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Removal of methylene blue dye from wastewater by using supported liquid memberane technology

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The present work describes the application of Supported Liquid Membrane (SLM) technology towards the removal and recovery of a cationic dye (Methylene Blue) from aqueous solutions. Natural and non-toxic vegetable oils have been impregnated on microporous polymeric films of polyvinylidene fluoride (PVDF) to constitute a liquid membrane. Different parameters affecting the transport, like pH of feed solution, acid concentration in the strip solution, initial dye concentration, oil types and stirring speeds have been investigated. Highest value of flux (1.7 x 10^{-5} mg/cm^2/sec^1) for methylene blue dye was achieved with sunflower oil impregnated on the PVDF support, with pH maintained at 12 in the feed solution and 0.3 M hydrochloric acid concentration in the strip solution. It took 6 hours to transport maximum amount of dye under optimum conditions.

Keywords: supported liquid membrane, vegetable oils, cationic dye, industrial wastes.

INTRODUCTION

Waste effluents being discharged from textile and printing industries are mostly colored along with other pollutants and suspended solids. Removal of color from textile industry waste water is challenging problem. Chemical species present in textile industry effluent belong to a broad range of functional groups but the color is because of dyes used in the process. Therefore, colored waste waters cannot be easily treated by conventional chemical and biological treatment methods[1]. Any bright colored synthetic organic compound whose molecule contains two groups of atoms (one acidic, such as a carboxylic group, and one color-producing, such as an azo or nitro group) can be called to be a dye. Basic dye is a class of synthetic dyes, that act as bases and when made soluble in water, they form a colored cationic salt, which can react with the anionic sites on the surface of the substrate. The basic dyes produce bright shades with high on textile materials.

In order to remove the dye from aqueous solutions, most of the techniques used are based upon physical adsorption, membrane filtration, precipitation, photo & bio-degradation, and electrolytic chemical treatment[2]. Membranes and membrane-based processes have attained technical and commercial importance with respect to their industrial and environmental applications. The possibility of utilizing thin layers of organic solutions, immobilized on microporous inert support interposed between two aqueous solutions, for removing selectively metal ions from a mixture was firstly proposed more than two decades ago. Such immobilized liquid layers, representing supported liquid membranes (SLM), have been attracted the interest of a number of researchers[3–5]. Removal of organic chemical species by transport through SLM has been reported in literature[6–9]. A recent literature survey indicated the scarcity of use of liquid membranes (LM) for the removal of dyes from wastewaters. Furthermore, all the reported literature on the use of LMs is based on employing synthetic solvents and chemicals, which are usually toxic. Therefore, edible, non-toxic and free from additives vegetable oils were used as membrane liquids. Vegetable oils are glycerides of fatty acids, and recently being used in industry as bio-fuel & bio-diesel[10–11].

Liu et al.[12] have studied degradation and sludge production of textile dyes by Fenton and Photo-Fenton process. Palanivelu et al.[13–14] have used vegetable oil as LM for the removal of Astacryl Golden Yellow dye and phenols. Roy et al.[15] have reported the use of colloidal gas aphrons for the removal of organic dye from wastewater. Lee et al.[16] have used pre-dispersed solvent extraction technique for the removal of solvent yellow dye from aqueous solutions.

Methylene blue is a cationic dye heavily used by printing industry. It is also used as a stabilizer and indicator in chemical industry. Wastewaters oozing out of the chemical industries contain significant amounts of this dye rendering water unsuitable for domestic purposes. In the present work, the recovery of the methylene blue, a cationic dye, from aqueous waste solution has been studied by using Supported Liquid Membrane (SLM). Vegetable oils are used as membrane liquid. Different factors controlling and influencing the transport of methylene blue dye have been studied. These factors include, pH range in the feed solution, hydrochloric acid concentration in the strip solution, stirring speeds in feed and strip solutions, initial dye concentrations, varieties of vegetable oils and stability of the membrane.

