

STUDIES OF SOLVENT EXTRACTION AND SUPPORTED LIQUID MEMBRANE WITH REACTIVE DYES FROM AQUEOUS SOLUTIONS USING ALIQUOT 336 AS CARRIER

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Article History: 02nd July, Revised on 05th October, Published on 05th January 2016

Abstract

The liquid-liquid extraction (LLE) and supported liquid membrane (SLM) studies of reactive dyes namely Gold Yellow (GYHE-R) and Reactive Green HE 4BD (RGHE-4BD) from aqueous solution using Aliquot 336 as the carrier has been investigated. Polytetrafluoroethylene (PTFE) membrane with 0.5 μm pore size has been used after impregnated with Aliquot 336 in dichloromethane. In liquid liquid extraction the following parameters had been optimized; pH of feed, diluent, carrier, strip and dye concentration and the same parameters have been applied to supported liquid membrane (SLM) study to transport dye from aqueous solution. The main advantages SLM study is; the extraction and stripping as single stage process and low consumption of carrier in the membrane phase compared to the solvent extraction process. The other parameters such as transport time, stirring speed and mechanism of dye transport has also studied by SLM. The percentage of transport of dye and flux rate increases with increasing time. The stability of membrane is satisfactory over 5 days.

Keywords: Feed phase; Aliquot 336; Extraction; Reactive dye; Transport.

INTRODUCTION

Natural and synthetic dyes are most widely used in many industries including textile, cosmetics, leather tanning and food. Reactive dyes are synthetic organic aromatic molecular structures such as anthraquinone, triarylmethane, vinylsulphone, chlorotriazine, trichloropyrimidine etc., and they are not biodegradable. Many dyes and pigments are toxic in nature with suspected carcinogenic and mutagenic effects that affects aquatic biota and humans. Therefore dye removal as necessary to remove from aquatic system. Many methods have been used to treat textile wastewater including photodegradation, ozonation, fenton's method, flocculation/coagulation and liquid-liquid extraction. Separation of reactive dyes namely in solvent extraction system require selective organic reagent which could form complex with the targeted analyte (dye) and extract based on their relative solubility in two different immiscible liquids [1-3].

Liquid membrane technique, which is an advanced liquid-liquid extraction, provides an effective and simple extraction/transport method for target species such as metal ions [4-7], amino acids [8], dyes [9-12] etc. Supported liquid membrane technique has specifically simultaneous extraction and stripping process of target species in one single step process [13]. Here, membrane support is impregnated by an organic carrier to facilitate the transport process.

Recently, numerous researchers have investigated liquid membrane based dye extraction process using with or without carrier. Muthuraman et al. [14] used supported liquid membrane and reported that the polypropylene (PP) membrane impregnated in vegetable oils (without carrier) to recover the dye from aqueous solutions. The transport and recovery of Levafix brilliant red E-4BA and Levafix brilliant red E-6BA were investigated using polytetrafluoroethylene (PTFE) fiber based supported liquid membrane containing tetrabutyl ammonium bromide (TBAB) in coconut oil as a carrier also studied [15]. In the present study, the reactive dyes (RGHE-4BD and GYHE-R) were removed using liquid-liquid extraction and transport through supported liquid membrane is investigated.

MATERIALS AND METHODS

Reagents and solutions

Materials

The reactive dyes GYHE-R [C.I. Reactive Yellow-84] and RGHE-4BD [C.I. Reactive Green-19] were obtained from local dyeing industry, Thiruvallur district, Tamil Nadu. It was used 'as received' without further purification. The structure of the dyes are presented in Fig. 1.

Aliquot 336 (88%, Merck), dichloromethane (98.5%, Merck), sodium nitrate (99.0%, Qualigens) were purchased and used without purification. A stock solution of GYHE-R and RGHE-4BD (1000 mg/L) were prepared and suitably diluted to the required initial concentration. A calibration curve of absorbance vs. concentration was constructed using a UV spectrophotometer (Shanghai mapada Instruments Co.Ltd., Model: UV 1100) at maximum wavelength of 405 nm and 630 nm for GYHE-R and RGHE-4BD respectively.

