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A Comparative Study on recovery of silk dyes Acid Red 10 B and Acid Pink BE by using Solvent extraction, Bulk Liquid membrane and Supported Liquid Membrane through tri-n-butyl phosphate as carrier

N.Hajarabeevi* and K.Palanivelu

***** Professor, B.S.Abdur Rahman University

Director of Centre for Climate Change and Adaptation Research, Anna University

***Corresponding author: Email: Hajarabeevi@bsauniv.ac.in**

ABSTRACT

The recovery of anionic silk dyes Acid Red 10 B and Acid Pink BE was compared in solvent extraction, bulk liquid membrane and Supported Liquid Membrane methods by using tri-n-butyl phosphate (TBP) as carrier and hexane as diluent. The effects of parameters such as pH of feed, stripping reagent concentration, recovery time, reusability of solvent and initial concentration of dye were examined. The optimum condition for recovery of dye was pH of the feed 1.0 ± 0.1 and 0.1 M- 0.5 M sodium hydroxide was used as a stripping phase. In solvent extraction method, the maximum recovery of Acid Red 10 B was 99.0% and Acid Pink BE was 91.3 ± 0.5. In Bulk liquid membrane method (BLM) 96.2 ± 0.5 % of Acid Red 10 B and 90.3 ± 0.5 % of Acid Pink BE was recovered. In Supported liquid membrane method (SLM) 94.2 ± 0.5 % of Acid Red 10 B and 85.7± 0.5 % of Acid Pink BE was recovered. The real dye effluent tested and gave satisfactory results. The reusability of dye in all the three methods was also studied. Even though the percentage of recovery is less in Supported liquid membrane method, only a small quantity of solvent/carrier is required.

Keywords: silk dyes removal, solvent extraction, bulk liquid membrane, recovery, TBP- hexane.

INTRODUCTION

The textile industry is one of the oldest and largest industries in the country. The textile dyeing industry produces large quantity of wastewater varying from 50-100 L / kg of the cloth processed. It is estimated that 10-15 % of the dye is lost during the dyeing process and released as effluent (1). The effluents from textile dyeing industries contain a variety of chemicals and dyes, which are carcinogenic and mutagenic (2). The disposal of wastewater causes significant environmental problems. Indeed these effluents are toxic and mostly non bio-degradable [3]. Various physico-chemical processes like chemical precipitation, adsorption (4), photo catalytic degradation (5) etc are currently used. In all these methods, valuable dyes are not recovered. In all these methods, valuable dyes are destroyed and they are not recovered.

Solvent extraction of dyes has been reported (6-8, 12). Two steps in solvent extraction are reduced to single step in Liquid Membrane (LM) process by combining them. Liquid membrane studies on dye removal have been reported (9). The optimum conditions such as effect of pH, effect of stripping reagent concentration, effect of TBP- hexane ratio, effect of equilibration time and initial dye concentration variation for the maximum removal of the dye was studied and applied for the recovery of dye in a real silk dyeing effluent. A comparative study has been made to recover anionic silk dyes Acid Red 10 B and Acid Pink BE from aqueous solution using solvent extraction and BLM method TBP- Hexane based liquid membrane was performed with H- type and SLM method to optimize the conditions for the removal and recovery of anionic dyes from aqueous solution.

MATERIALS AND METHODS

Tri-n-butyl phosphate, hexane, sodium hydroxide were purchased from Merck, India. Hexane and TBP were used without any purification. Sulphuric acid used was supplied by Excel Chemicals India. All the reagents used were of AR grade. The commercially available silk dye Acid red 10 B and Acid Pink BE (Figure-1) anionic dyes was kindly donated by Uma Dyeing works, Kancheepuram, Tamil Nadu.

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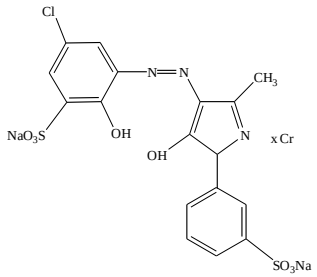

Figure .1.Structure of Acid Pink BE (CI Acid red 183)

Apparatus and measurement: The spectrophotometer used for the measurement of dye concentration in the aqueous phases was a Spectronic 20 Genesys (Germany). The pH measurements were made using WTW pH meter (Germany) with combined electrode. Electrophoresis apparatus (submarine Gel system, India) was used to find out the nature of dyes. The λ_{max} value for Acid Red 10 B was found to be 566 nm and for Acid Pink BE was found to be 519 nm.