MATERIAL AND METHODS

Reagents & Membranes

All vegetable oils purchased from the local market were of commercial grade. Methylene blue (MW 319.85 g/mol) (Aldrich) was used as received. All other chemicals were of AR-grade. The support for the organic phase was a Durapore microporous PVDF film. This support has a 75% porosity, thickness 125 μm, pore diameter 0.2 μm and tortuosity 1.67. This is a chemically stable and hydrophobic porous synthetic polymer support, and the supported liquid membrane has an organic phase containing the carrier in the polymeric porous medium. The carrier was incorporated into the membrane by capillary action/soaking the film in the carrier solution for

24 hours. For the analysis of dye, samples were analyzed on an UV/Vis spectrophotometer (Shimadzu 5301PC, λ_{max} 640 nm). For the measurement of viscosities, Brookfield (BII+) system was used.

The Permeation Cell

The apparatus to carry out permeation studies has been fabricated with perspex. It is a batch lab-scale reactor. It comprises of two compartments of identical size and shape. The volume of each cell is 140.0 mL and a membrane of effective surface area 14.2 cm^2 could be fixed amid the two chambers.

Each compartment/chamber is provided with two openings; one for variable speed stirrer to minimize the boundary layer resistance, and other to withdraw samples. The reactor could be placed in a constant temperature bath and experiments could be run at desired temperatures. Figure 1 and Figure 2 show the schematics representation and photographs of the set up. A variable power supply was also set up to control the speeds of stirrers.

The flux of the chemical species through the membrane is defined as mass transfer per unit area of the membrane, per unit time. The relationship which correlates the membrane flux (J) to concentration C, the aqueous feed volume V, and to the membrane area A, is

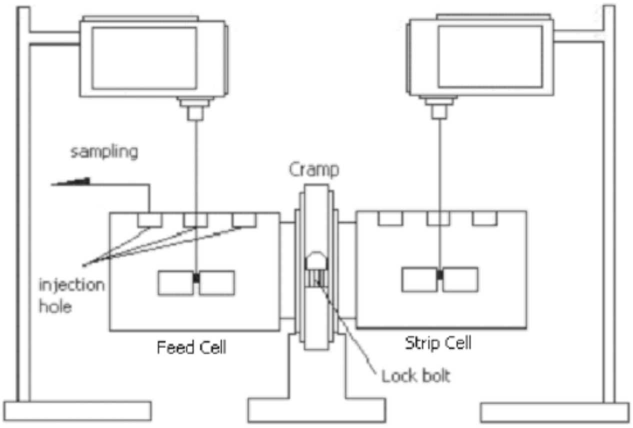

Figure 1. Schematic diagram of Permeation Cell

$$J = -\frac{dC}{dt}\frac{V}{A} \quad (1)$$

The integrated form of the flux equation is

$$\ln \frac{C}{Co} = -\frac{A}{V} Pt \quad (2)$$

C_o is the value of C at time zero. Equations 1 and 2 are very useful to predict the permeation behavior of SLMs when the feed solutions are relatively dilute in metal species[4].

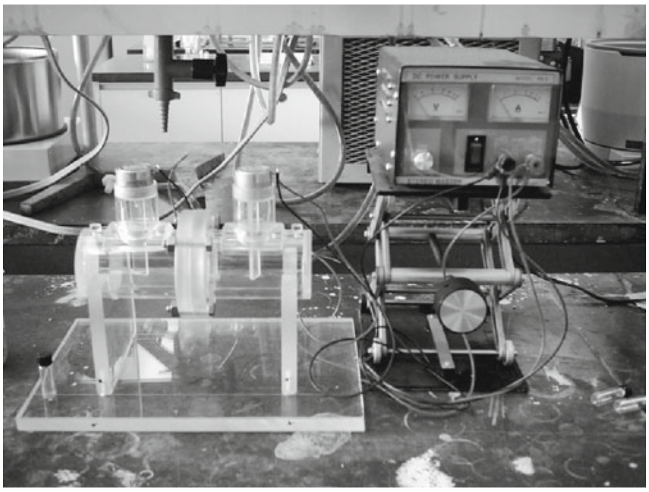

Figure 2. Picture of permeation cell (assembled)

RESULTS AND DISCUSSIONS

Different types of vegetable oils that have been selected to be used as membrane liquids for the dye transport are presented in Table 1 along with values for flux and viscosity. In order to establish the flow ability, viscosity of all oils was determined. The results showed that refined palm oil, sunflower oil and coconut oil can be used as membrane liquids for the transport of the dye. No transport of the dye was observed with castor oil as membrane liquid. This behavior can be attributed to high viscosity of castor oil (570 centiPoise) due to which the transport process was hindered. When olive, groundnut, and mustard oils were used as membrane liquids, it was observed that there was a dye accumulation on the membrane surface during the transportation process, therefore, these oils were not considered for further investigations. Also no transport of the dye was observed without oil impregnation of the membrane. This observation suggested the need for a hydrophobic carrier for the transport of dye across the membrane.