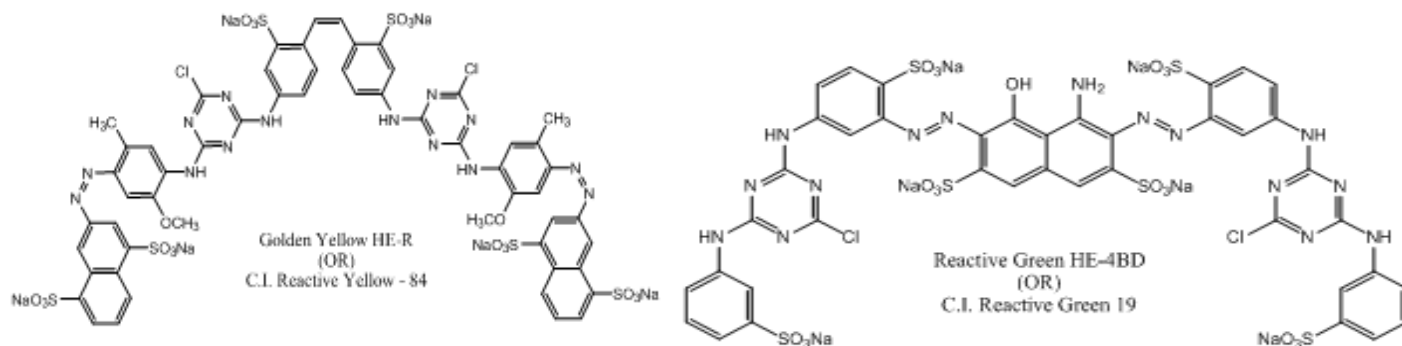


Figure 1: Structure of reactive green HE-4BD ($\lambda_{\text{max}} = 630 \text{ nm}$) & gold yellow HE-R ($\lambda_{\text{max}} = 405 \text{ nm}$).

Instrument

The pH of the dye solution was measured with a pH meter, Elico LI 120 pH meter with a combined electrode. An Elico SL 159 UV visible spectrometer was used for absorbance measurements. Magnetic stirrer was used for stirring REMI 1MLH (in india). The Whatman PTFE plain membrane with a pore size 18 μm thickness, 0.45 μm porosity and 47 mm diameter was used in the study that was obtained from GE Healthcare UK Ltd (Made in Germany).

Experimental

Solvent extraction

Solvent extraction experiments were carried out at $30 \pm 0.5^\circ \text{C}$. The pH of the dye solution was adjusted by using acid (dilute hydrochloric acid) and base (dilute sodium hydroxide). A feed phase containing dye (100mg/L, $V=25\text{mL}$) and the organic phase ($V=25\text{mL}$) were introduced in a separating funnel. The two phases were immiscible with each other. The two phases were mixed gently for known time and then left to separate. The raffinate was collected for measurement of the remaining dyes is calculated as per the following equations.

$$E = 1 - [\text{Dye}]_{\text{aq}} / [\text{Dye}]_{\text{aq0}} \times 100 \quad \text{----- (1)}$$

Where $[\text{dye}]_{\text{aq}}$ = dye concentration (mg/L) in the aqueous phase after extraction, $[\text{dye}]_{\text{aq0}}$ = initial dye concentration (mg/L) in the aqueous phase, E = percentage of extracted dye.

In the stripping, the loaded organic dye ($V=25\text{mL}$) and the stripping solution ($V=25\text{mL}$) were added together into a separating funnel and shaken well. The aqueous strippant was taken for measurements of absorbance. From this value, the percentage of stripped dye was calculated by the following equation.

$$R = [\text{Feed}]_{\text{s}} / [\text{feed}]_{\text{aq0}} \times 100 \quad \text{----- (2)}$$

Where R = percentage of stripped dye, $[\text{feed}]_{\text{s}}$ = concentration of stripped feed phase and $[\text{Feed}]_{\text{aq0}}$ = initial concentration of feed phase [8].