Extraction Procedure: All the experiments were carried out at ambient temperature (27°C). The preparation of dye solutions was as follows. 0.1 g of Acid Pink BE and Acid Red 10 B (as received) was dissolved in 1000 mL of distilled water to make a dye solution typical of dye bath rinse effluents (100 mg/ L). About 30 mL aqueous solution of dye (adjusted pH to 1.0 ± 0.2) containing 100 mg/L was taken in a separating funnel along with 30 mL mixture of TBP+hexane (1:1 ratio). The phases were mixed gently for five minutes and allowed to stand for separation of phases. The aqueous layer was analysed for remaining dye using spectrophotometer at 566 nm for Acid Red 10 B and 519 nm for Acid Pink BE. The extracted dye was shaken with 0.5 M sodium hydroxide solution for five minutes and allowed to stand for separation of phases. The aqueous layer (sodium hydroxide) was neutralised and analysed for recovered dye using spectrophotometer.

The BLM reactor used during this study, consisted of two half cells like H Type. The feed solution (containing 100 ml of 50 mg dye solution) was fed on one side and strip solution (containing 100 ml of 0.1 M NaOH) on another side and liquid membrane (200 ml TBP+Hexane) contacting both feed and strip solution with two mechanical stirrers were fixed at the top to agitate the liquid confined in the half cells. The inner dimension of the transport cell was 75-mm diameter X 190-mm depth X 45-mm height (from the bottom). The reactor was also equipped with outlets for draining the liquid and collecting samples. Determination of the dye concentration in both aqueous phases was carried out by spectrophotometer at 566 for Acid Red 10 B and 519 nm for Acid Pink BE. A similar transport experiment was carried out in the absence of carrier for reference. Each experiment was duplicated under identical conditions and the analysis was carried out in triplicate. The results were found to be reproducible within ± 4.0 %.

SLM reactor consists of two cylindrical cells one for feed solution and another for strip solution with the capacity of each cell was 150 mL for dye removal. Polytetrafluoroethylene (Teflon) was used as support and the membrane containing carrier was placed in between the cells. Magnetic stirrers were used to mix the aqueous feed and strip solution. The polymeric supported membrane was impregnated with a carrier solution by immersion for 24 hours and then leaving it to drip for a few seconds before being placed in the transport cell. The concentration of dyes in the feed and strip side was measured periodically by sampling a small amount from both feed and strip side. The photographic view of the SLM reactor is shown in Figure-2.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on the extraction of anionic dyes was studied by varying the pH from 1.0 to 7.0 in solvent extraction (SX) method and from 1.0 – 4.0 in BLM process was studied and the results are shown in Table-1. The extraction of dyes was maximum at lower pH. The percentage of extraction of dyes was found to decrease with the increase in pH and there was no extraction at pH 7.0. This study reveals that maximum extraction (91.0 % in solvent extraction, 90.0 % in BLM and 85.7 % in SLM for Acid Pink BE) was achieved at pH 1.0 ± 0.2. This may be due to the fact that at lower pH, H^+ ion concentration is high and hence the anionic dye readily forms an ion-pair complex with

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cationic TBP. At higher pH, TBP does not form an ion pair with dye because TBP remains neutral and not present in cationic form, thus resulting in poor extraction. Hence for further studies pH 1.0 ± 0.1 was chosen.

Figure.2.Photographic View of the SLM Reactor

Table.1.Effect of pH on Extraction of Acid Pink BE.

pH	Amount of dye of Extracted (mg/L)		
	SX	BLM	SLM
1.0	**91.0**	**90.0**	**85.7**
2.0	**81.0**	**73.8**	**70.5**
3.0	**65.8**	**55.5**	**54.2**
4.0	**30.5**	**25.0**	**22.5**

Experimental conditions: Dye initial concentration 100 mg/lit for SX and 50 mg/L for BLM, Aqueous/ solvent ratio (1:1), equilibration time 5 min for SX and 120 min for BLM.

