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Recovery of Dye from Wastewater Using Liquid-Liquid
Extraction and Bulk Liquid Membrane Techniques

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Abstract: The attention that natural dyes and pigments are getting is due to the functional properties attributed to some of these colorants. Although synthetic dyes and/or pigments have lower production costs and greater stability, that is why widely used in textile industries. The aim of this work is liquid- liquid extraction followed by bulk liquid membrane techniques have been applied to recovery of Gold yellow HE-R (GYHE-R) dye from wastewater has been studied. In liquid-liquid extraction, diluent and carrier concentration on the organic phase and stripping acid concentration have been investigated. The maximum percentage of extraction (96.0%) was achieved at at neutral medium (pH 6.5-7.0). In bulk liquid membrane, the above optimum conditions were applied and carry out further studies. The affecting parameters include were; stirring speed, time and transport mechanism has been studied. Real effluent was also extracted and found to give satisfactory result.

Keywords : Feed phase; aliquot 336; recovery; liquid membrane; transport.

Introduction

There are many methods have been treated to remove dyes form wastewater. These methods can be divided into physical, chemical and biological methods such as adsorption, ion exchange and membrane, coagulation, flocculation, ozonation, fenton's method, solvent extraction and photodegradation etc¹⁻¹⁴., the removal of color form dye bearing effluents is one of the major problem due to the difficulty in treating such wastewaters by conventional treatment methods. Liquid-liquid extraction (LLE) is significant potential to remove the dyes from wastewater.

In recent years, much attention has been focused on a separation technique such as solvent extraction or liquid – liquid extraction (LLE) and liquid membrane. LLE is based on the principle that a solute can distribute itself in a certain ratio between immiscible solvents, and the extraction process depends on its mass transfer rate¹⁵. The advantages of LLE methods are: the method lends itself to rapid and very selective separations that are usually highly efficient, the composition of the organic phase and the nature of complexing (or) binding agents can be varied so that the number of practical combinations is virtually unlimited and it can be performed with simple equipment, but can also be automated. The disadvantages of solvent extraction technique: it

requires toxic or flammable solvents, generates large amounts organic waste and formations of emulsions can interfere with the phase separation process.

Ultimately, a simple, cost effective and safe alternative for color removal and recovery of dyes from textile effluent is required and membrane technology may provide this alternative. There are three basic configurations in liquid membranes (LMs) such as bulk liquid membrane (BLM), supported liquid membrane (SLM) and emulsion liquid membrane (ELM) among which BLM is the simple, lowest and efficient type used by numerous researchers in a wide variety of applications. Such experimental rig on a laboratory scale to evaluate new means of improving the efficiency of separation processes is suggested¹⁶. In its simplest form, this technique can be carried out in either H-type or a U-type configuration depending on the density of the solvent used^{17,18}.

Experimental

Materials and Methods

The reactive dye GYHE-R [C.I. Reactive Yellow-84] was obtained from local dyeing industry, Thiruvallur district, Tamil Nadu. It was used 'as received' without further purification.

Aliquat 336 (88%, Merck), xylene (99.0%, Merck), toluene (99.5%, Merck), benzene (99.5%, Merck), dichloromethane (98.5%, Merck), sodium nitrate (99.0%, Qualigens) were purchased and used without purification.

The absorbance of dye sample was determined using UV visible spectrophotometer (Elico SL 159). The pH adjustment of source phase (dye solutions) was used by Elico LI 120. The three phases were stirred with mechanical stirrer using REMI lab stirrer.

Liquid-liquid 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 (hydrochloric acid) and base (sodium hydroxide). A feed phase containing dye (100mg/L, V=25mL) and the organic phase (V=25mL) 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.

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

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=25mL) and the stripping solution (V=25mL) were added together into a separating funnel and shaken at 200rpm. The aqueous strippant was taken for measurements of absorbance. From this value, the percentage of stripped dye was calculated by the following equation.

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

Where R = percentage of stripped dye, $[\text{feed}]_s$ = concentration of stripped feed phase and $[\text{Feed}]_{\text{aq0}}$ = initial concentration of feed phase¹⁹.

