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Transport of textile dye in vegetable oils based supported liquid membrane

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Abstract

A laboratory study on supported liquid membrane (SLM) system has been investigated for removal and recovery of textile dye from the aqueous solution using renewable, non-toxic, natural vegetable oils, never used before as a liquid membrane. A flat sheet polypropylene (PP) supported Teflon membrane impregnated with vegetable oils has been tested for transport of Astacryl golden yellow a cationic dye. The fundamental parameters influencing the transport of dye such as pH in the feed solution, H_2SO_4 concentration in the strip solution and different type of oils, stirring speed, initial dye concentrations have been determined. At the end, stability of membrane was checked.

Keywords: Supported liquid membrane; Vegetable oils; PP supported Teflon membrane; Textile dye; Recovery

1. Introduction

One of the more pressing environmental problems associated with the textile industry is the removal of colour from textile effluent prior to discharge into the environment. Textile wastewater may be highly coloured and toxic. The molecules present in the textile effluent belong to very diverse chemical classes. Hence textile wastewater presents a challenge to conventional physico-chemical and biological treatment methods [1]. The majority of the dye removal techniques are based on adsorption, membrane filtration, precipitation, photodegradation, biodegradation, and electrolytic chemical treatment. The advantages and disadvantages of some methods of dye removal from wastewater are given in Table 1. Conventional chemical techniques have been found to be inadequate and not cost effective in removing organic dyes from wastewater [2] and moreover dyes are not recovered.

A method using colloidal gas aphrons (CGA) was proposed by Roy et al. [3] for the removal of organic dye from wastewater. Removal of an organic dye (solvent yellow 1) from wastewater using a pre-dispersed solvent extraction has also been reported by Lee et al. [4]. Removal and recovery of dyes by liquid–liquid extraction have also been reported [5,6].

Membrane technology is one of the most important topics in today's research [8]. A liquid membrane (LM) technique known as "Supported Liquid Membrane" (SLM) has the advantage of achieving selective removal and concentration in single stage, thus having great potential for reducing cost significantly [9]. There have been a number of papers dealing with organic compounds transport through SLM in synthetic solutions [10–12]. To the best of our knowledge no work has been carried out to recover dyes by liquid membrane technology. Further all the studies reported on LM were based on synthetic solvents and chemicals as liquid

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Table 1
Advantages and disadvantages of the methods used for dye removal from industrial effluents [7]

Physical/chemical methods	Advantages	Disadvantages
Fenton's reagent	Effective decolourisation	Sludge generation
Ozonation	No change in effluent volume	Short half life
Photochemical	No sludge generation	Formation of byproducts
NaOCl	Initiate azo-bond cleavage	Release aromatic amines
Cucurbituril	Good sorption capacity of dyes	High cost
Electrochemical	Non-hazardous end products	High cost of electricity
Activated carbon	Highly effective for various dyes	Very expensive
Peat	Good adsorbent	Surface area is low
Silica gel	Effective for basic dyes	Side reactions in effluent
Membrane filtration	Removes all dyes	Concentrated sludge production
Ion exchange	No adsorbent loss	Not effective for all dyes

membranes. Hence, it was felt to investigate the naturally occurring, renewable and non-toxic vegetable oil as LM. Chemically vegetable oils are glycerides of fatty acids. Vegetable oils are gaining importance as a bio-fuel and bio-diesel [13–16]. Polycyclic aromatic hydrocarbons were extracted from soil using peanut oil [17] for analytical purpose.

In this paper, the recovery of textile dye from an aqueous solution has been studied by SLM using vegetable oil as LM. The parameters influencing the transport of dye such as pH in feed, H_2SO_4 concentration in strip, rate of stirring, initial dye concentrations, different kind of vegetable oils, and membrane stability have been studied and reported here.

2. Experimental methods

2.1. Reagents and chemicals

All vegetable oils purchased from local market were of commercial grade except olive oil (Berrotolli, Italy). Astacryl golden yellow dye was kindly donated by Dy Star India Ltd. All other chemicals used in the present study were of AR grade. PP supported Teflon membranes were purchased from PALL Pharma Lab filtration Mumbai, India. PP supported membrane was used as flat sheet membrane (47 mm). These polypropylene membranes with sub microns porosity offer excellent product uniformity, strength and chemical stability.

2.2. SLM preparation

Supported liquid membrane was prepared by impregnating the membrane support disc (47 mm, 1.0 μm pore size, 15.0 μm thickness) with vegetable oil for 3 h before use, the support was taken out from the oil and the excess of oil attached to the surface of the membrane was removed gently with a tissue paper. The prepared membrane was clamped into the SML cell.