Effect of stripping reagent concentration: Since sodium hydroxide showed good stripping efficiency among the various alkaline chemicals, to check out the effect of stripping reagent concentration, the concentration of receiving (sodium hydroxide) was varied in the range of 0.01 M to 0.50 M for SX and 0.05 to 0.7 M.for BLM and SLM. It is clear that, the recovery of dye increases with increasing the concentration of sodium hydroxide from 0.05 to 0.7 M. The recovery of Acid Pink BE dye in 300 seconds was found to be 55.6 mg/L at 0.05 M NaOH and slightly increases to 82.5 mg/L at 0.2 M NaOH. In the range of 0.4 M – 0.70 M NaOH, stripping efficiency is still increased to 91.2 mg/L. This is probably due to increase in the concentration of hydroxyl ions. Hence 0.5 M sodium hydroxide solution was selected for further studies in SX. In BLM and SLM methods, the percentage of recovery is increased with increase of sodium hydroxide concentration up to 0.1 M. Later it was constant. The maximum recovery of dye in 120 minutes was 90.0 % for BLM from loaded Hexane + TBP mixture with 0.1 to 0.5 M sodium hydroxide respectively. The maximum recovery of dye in 7 hrs was 85.7 % ± 0.5 for SLM method. Hence for further studies 0.1 M NaOH was chosen BLM. Similar effects were observed for Acid red 10 B. The results are shown in Figure -3

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 %.

Transport Mechanism: The dye was found out as an anionic by electrophoresis method. 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. This mechanism is proved by plotting log D versus log TBP concentration for Acid Red 10 B and Acid Pink BE and the plots of are given in Figures 4 and 5 respectively

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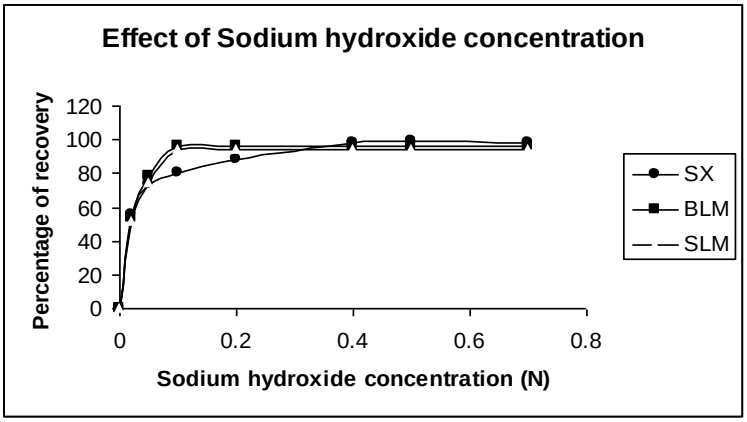

(Conditions: Source phase 100 mL of 100 mg/L Acid Pink BE dye solution at pH 1.0 ± 0.1, receiving phase 100 mL of NaOH, rate of stirring 220 rpm, time of transport 2 hours for BLM, rate of stirring 600 rpm, time of transport 7hours for SLM).

Figure.3.Effect of Stripping Concentration on Recovery of Anionic Dye Acid Red 10 B

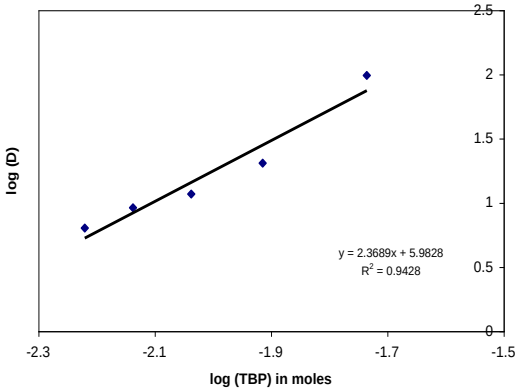

Figure.4.Relationship between log D and log (TBP) for Acid Red 10B

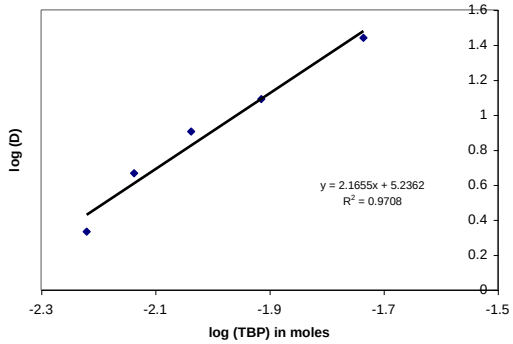

Figure.5.Relationship between log D and log (TBP) for Acid Pink BE

(Conditions: Source phase 100 mL of 100 mg/L Acid red 10 B and Acid Pink BE dye solutions at pH 1.0 ± 0.1, receiving phase 100 mL of NaOH, rate of stirring 220 rpm, time of transport 2 hours for BLM, rate of stirring 600 rpm, time of transport 7hours for SLM).