Bulk liquid membrane

BLM: H-type BLM contains three phases, two of the phases are aqueous namely feed (donor) and strip (acceptor) phase and the third phase is membrane phase shown in Fig 1. The aqueous phase Gold yellow HE-R dye solution (100mg/L, V=280mL) and the receiving phase nitric acid (0.2 M, V=280mL) were filled. Equal volumes (280mL) of aqueous solutions for the feed and stripping phase were placed into the two compartments. These two compartments were separated by the organic solvent in carrier such as Aliquat 336 in dichloromethane which present in the liquid membrane (LM) phase. These three phases were stirred using mechanical stirrer. Sample of aqueous solution was collected for the measurement of dye concentration. The dye concentration in the membrane phase was calculated on the basis of mass balance.

Results and Discussion

Liquid-Liquid Extraction

Effect of diluents

In this experiment two different kinds of organic diluents were mixed to prepared 3×10^{-3} mol/L aliquat 336. Low density and high density solvents used were; hexane, toluene, xylene, benzene, carbon tetra chloride, chloroform and dichloromethane. The results were presented in Table 1. It shows that the maximum percentage of extraction (96.0%) was obtained using dichloromethane used as a diluent. This is due to dichloromethane has high polarity interacted well with aliquat 336²⁰. Hence 3×10^{-3} mol/L aliquat 336 has been used for further studies.

Table 1 Effect of diluents

Diluents	Percentage of extraction
Low Density Solvents	
Benzene	73.5
Toluene	62.5
Xylene	65.0
Hexane	-
High Density Solvents	
Dichloromethane	96.0
Chloroform	92.5
Carbon tetra chloride	68.0

The effect of extractant concentration

The extractant concentration was varied from 0.9×10^{-4} to 4×10^{-3} mol/L. Fig. 2 shows the plot between the percentage of extraction of dye against extractant concentration. Usually we expect the percentage of extraction increases with increasing extractant concentration the similar results were obtained. The maximum percentage of extraction (96.0%) was occurred at 3×10^{-3} mol/L aliquat 336 in dichloromethane. After increases the aliquat 336 concentration there is no change in extraction efficiency. Hence 3×10^{-3} mol/L aliquat 336 concentration was recommended for further studies.

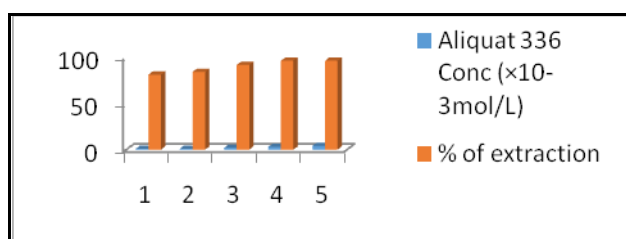


Fig.2. Effect of Aliquat 336 concentration: Experimental conditions (Experimental conditions: volume of feed phase = 25 mL, volume of organic phase = 25 mL and pH = 6.5-7.0).

Effect of stripping reagent concentration

It is an important parameter in liquid-liquid extraction the dye was back extract from loaded organic phase into aqueous phase. Here sodium hydroxide used as a stripping reagent and its concentration ranges from 0.05 to 0.3 mol/L. Table. 2 indicates that the stripping efficiency increases with increasing sodium nitrate concentration. The maximum stripping efficiency (98% for GYHE-R) was obtained at 0.2 mol/L of sodium nitrate.

Table 3. Effect of Sodium nitrate concentration

Sodium nitrate Concentration (mol/L)	% of stripping
0.07	76.5
0.08	84
0.09	90.2
0.1	95.5
0.2	98.0
0.3	98.0

Bulk Liquid Membrane

Effect of time on the transport of GYHE-R

The experiment was carried out using 3×10^{-3} mol/L aliquat 336 in membrane phase, 100 mg/L MO in donor phase, 0.2 mol/L NaNO_3 in receiving phase and stirring speed 200 rpm with different time intervals has been investigated. Fig. 3 shows that, in donor phase the transport efficiency (R_d) decreases steadily with increasing of time. It indicates that the dye MO was successfully extracted from donor phase into membrane phase. The maximum transport rate (R_a) was observed at 210 min. Hence the time 210 min was recommended for further studies.