2.3. SLM apparatus

The SLM cell consisted of two halves of a cylindrical chamber (30 mm id × 95 mm length) separated by the membrane as shown in Fig. 1. A mechanical stirrer agitated aqueous solution in each chamber. The effective volume of each chamber was 60 ml. The whole membrane disc was 47 mm in diameter and the central part contacting aqueous solution was 40 mm in diameter.

2.4. Determination of flux, permeation coefficient, removal efficiency

The dye flux [18] was obtained by the following relation.

$$J = \frac{-V\mathrm{d}C}{A\mathrm{d}t} \tag{1}$$

where V is the volume of feed solution, A is the membrane area in contact with the aqueous solution and C is the concentration of dye.

The permeation coefficient (P) was calculated by the following equation [19]

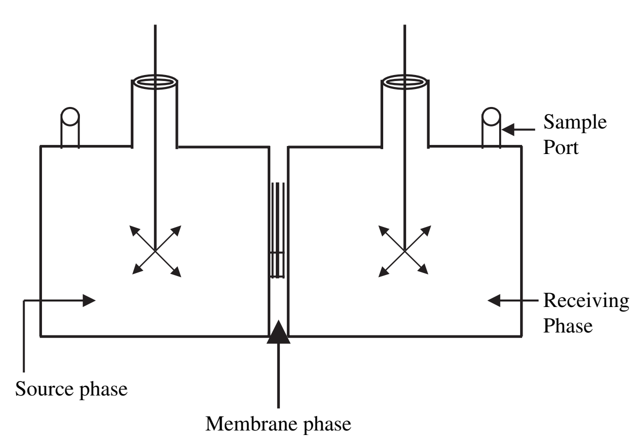

Fig. 1. Schematic diagram of supported liquid membrane (SLM) reactor.

$$\ln C_t/C_0 = -\frac{A}{V}Pt \qquad (2)$$

where C_0 is the initial dye concentration in the feed solution, C_t is the feed concentration at the operating time of t, V is the volume of the feed solution, A is the membrane area in contact with aqueous solution and t is operating time (s).

The removal efficiency [9] was calculated as follows:

$$\text{Removal}\,(\%) = 100 \times (C_{F_0} - C_{F_t})/C_{F_0} \qquad (3)$$

2.5. Experimental procedures

The feed containing 60 ml of 50 ppm of aqueous dye solution at pH 11 ± 0.1 and strip containing 60 ml of 0.3 N H_2SO_4 solutions were taken in the SLM reactor. The feed and stripping phases were mechanically stirred at 350 rpm (see Section 3.4) at room temperature 27 °C to avoid concentration polarization conditions at the membrane interfaces. After a preset time, 3 ml of sample were taken from feed chamber and absorbance of dye was measured spectrophotometrically at 445 nm. The samples were diluted with double distilled water if the absorbance of sample exceeded 0.800.

All experiments were carried out in duplicate or triplicate and variations between replicate samples within an experiment range less than 3%. Variations in reproducibility between experiments were less than 5%.

3. Results and discussions

Preliminary studies on solvent extraction resulted in emulsion formation and hence not continued. However, these studies revealed that the dye was extracted in alkaline condition.

3.1. Selection of oil for the transport of cationic dye

Different type of vegetable oils as LM have been studied for the transport of dye and presented in Table 2 along with the experimental conditions. Among these, it was found that palm oil, sunflower and coconut oils are very suitable liquid membranes for transport of dye from aqueous feed solution to strip solution. There was no transport of dye with castor oil as LM, may be due to high viscosity which might have prevented the mass transfer. Using olive, gingely, groundnut, and mustard oils as a liquid membrane, there was a dye accumulation on the surface of the membrane during the transportation, so these LMs are skipped out for further studies. There was also no transport of dye without oil impregnation of the membrane suggesting the need for the hydrophobic oil for the transport of dye.

3.2. Influence of the pH in the source phase

In order to explore the significant role being played by pH in the source phase during the transport of the dye in SLM system, the transport studies were carried out at different pH (7–14) in the source phase. Dye transport rate increases with increasing the pH, maximum extraction as well as maximum transport was achieved at pH 11.0 ± 0.1. However, at higher pH values (>12) dye transport efficiency diminished slowly as shown in Fig. 2. This might be due to the fact that at very high pH values the solubility of dye in oil is decreased. For further studies, it was decided to maintain the transport study at pH 11.0 ± 0.1.

