

Emulsion Liquid Membrane Extraction of Turquoise Blue Reactive Dye-Study on Membrane Breakage and Swelling

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ABSTRACT

Reactive dyes are the principal dyes used in batik industry in Malaysia. From the environmental point of view the dyes should be removed from wastewater because they are toxic in nature. Therefore, the removal and recovery of dyes from batik industry wastewater is absolute necessity in order to save raw materials and to protect environment from hazardous compounds. An experiment was carried out using emulsion liquid membrane (ELM) process in batch system to study the extraction behaviour of Turquoise Blue which is commonly used in batik industry. Several parameters have been studied such as carrier and surfactant/emulsifier concentrations, stripping agent and extraction time. The liquid membrane was formulated using kerosene as diluent, SPAN 80 as emulsifier and tri-dodecylamine (TDA) as a carrier. Hydrodynamic condition to generate extraction process was at 1:3 treat ratio and 250 rpm stirring speed for 10 minutes while the emulsification was done at 12000 rpm for 5 minutes using homogenizer. The result obtained shows that, more than 70% of Turquoise Blue was extracted at favourable condition of 0.07 M TDA, 7% (w/v) SPAN 80 and 0.5 M Thiourea in 1 M NaOH.

Keywords: Batik industry, emulsion liquid membrane, extraction, reactive dyes, wastewater

1.0 INTRODUCTION

Disposal of synthetic dyes in the form of wastewater effluents poses severe hazards to the environment as these effluents contain large amount of surfactants, suspended solids, trace metals, color and have high chemical oxygen demand (COD) [1]. Textile wastewater is coloured effluent and the released of these wastes into receiving waters are contributed to the water pollution. Coloured effluents have been produced, most certainly, since the dyeing technique was invented. Dyes have an adverse aesthetic effect because they are visible pollutants which affect photosynthetic activity in aquatic life due to reduced light penetration [2]. Recently, more researchers had concerned on the treatment of dye wastewater as the environmental

contamination by dye wastewater has becomes a great environmental problem [3]. The majority of synthetic dyes currently used are the highly water soluble azo-reactive dyes. Azo dyes are characterized by the existence of nitrogen-nitrogen double bonds ($-N=N-$) and the bright color of their aqueous solutions. The azo-reactive dyes are used extensively in textile industries to their favourable characteristics of bright color, water-fast and simple application techniques with low energy consumption [4]. The main pollution source of textile wastewater as in batik industry comes from the dyeing processes.

Therefore, dyes colour is the most important environmental concern in the textile industrial wastewater since the colour must be removed from the wastewaters before discharge to any water body. Textile dyes are classified into three categories which are cationic, anionic and non-ionic reactive dyes [5]. Cationic dye referred to

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one which is basic in reaction and unites with negatively charged ions of the material acted upon, anionic referred to one which is acidic in reaction and unites with positively charged ions of the material acted upon such as Red 3BS, Turquoise Blue, Black B and Orange 3R. Non-ionic dye referred to one containing both reactive basic and reactive acidic groups and staining both acidic and basic elements. Due to toxicity level, cationic is the most toxic followed by anionic and non-ionic dyes [5].

Reactive dyes with the benzidine and aromatic compound were found to potential carcinogenic amines have already been proved [6]. Turquoise Blue (TB) as shown in Figure 1 is anionic reactive dye where sodium ion (Na^+) which positive charge attached at dye compound contains benzidine and aromatic structure make it hazardous waste in batik industry effluents.

