text{pH } 4.0 \pm 0.1$ and studies were carried out in supported liquid membrane method (SLM) using D2EHPA as carrier in coconut oil under the optimised conditions obtained from SLM. For Rhodamine B, the maximum dye recovery was 76.0 %. For Methyl Violet, the maximum dye recovered was found to be 73.0 %. During the initial concentration variation, it was observed that up to 30 mg/L of dye

concentration, there was no change in permeability and with maximum recovery. Hence the effluent was diluted to 10 times and subjected to SLM transport. The maximum dye recovered was 93.0 % for Methyl Violet and 87.0 % was Rhodamine B. The results are summarized in Table 4.22.

Table 4.22 Removal Efficiency of Silk Dyeing Effluent

Sl. No.	Process	Aqueous dye solution	% of recovery	
			Rhodamine B (9 hours)	Methyl Violet (9 hours)
1.	SLM/ D2EHPA in Coconut oil	Synthetic	90.5	95.7
		Real effluent	76.0	73.0
		Effluent diluted (10 times)	87.0	93.0

It is evident from the data that the method works satisfactorily for the recovery of cationic dyes as the recovery of Rhodamine B and Methyl Violet were found to be near quantitative.

CHAPTER 5

SUMMARY AND CONCLUSIONS

With the growing use of a variety of dyes, pollution from textile effluent is one of the major environmental problems of the world. There are about 3000 types of dyes in the world market. Dyes that have low biodegradability greatly influence natural ecosystems and humans. Although research has been carried out on the development of the economic removal of dyes still remains a significant problem.

Solvent extraction process, which involves extraction and stripping steps, is not economical to extract trace amount of dye molecules present in very dilute solutions. Now-a-days liquid membrane process is found to attract worldwide attention, and much work has been directed toward developing methods for its application to the separation of various metals and to a lesser degree of separation of organic substances. The two-step process of solvent extraction is modified to single step liquid membrane (LM) process by combining them.

A significant advantage of using SLM over conventional liquid-liquid extraction is that only a trace amount of organic ligand (LM) is required for transferring solute from the source phase into the receiving phase.

In the present work, a study on the recovery of anionic silk dyes (Acid Red 10 B and Acid Pink BE) and cationic dyes (Rhodamine B and Methyl Violet) from dye solution using TBP carrier and D2EHPA carrier through liquid-liquid extraction and liquid membrane processes were carried

out and the developed method was tested for its applicability with real silk dyeing effluent. The major findings and conclusions drawn are summarized below.

CONCLUSIONS

1. In the LLE process, maximum extraction of 99.0 % for Acid Red 10 B and 91.5 % for Acid Pink BE was achieved at pH 1.0 ± 0.1 with 1: 1 TBP/Hexane ratio and the maximum stripping obtained with 0.5 M NaOH.
2. The presence of chloride and sulphate slightly decreased the extraction efficiency. The dye to TBP mole ratio was found to be 1:2 indicating that one mole of dye forms a complex with two moles of TBP.
3. In BLM process, an increase in dyes transport was observed as the sodium hydroxide concentration of stripping solution was increased to around 0.1 M.
4. A maximum dye extraction was achieved with 50 % TBP carrier concentration. Intermixing of solution was observed, when the stirring speed was increased beyond 220 ± 10 rpm.
5. The transport studies in SLM revealed that PTFE plain membrane with 1.0 μm pore size has more transport efficiency than 0.5 μm pore size.
6. The presence of sulphate and chloride ions in dye solutions decreased the dyes transport beyond 1000 mg/L. The maximum permeability observed was 11.0×10^{-6} m/s for Acid Red 10 B and 7.7×10^{-6} m/s for Acid Pink BE.
7. Under the optimum conditions, the recovery of anionic dyes from silk dyeing wastewater was found to be satisfactory by

applying solvent extraction, bulk liquid membrane and supported liquid membrane methods.

8. The results provided that the maximum transport was obtained at pH 4 in the feed phase and pH 2.5 in the strip phase. Increase of dye initial concentration, the % of extraction was decreased.
9. The reusability was investigated by using the same membrane consecutive reactions without re-impregnation of the D2EHPA carrier and the membrane can be used up to 8 runs.
10. The mass transfer coefficient k value calculated was 6.5×10^{-6} m/s for Rhodamine B, 5.3×10^{-6} m /s for Methyl Violet respectively.
11. Under the optimum conditions the recovery of cationic dyes from silk dyeing wastewater was found to be satisfactory for supported liquid membrane methods by using D2EHPA as carrier and coconut oil as a diluent. It is hoped that the methods developed using simple equipments can find use in recovery of dyes in effluent.

SCOPE FOR FUTURE WORK

- The studies may be extended by using different carriers like Cyanex 923, TOPO etc., for anionic dyes.
- Reusability of the treated water and reuse of the recovered dyes can be studied.
- Scale up and application to similar types of silk dyeing effluent can be analysed.