3.3. Influence of stripping phase concentration on the permeability

The transport of dye from aqueous feed across the membrane is dependent upon the concentration of the stripping reagent (H_2SO_4), present on the product side

Table 2
Selection of vegetable oil for the transport of cationic dye

S. No.	Vegetable oil	Viscosity (Pa s)	Flux (mg/ cm^2 s)	Permeability coeff. (mg/cm^2 s)
1.	Coconut oil refined	0.05	1.1×10^{-5}	4.6×10^{-7}
2.	Coconut oil unrefined	0.04	1.1×10^{-5}	4.6×10^{-7}
3.	Castor oil	0.59	No dye transport	No dye transport
4.	Sunflower oil	0.07	1.2×10^{-5}	5.2×10^{-7}
5.	Olive oil	0.09	0.9×10^{-5}	4.4×10^{-7}
6.	Gingelly oil	0.09	0.8×10^{-5}	3.7×10^{-7}
7.	Groundnut oil	0.092	0.9×10^{-5}	4.0×10^{-7}
8.	Palm oil	0.106	1.3×10^{-5}	7.5×10^{-7}
9.	Mustard oil	0.09	0.8×10^{-5}	3.2×10^{-7}
10.	Membrane without impregnation of oil		No dye transport	No dye transport

Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml of 0.3 N H_2SO_4. Stirring rate 350 rpm, time of transport 5 h.

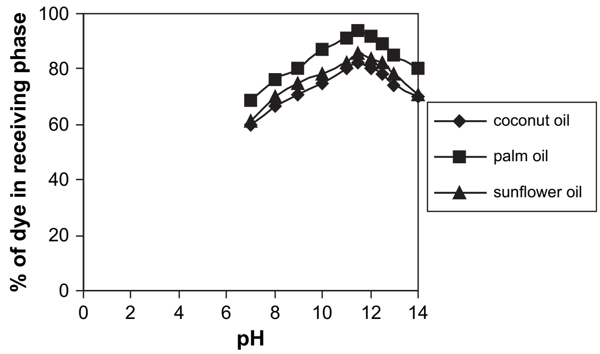

Fig. 2. Effect of pH in the source phase. Experimental conditions: source phase 60 ml of 50 ppm dye, receiving phase 60 ml 0.3 N H_2SO_4. Stirring rate 350 rpm, time of transport 5 h, LM (coconut, palm, sunflower oils).

of the membrane. The results of dye permeation using various H_2SO_4 concentrations (0.05–0.5 N) are thus shown in Table 3. It means that the presence of H_2SO_4 in the stripping phase helps the transport of dye by converting the dye hydrophilic moiety. The transport linearly increased with the H_2SO_4 acid concentration and reached a plateau at concentration greater than 0.3 N H_2SO_4.

3.4. Influence of the stirring speed of the feed and stripping phases

The effect of stirring speed in the feed phases was studied in order to obtain uniform mixing and to minimize the thickness of the aqueous boundary layer. The source and receiving phases were independently stirred over the range 50–400 rpm (Fig. 3). The flux increases for the range 50–300 rpm which indicates that the thickness of diffusion layer decreases. This region responds for the achievement of minimum diffusion layer thickness at the interfaces. Beyond 300 rpm the flux coefficient remains constant. Further research studies were done at 350 rpm.

Table 3
Influence of the stripping phase concentration on the permeability

Normality of H_2SO_4	Permeability coefficient ($\times 10^{-7}$ mg/cm^2 s)		
	Coconut oil	Palm oil	Sunflower oil
0.05	4.1	7.0	4.8
0.10	4.3	7.3	4.9
0.20	4.4	7.4	5.1
0.30	4.6	7.5	5.2
0.40	4.6	7.5	5.2
0.50	4.6	7.5	5.2

Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml various normality of H_2SO_4. Stirring rate 350 rpm, time of transport 5 h, LM (coconut, palm, sunflower oils).

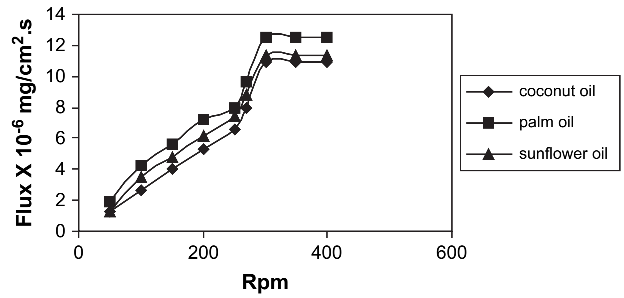

Fig. 3. Rate of stirring. Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml of 0.3 N H_2SO_4, time of transport 5 h, LM (coconut, palm, sunflower oils).