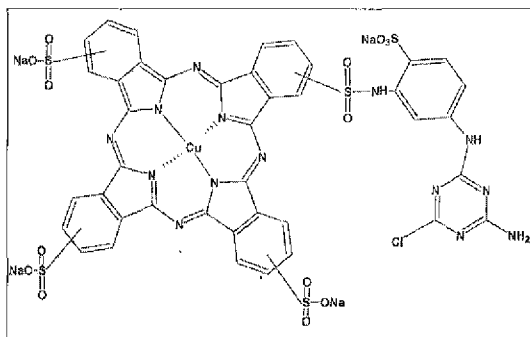


Figure 1 Chemical structure of turquoise blue dye

Various techniques have been found and investigate to remove dye stuffs from wastewater effluent. Adsorption of dye stuffs on cotton fabric wastewater using semi-activated carbon has been proposed by Ozoh [7]. The problem regarding to this method is disposal approach of the spent activated carbon after removing of dye stuffs. Removal and recovery of dyes using ion exchange were investigated by many researchers such as Naim and Yehia [8] and Farag *et al.* [9] on recovery of acid dyes from wastewater. Ahmad *et al.* [10] and Djenouhat *et al.* [11] were reported that membrane separation process offered the method for increasing the removal of dyes. However, fouling of membrane is the main problem for this technique. Solvent extraction or liquid-liquid

extraction has been proposed by Panjit and Basu [12], Muthumaran and Palanivelu [13] and Muthumaran *et al.* [14] for both anionic and cationic dyes from wastewater.

Recently removals of dye stuffs have been employed rather than recovery process. Removal dyes from wastewater was concerned by environmental point of view due to colour and toxicity of dye compounds contribute pollution impact to water bodies. However, the purpose of recovery process will be more excellent than removal of dyes since the spent dyes will be reuse back using emulsion liquid membrane (ELM) technique. Emulsion liquid membrane is one of the promising techniques used in industrial separation process such as metals and chemicals removal from wastewaters. ELM is a heterogeneous mixture of two immiscible liquids. One of the liquid is dispersed in other phase to form globules or droplets in stable membrane (primary emulsion). The primary emulsion will be dispersed into external phase or phase to be treated to form double emulsion system. In this stage the extraction and stripping process occurred simultaneously in one step operation process.

This paper will present the membrane stability and efficiency of removal of TB anionic dye from simulated batik industry using ELM technique with tridodecylamine (TDA) as a mobile carrier [15]. The studies are carried out involving process parameters such as the carrier concentration, contact time, stripping agent concentration and agitation speed.

2.0 EXPERIMENTAL PROCEDURES AND MATERIALS

All the chemicals are used as received. Kerosene as diluents was obtained from Acros Organic, TDA as carrier and sodium hydroxide (NaOH) as stripping agent from Merck Schuchardt OHG Germany, thiourea (Tu) as additive or co-stripping agent from GCE Laboratory Chemicals and SPAN 80 from Fluka. Turquoise blue reactive dye was obtained from Batik Industry in Kuala Terengganu, Malaysia. The apparatus used are agitator IKA C-MAG, homogeniser Heidolph Silent Crusher M and 1100 Series Spectrophotometer.

TB dye solution was prepared by dissolving desired amount of dye concentration before each experiment. An equal volume of 5 ml of organic solution and an aqueous strip solution will be stirred continuously at 12000 rpm using homogeniser for 5 minutes to obtain a stable primary emulsion system. Then, the emulsion will be dispersed into external phase of 50 ppm TB solution with treat ratio 1:3 (volume of emulsion: volume of external phase) to form the double emulsion (W/O/W) system for 10 minutes extraction at 250 rpm agitation speed. The emulsion must be freshly prepared each time before dispersion experiments. After that the mixtuer was allowed for phase separation for 15 minutes. Then, the primary emulsion was separated from the aqueous treated wastewater and dye concentration in the aqueous was analysed.

The quantitative determination of reactive TB dye was made using a spectrophotometer at wavelength $\lambda = 635$ nm. To determine dye mass balance for all phases, after separation of aqueous phase the external aqueous phase was analysed using this formula of percent removal efficiency, R:

$$E = \frac{[Dye]_i - [Dye]_f}{[Dye]_i} \times 100\% \quad (1)$$

$$D = \frac{[Dye]_{org}}{[Dye]_{aq}} \quad (2)$$

Symbols:

- $[Dye]_i$ = Initial dye concentration
- $[Dye]_f$ = Final dye concentration
- $[Dye]_{org}$ = Concentration of dye in organic phase
- $[Dye]_{aq}$ = Concentration of dye in organic phase

The experimental setup for extraction for removal and recovery of TB reactive dye using ELM system is shown in Figure 2. TB reactive dye is extracted into TDA-kerosene under neutral condition and the extracted dye is stripped into 1 M NaOH with Tu. The reaction for extracting and stripping of the dye were represented by equation (I) and (II) in Figure 3. Equation (I) shows the mechanism of extraction between TDA in organic phase (org) and TB reactive dye to form the complex of dye and TDA. The mechanism of stripping process is shown in equation (II) using NaOH to strip the complex was formed.