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 $(SO_3)^- Na^+$ 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 and the mechanism is shown below.

$$2\,[RO_3P^+O\,H]_{org} + Dye^{2-}{}_{aq} \rightleftharpoons [(RO_3P^+O\,H)_2\,Dye^{2-}]_{org}$$

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.

$$[(RO_3P^+O\,H)_2\,Dye^{2-}]_{org} + OH^-{}_{aq} \rightleftharpoons 2[RO_3PO]_{org} + 2H_2O + Dye^{2-}{}_{aq}$$

Figure -6 depicts schematically the dye transport processes in the LM process. At the source phase –membrane interface, $[RO_3PO\,H^+Dye]_{org}$ ion pair complex is formed. At the membrane-receiving phase interface, OH^- with high

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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) extraction (Santhanalakshmi et al, 1998).

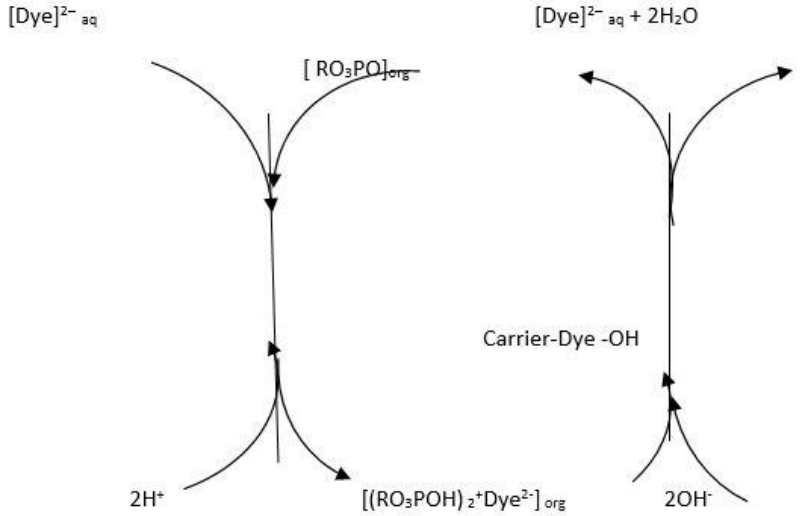

Figure.6. Schematic Representation for Transport of Anionic Dyes by Supported Liquid Membrane

Reusability: Stability of PTFE-TBP system was studied by using one disc for different runs without further impregnation of carrier. Stability of the SLM was quite remarkable when ten consecutive experiments were performed without re impregnation of the TBP carrier. This shows that the TBP has performed a stable SLM system in PTFE membrane. This may be due to high viscosity of TBP (3.8 m pa/ s at 25° C, R.H.Perry and Dongreen, 1984). No water transport through the SLM was observed during the experiment because of there is 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.

Application to textile dyeing 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 2. 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.

Table.2. Characteristics of Silk Dyeing Effluent

Parameter	Dye effluent
pH	8.65
Conductivity m S/cm	2.46
Total dissolved solids (mg/L)	2350
Total suspended solids (mg/L)	39.5
Dye Concentration (mg/L)	500
Chloride (mg/L)	750
Colour	Pink
λ_{max}	519

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Table.3.Removal Efficiency of Silk Dyeing Effluent

Process	Aqueous dye solution	% of Acid Red 10 B recovery	% of Acid Pink BE recovery
LLE	Synthetic	99.0	91.5
	Real effluent	97.7±0.5	89.2±0.5
BLM	Synthetic	96.2±0.5	90.3±0.5
	Real effluent	95.0±0.5	89.0±0.5
SLM	Synthetic	94.2	70.0±0.5
	Real effluent	74.0±0.5	85.0

CONCLUSIONS

A recovery of Acid Pink BE through a bulk liquid membrane system and solvent extraction was studied using TBP as carrier and hexane as diluent. It was found that TBP is a good carrier for selective and efficient transport of anionic dye molecules. This study reveals that the usefulness of the bulk liquid membrane technique for making it possible to combine extraction and stripping operations in a single process where as in solvent extraction it has to be done in two step process. The optimum condition selected for anionic dyes are feed pH 1± 0.1, time 120 minutes fpr BLM and 5 minutes for SX, 0.1 M sodium hydroxide as stripping phase for BLM and 0.5 M for SX. The dye recovered under optimum conditions were observed as 90.0% in BLM and SX respectively with an initial concentration of 500 mg/L. Under the optimum conditions real dye effluent tested and gave satisfactory results. Even though the percentage of recovery is less in Supported liquid membrane method, only a small quantity of solvent/carrier is required. The best method suggested is Supported liquid membrane method.

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