3.5. Effect of the initial dye concentration

The variation of dye concentrations at the optimum conditions have been done over the range of 25–300 ppm. It was observed from Fig. 4, the flux values increased along with increase in the dye concentration up to 200 ppm. At higher dye concentrations (230 ppm onwards) the flux became independent of the initial dye concentration this may be due to membrane saturation and lower effective membrane area of LM and also to maximization due to saturation of membrane interface which assists the retention of the separating constituent on the entry side and leads to a constant flux. This behavior has also been shown in a number of different metal carrier liquid membrane systems [20,21].

3.6. Transport performance

The cationic dye can be transferred from the alkaline solution to acidic solution against the concentration gradient. The dye distribution profiles in the two phases during a transport experiments are shown in Fig. 5. In the initial stages of the test, the decrease in dye concentration in the feed phase was accompanied by corresponding increase in the receiving phase concentration. The mass balance of the dye in the feed and strip

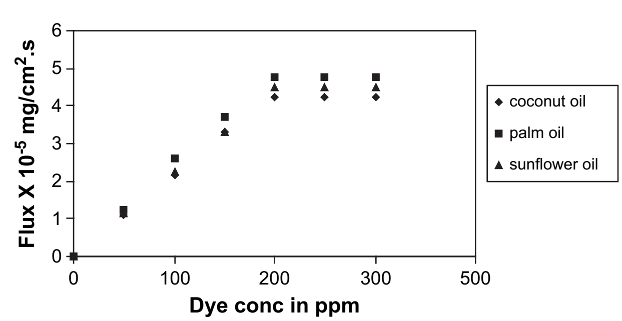

Fig. 4. Initial dye concentration. Experimental conditions: source phase 60 ml of dye at pH 11.0 ± 0.1, receiving phase 60 ml of 0.3 N H_2SO_4. Stirring rate 350 rpm, time of transport 5 h, LM (coconut, palm, sunflower oils).

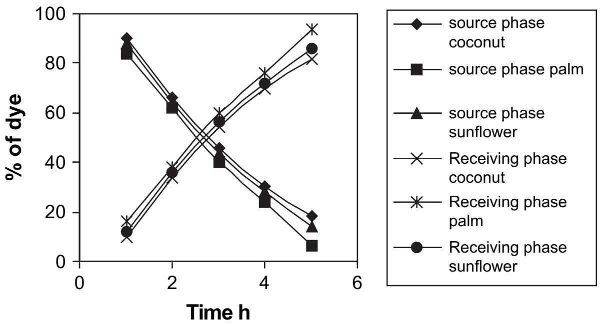

Fig. 5. Transport performance. Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml of 0.3 N H_2SO_4. Stirring rate 350 rpm, LM (coconut, palm, sunflower oils).

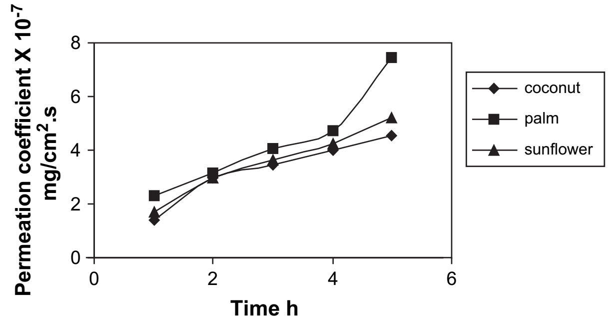

Fig. 7. Effect of permeation coefficient. Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml of 0.3 N H_2SO_4. Stirring rate 350 rpm, LM (coconut, palm, sunflower oils).

side was obeyed indicating that there is nearly no accumulation of dye in or on the membrane. It can be seen from Figs. 6 and 7, flux and permeability increases with increasing time. Maximum amount of dye transport to strip side in 5 h under optimized conditions.