Membrane preparation

Polytetrafluoroethylene flat sheet membranes (PTFE) were used for the transport of reactive dyes. The PTFE flat sheet membrane is 18 μm thickness, 0.45 μm porosity and 47 mm diameter. The polymeric supported membrane was impregnated with a carrier solution containing Aliquot 336 in dichloromethane by immersion for 24 h before use, which is present in petry dish. The polymeric support was taken out from the carrier solution and then this membrane was clamped into the SLM cell.

SLM Transport experiments

The SLM experiment was carried out in a glass cell consisting of two cubic compartments and separated by the microporous membrane impregnated with Aliquot 336 in dichloromethane. The feed phase containing 120 ml of 100 mg/L of aqueous dye solution at $\text{pH} = 7.0 \pm 0.5$ and strip phase containing 120 ml of 0.2 mol/L sodium nitrate solutions were taken in SLM reactor. Agitation was performed in both (feed and strip) compartments by using Teflon pellets of 12 mm length. After different time intervals 2-3 ml of sample were taken from feed as well as strip chamber and then the dye concentration was measured spectrophotometrically. The samples were diluted with double distilled water if the absorbance of sample exceeded 0.900. The experimental setup of SLM is given in Fig. 2.

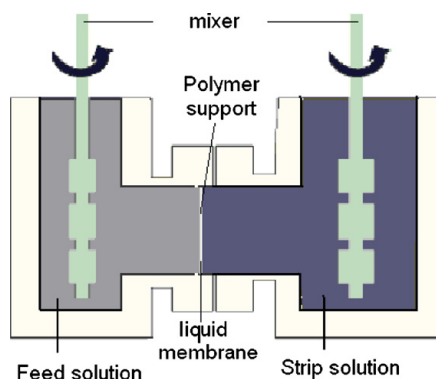


Figure 2: Schematic diagram of supported liquid membrane

The percentage of transport of dye was calculated as following Eq. (3)

$$\text{Transport (\%)} = \frac{[\text{Dye}]_{f,0} - [\text{Dye}]_{f,t}}{[\text{Dye}]_{f,0}} \times 100 \quad \text{-----(3)}$$

Following the equation using, measures the quantity of a dye transported through a specific area of membrane surface area in given unit of time

$$\log \left\{ \frac{[\text{Dye}]_{f,t}}{[\text{Dye}]_{f,0}} \right\} = -\frac{A}{2.303V} P t \quad \text{-----(4)}$$

where $[\text{Dye}]_{f,t}$ is the dye concentration in feed phase at time t , $[\text{Dye}]_{f,0}$ is the dye concentration in feed phase at initial time, A is the area of membrane (m^2), V is the volume of feed phase (ml), t is the time (min or sec) and P is the permeability (m/s).

RESULTS AND DISCUSSION

Liquid-liquid extraction

Effect of diluent

In this study various diluent used such as hexane, benzene, xylene, carbon tetra chloride, chloroform and dichloromethane. Among them dichloromethane extract the dye very well which is given in Table 1. Dichloromethane has high polarity hence well interacted with carrier and the extraction efficiency increased. The maximum percentage of extraction (96.0% for GYHE-R and 97.5% for RGHE-4BD) achieved using dichloromethane as diluent.

Table 1: Effect of diluent

Diluents	Percentage of extraction	
	Golden Yellow HE-R	Reactive Green HE-4BD
Low Density Solvents		
Benzene	73.5	78.0
Toluene	62.5	70.0
Xylene	65.0	71.0
Hexane	No extraction	No extraction
High Density Solvents		
Dichloromethane	96.0	97.5
Chloroform	92.5	91.0
Carbon tetra chloride	68.0	74.5

Effect of extractant concentration

In this experiment Aliquat 336 concentration was varied from 9.0×10^{-4} to 4.0×10^{-3} mol/L at neutral medium. Figure 3 shows that the percentage of extraction increased with increasing extractant concentration. The maximum percentage of extraction was achieved at 3.0×10^{-3} mol/L. Beyond 3.0×10^{-3} mol/L the extraction efficiency did not change. Hence Aliquat 336 concentration 3.0×10^{-3} mol/L has been recommended for further studies.