Optimum pH value in the feed solution was established by conducting transport experiments at different pH values ranging from 6 to 14. The results along with experimental conditions are depicted in Figure 3. It is clear that percentage of the dye extracted and transported increased with increasing pH, till a maxima is reached at pH 12 ±0.5. However, at higher pH values (>13) transport efficiency decreased. This can be attributed to the fact that at considerably high pH values, the solubility of the dye in oil decreases, therefore, further studies were conducted by maintaining pH at 12.0 ±0.5 on the feed side. Muthuraman & Palanivelu[13] have reported that at high pH values the dissociation of hydroxyl groups is suppressed, resulting in decreased solubility.

The concentration of hydrochloric acid in the strip solution plays an important role to enhance and facilitate the transport process. Different concentrations of HCl

Table 1. Fluxes obtained for different oils. Conditions: Feed Side, 100 ppm dye, pH 12 ±0.5; Strip Side, 0.3 M HCl; Stirring Speed 500 rpm; Time of Transport 7 hours

S.No.	Type of oil	Flux (mg – cm^{-2} – sec^{-1}) x 10^{-6}	Viscosity [cP]
1	Sunflower oil	1.53	66.3
2	Olive oil (virgin)	0.92	91.4
3	Coconut oil	1.18	54.1
4	Palm oil	1.35	104
5	Mustard oil	0.79	97

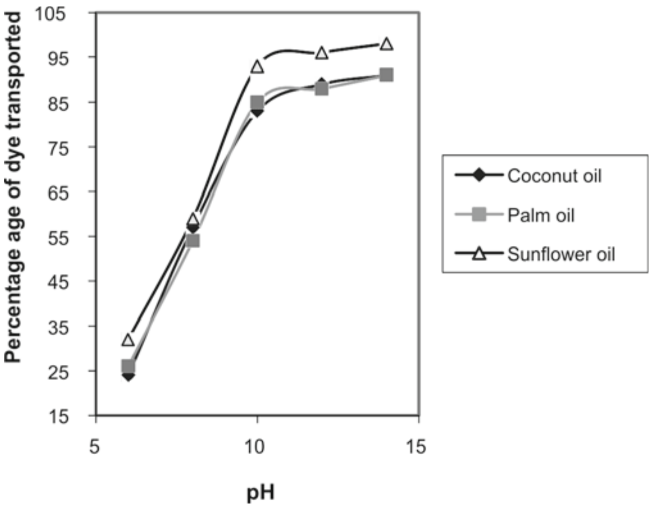

Figure 3. Effect of pH in feed phase. Feed Side:Dye 100 ppm, Strip Side: 0.3 M HCl; Transport Time: 10 hrs; Membrane liquids (Coconut, palm & sunflower oils)

in the strip solution ranging from 0.1 M to 0.4 M were tried to achieve maximum transportation of dye. The results along with experimental conditions are presented in Figure 4. It is shown that HCl facilitates the transport process and transport increases linearly with concentration till maxima is achieved at 0.3 M HCl concentration. This shows that at high acid concentration, the dissociation of dye-oil complex is decreased. Hydrochloric was preferred over sulphuric and phosphoric acids because of their higher viscosities.