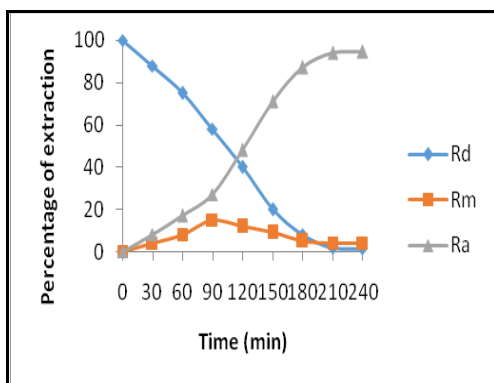


Fig. 3 Effect of Time (Experimental conditions: dye conc 100 mg/L, receiving phase = 0.2 M NaOH, carrier concentration 3×10^{-3} M, stirring speed = 200 rpm and pH 2.0 ± 0.1).

The effect of stirring speed

The effect of stirring speed in the donor phase and receiving phase was studied in the range of 100-300 rpm in order to obtain optimal stirring speed that allows effective transport through liquid membrane. The results were presented in Fig. It indicates that the transport efficiency of dye decreases on the donor phase as well as increases on the receiving phase with increasing time. The maximum percentage of transport (94.0%) of dye was achieved at 200 rpm. Hence 200 rpm has been recommended for further studies.

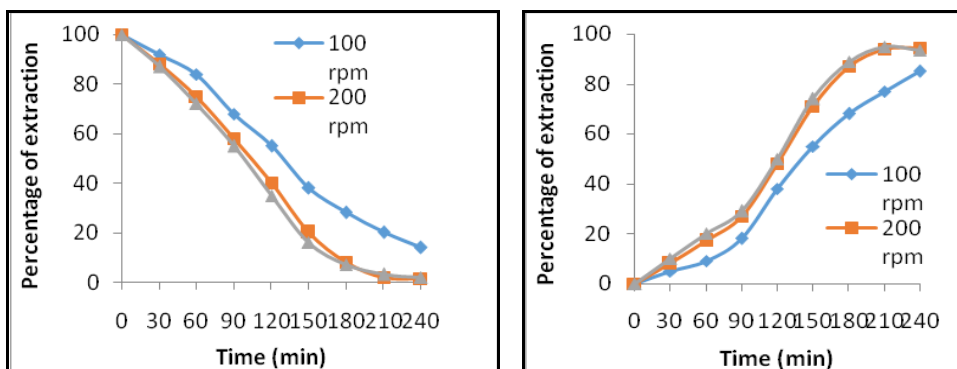


Fig 4a and 4b. Effect of R_d and R_a of stirring speed: (experimental conditions: dye conc 100 mg/L, receiving phase = 0.2 M NaOH, carrier concentration 3×10^{-3} M and pH 6.5-7.0).

Application of the developed BLM for textile wastewater

The wastewater from a local textile industry was selected for testing the applicability of the developed bulk liquid membrane system which was neutral in nature (pH 6.5-7.0). Underoptimized condition (donor phase = 280 mL of 100 mg/L dye solution, membrane phase = 280mL of 3×10^{-3} mol/L Aliquat 336, receiving phase 280 mL of 0.2 mol/L NaNO₃, transport time = 210 min and stirring speed = 200 rpm) the textile dye wastewater was extracted and the extracted dye was stripped into the sodium nitrate.

Conclusion

The removal and recovery of reactive dye Gold yellow HE-R (GYHE-R) from aqueous solutions has been investigated. Aliquat 336 extractant found to extract 96% for GYHE-R from aqueous solutions at neutral medium (pH 6.5-7.0). This study demonstrates that the usefulness of the LM technique for making it possible to combine extraction and stripping operations in a single step process. It also applied for recovery of dyes from textile effluent in textile industry which give satisfactory result.

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