3.7. Stability of membrane

The reason for an SLM to become unstable is the loss of the liquid membrane phase (extractant and/or solvent) out of the pores of the support material. This loss of extractant and/or membrane solvent can be due to several parameters, such as pressure different over the membrane, solubility and extractant and membrane solvent in adjacent feed and strip solution, wetting of support pores by aqueous phases [22]. Ageing tests were with PP supported membrane. A flux or permeability decrease of the transported species can give an indication for membrane instability. Therefore, the flux value was tested by means of ageing experiments. Almost all the dyes were transported to strip side in 5 h at an initial concentration of 50 ppm of dye. The results are shown in Fig. 8 where the dye flux was constant up to 30 h (6 experiments run, every 5 h feed and strip solutions were changed but membrane was not reimpregnated) after that flux decreased slowly. This instability and limited lifetime of SLMs have been found to be caused by a number of factors such as SLM preparation protocol, surface shear forces, changes to membrane morphology, Margoni effect and Bernard instability [23,24]. One of the methods to enhance the SLM lifetime is the reimpregnation of the support with LM to keep the flux at a constant level.

3.8. Suggested mechanism

Based on the results obtained, the dye transported across the SLM system can be explained as follows (Fig. 9):

1. In alkaline medium the cationic dye remains as unionized dye molecule (neutral) similar to aniline [25].
2. Diffusion of the unionized dye into the oil phase takes place due to the like nature of dye and oil (hydrophobic).
3. At the membrane–strip solution interfaces (i.e.) acidic condition, unionized dye molecule is converted

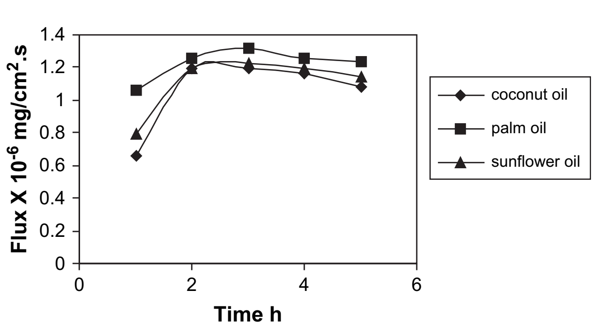

Fig. 6. Effect of Flux. Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml 0.3 N H_2SO_4, Stirring rate 350 rpm, LM (coconut, palm, sunflower oils).

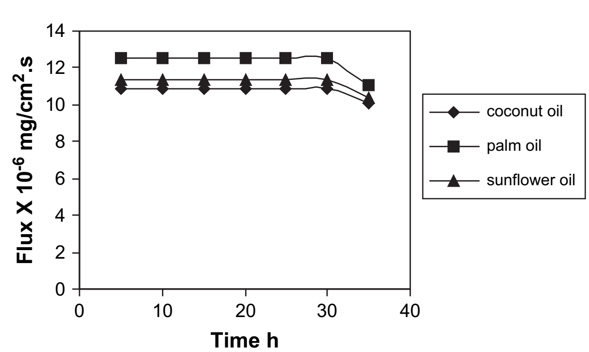

Fig. 8. Stability of membrane. Experimental conditions: source phase 60 ml of 50 ppm dye at pH 11.0 ± 0.1, receiving phase 60 ml of 0.3 N H_2SO_4. Stirring rate 350 rpm, LM (coconut, palm, sunflower oils).

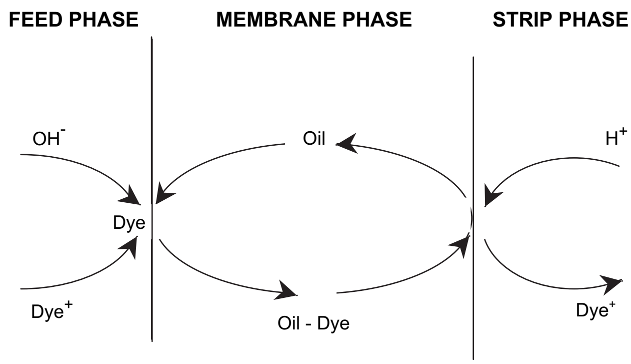

Fig. 9. Schematic description of transport of dye through SLM.

into ionized molecule (i.e.) stripping of the dye takes place.

4. The dye comes to the aqueous strip side and oil is ready for another cycle.

The cycle starts again and it was confirmed without reimpregnation of membrane for dye transport.

Transport of dye was not decreased up to 5 runs.

4. Conclusion

Vegetable oils have been demonstrated to be effective in recovery dyes from aqueous solution. The dye transport is influenced by number of variables like pH of source phase, sulphuric acid concentration in the receiving phase, suitable LMs and dye concentration etc., The permeation coefficient is increased by increasing the stirring speed up to 350 rpm after that it was constant. The dye flux increases with increasing the initial concentration but tends to be constant at higher dye concentration. PP supported membrane can be used many times. This discovery could be very useful in the development of SLM with improved stability and lifetimes using renewable substance as LM.

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