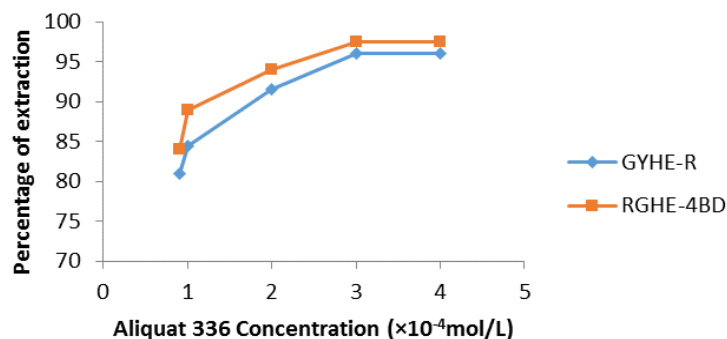


Figure 3: Effect of Aliquat 336 concentration (Experimental conditions: volume of feed phase = 25 mL, volume of strip phase = 25 mL, pH = 7.0 ± 0.5 and equilibrium time = 5 min).

Effect of stripping reagent concentration

The concentration of stripping reagent plays an important role for stripping dye from loaded organic phase and the results were given in Table 2. Sodium nitrate was used as the stripping agent and its concentration was varied from 0.009 to 0.3 mol/L. Table 2 shows that the percentage of stripping increases with increasing sodium nitrate concentration. The maximum amount of dyes were stripped into 0.2 mol/L NaNO_3 solutions. Further increase in NaNO_3 concentration did not vary stripping efficiency hence 0.2 mol/L NaNO_3 solution was chosen for further studies.

Table 2: Effect of sodium nitrate concentration

Sodium Nitrate Concentration (mol/L)	Percentage of extraction	
	Golden Yellow HE-R	Reactive Green HE-4BD
0.07	76.5	80.0
0.08	84	86.5
0.09	90.2	91.5
0.1	95.5	96.2
0.2	98.0	98.0
0.3	98.0	98.0

Supported liquid membrane

Effect of stirring speed

In order to investigate the effect of stirring speed on transport of reactive dyes, stirring speed was varied from 200 to 800 rpm while other experimental conditions were kept the optimum ones and the results were presented in Fig 4. It shows that the transport efficiency increases with increasing stirring speed up to 600 rpm and then decreases gradually. It might be due to high turbulence caused by stirring, resulting in displacement of carrier from the membrane pores [16]. Further studies were carried out at 600 rpm as a stirring speed.

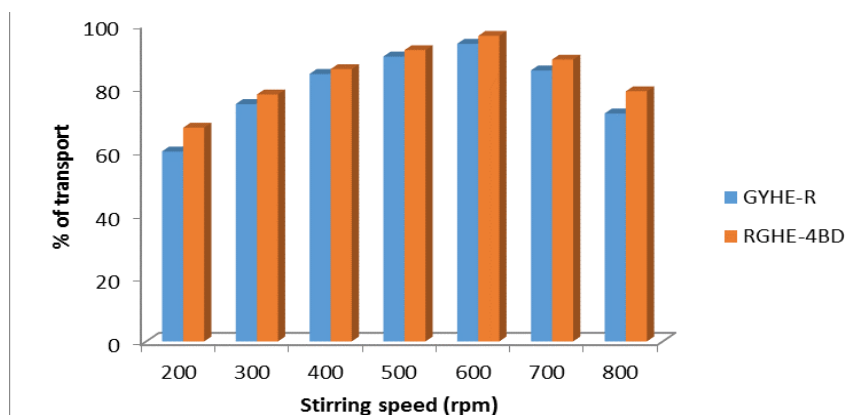


Figure 4: Effect of stirring speed (Experimental conditions: carrier concentration = 3.0×10^{-3} mol/dm³ volume of feed phase = 120 mL, volume of organic phase = 120 mL, pH = 7.0 ± 0.5 and transport time = 6 hrs).

Effect of transport time

To study the transport time of reactive dyes, an experiment was performed at optimum experimental conditions and the results were shown in Fig 5. It shows that the transport efficiency increases with increasing transport time. The maximum percentage of transport of dyes (94.0% for GYHE-R and 96.5% for RGHE-4BD) was obtained at 9 hrs. After 9hrs, the transport efficiency did not varied. Hence the transport time 9hrs was fixed for further studies.