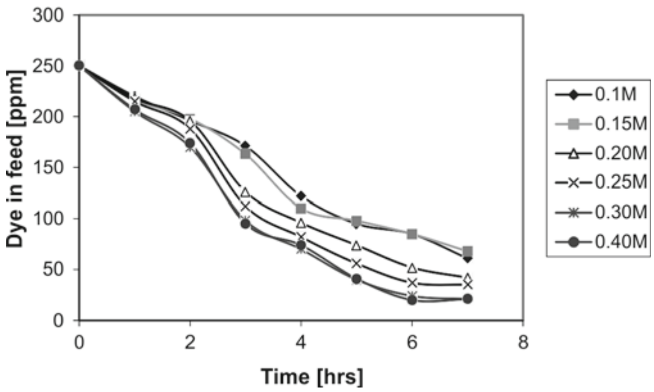

Figure 4. Influence of acid concentration in strip. Feed: 100 ppm dye at pH 12 ±0.5; Membrane liquid: sunflower oil; Strip: 0.1 M–0.4 M HCl; Transport Time: 7 hrs

Stirring of feed and strip solutions is crucial to reduce the formation of boundary layers at the solution-membrane interface. Therefore, the effect of stirring speeds on the flux was studied ranging from 150 to 600 rpm (Fig. 5). The value of flux increased with stirring speeds up to 500 rpm. Stirring speeds higher than that may cause membrane liquid to leave membrane pores[14]. This shows a value where thickness of boundary layer was minimum, so stirring speed was fixed at 500 rpm for all experiments.

The variation of flux with changing concentration of dye in the feed solution is presented in Figure 6. A wide range of dye concentration, from 50 to 300 mg/L was used to study this parameter. A directly proportional relationship was observed between flux and dye concentration up to 250 mg/L. Any more increase in dye concentration does not affect the flux. This may be due to limited surface

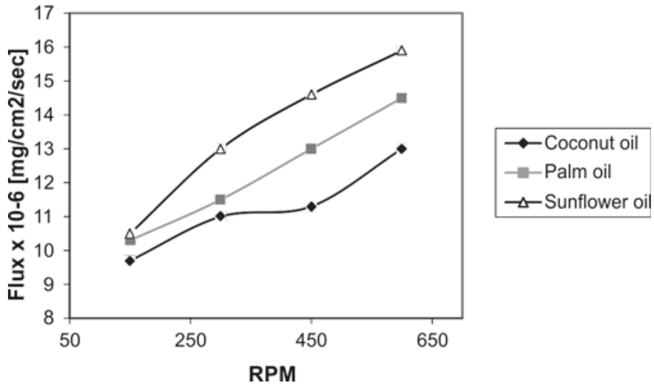

Figure 5. Effect of stirring speeds. Feed: 250 ppm dye at pH 12 ±0.5; Strip: 0.3 M HCl; Transport Time: 5 hrs

area of the membrane (14.2 cm^2) that caused saturation of the flux. Similar findings have reported for different metalo-organic SLM systems[13–19].

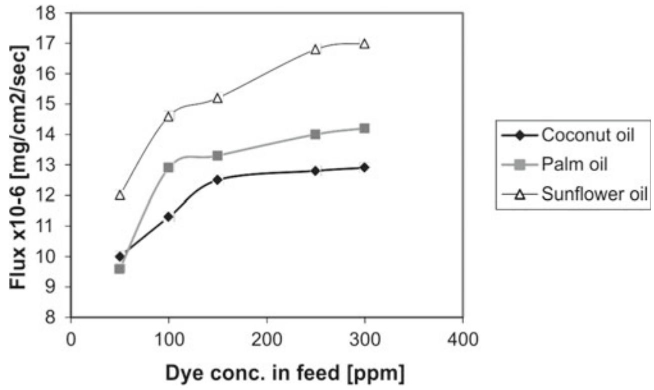

Figure 6. Effect of initial dye concentration in feed. Feed: 50–300 ppm dye at pH 12 ±0.5; Strip: HCl 0.3 M; Transport Time 7 hours