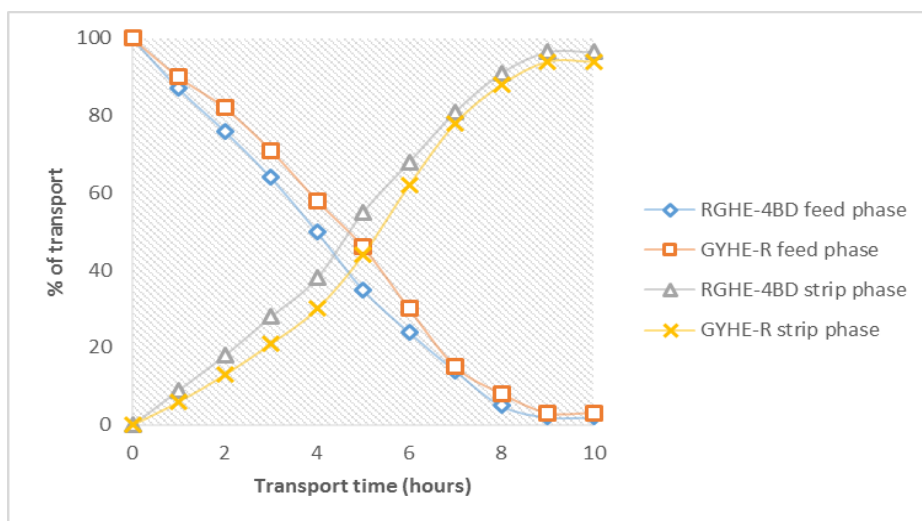


Figure 5: Effect of transport time (Experimental conditions: carrier concentration = 3.0×10^{-3} mol/L, volume of feed phase = 120 mL, volume of strip phase = 120 mL, stirring speed = 600 rpm and pH = 7.0 ± 0.5).

Mechanism of the transport

Anionic dye molecules well interacted with positively charged carrier Aliquot 336 (tricaprylylmethyl ammonium chloride) at feed/membrane (F/M) interface, hence the production of ion-pair complex was formed. This ion-pair complex was associated only in an electrostatic force of attraction of positively charged carrier and negatively charged dye molecules. This ion-pair complex was interacted with sodium nitrate and dissociation takes place at membrane/strip (M/S) phase, when electrostatic force of attraction was disappeared in the presence of base (strip phase containing sodium nitrate). Therefore the dye molecules enter into the strip aqueous phase and the carrier diffuses back into the membrane phase where the cycle starts again. The mechanism of the transport of dye has been given in Fig. 6.

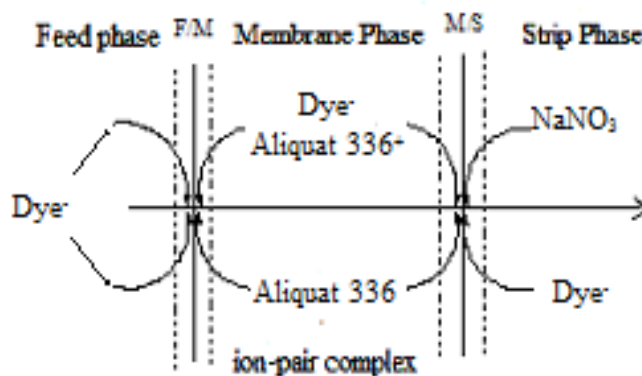


Figure 6: The mechanism of transport

CONCLUSION

The extraction and stripping of reactive dyes namely RGHE-4BD and GYHE-R has been studied by liquid-liquid extraction and SLM. The maximum amounts (96.0% for GYHE-R and 97.5% for RGHE-4BD) of dyes were removed from organic phase by using 3.0×10^{-3} mol/L Aliquat 336 as carrier at $\text{pH } 7.0 \pm 0.5$. The extracted dye has been successfully recovered from organic phase using 0.2 mol/L NaNO_3 solutions. The transport efficiency is increased with increasing stirring speed. The recovered dye can be reused.

ACKNOWLEDGEMENT

The authors are thankful to UGC sanctioned the fund to carry out this research work.

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