Vegetable Oil Membrane stability

In order to study the stability of Oil-Membrane system, prolonged time experiments were conducted. The stability of the membrane is referred to the loss of the membrane liquid (extractant and/or solvent) out of the pores of the polymeric support material. The loss of extractant and/or membrane liquid can be due to several reasons, such as pressure gradient over the membrane, solubility of extractant and membrane liquid in feed and strip solution, and wetting of support pores by aqueous phases. Membrane instability leads to decrease in flux over the period of time, therefore, the change in flux value was tested by means of ageing experiments. Ageing tests were performed with optimized parameters. The results are shown in Figure 7 where the dye flux was constant up to 20 hours, after that flux decreased slowly. All dye was transported to strip side within 6 hours at an initial concentration of 100 ppm. Seven experiments run in total. After regular intervals of time (5 hours) feed and strip solutions were changed but membrane was not re-impregnated. This instability and limited lifetime of SLMs have been attributed to a number of parameters like, SLM preparation protocol, surface shear forces, changes in membrane morphology, Margoni effect and Bernard instability[20–22]. If the membrane morphology does not change, the lifetime can be increased by re-impregnation of the support with membrane liquid after regular intervals of time.

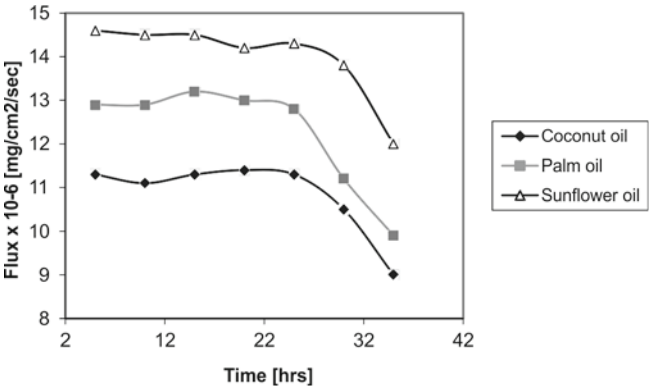

Figure 7. Stability studies. Feed: 100 ppm dye at pH 12 ±0.5; Strip: HCl 3.0 M

Probable mechanism of transport

Methylene Blue is a basic dye as indicated by the presence of a nitrogen ion in its structural formula. The structural formula is shown in Figure 8. On dissolution, the chloride ions enter the aqueous solution securing an overall positive charge over the dye. The cationic nature of the dye ensures that it is attracted by the membrane liquid. The cationic charge is attracted by hydroxyl groups of vegetable oils. Based upon the experimental results obtained, the mechanism of dye transport across vegetable oil supported liquid membrane can be interpreted as follows (Fig. 9):

1. In the basic medium (higher pH) the methylene blue dye remains in the unionized form (Feed Side).
2. Unionized methylene blue molecules diffuse into the oil phase because both oil and dye are hydrophobic in nature.
3. On the strip side, unionized methylene blue molecules are converted into ionized molecules, thus causing stripping of the dye.
4. The dye comes to the aqueous strip side and oil is ready for another cycle.

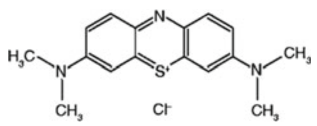

Figure 8. Structural formula of Methylene Blue

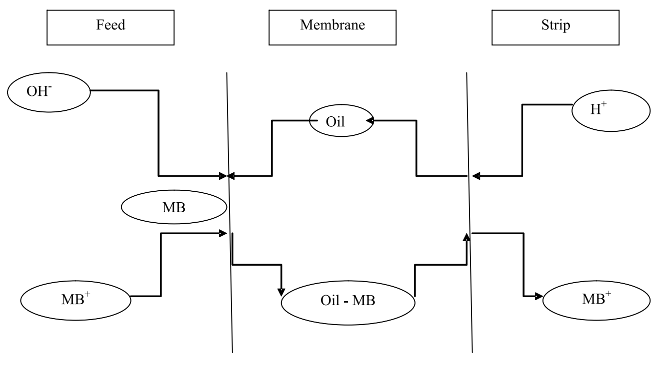

Figure 9. Schematic description of transport of cationic dye through SLM

CONCLUSIONS

Vegetable oils have been found to be effective in selective recovery of methylene blue dye through supported liquid membranes. The dye transport is effected by a number of parameters like pH of feed phase, hydrochloric acid concentration in the strip phase, appropriate membrane liquids, dye concentration in the effluent and so on. Flux through the membrane increases by increasing the stirring speed up to about ≈500 rpm after that it becomes constant. The transport flux of the dye increases with increasing initial concentrations but tends to be constant at higher concentrations.

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