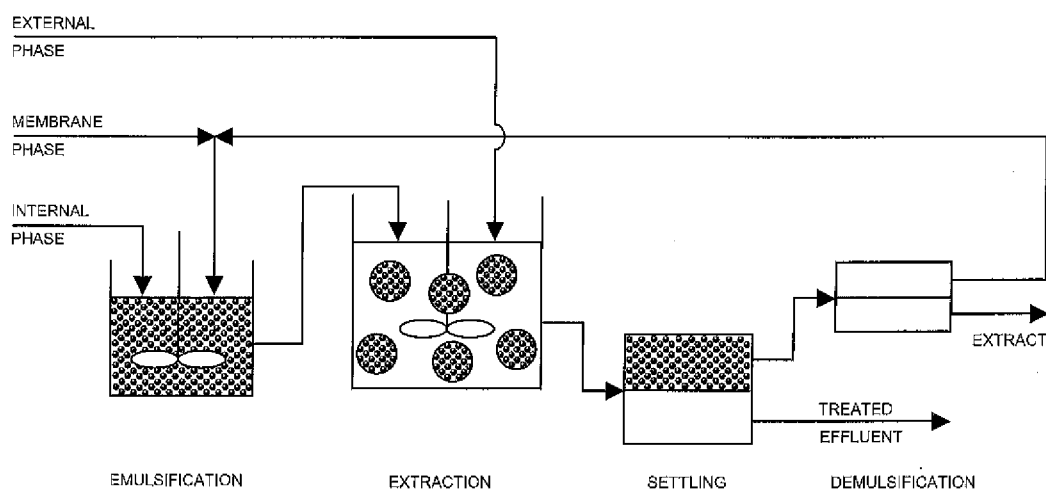
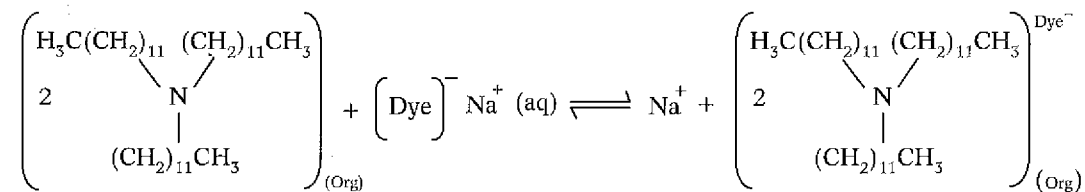


Figure 2 A schematic diagram of mixer-settler extraction using in emulsion liquid membrane

Equation 3.1: Mechanism of reaction between TDA and dye ion in extraction process.



Equation 3.2: Mechanism of reaction between NaOH and dye ion in stripping process.

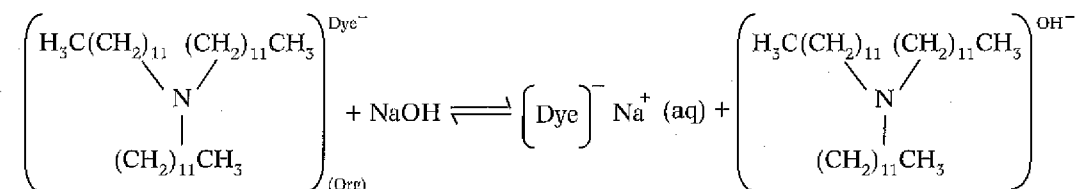


Figure 3 Reaction mechanism of extraction and stripping TB dye with TDA and NaOH

3.0 RESULTS AND DISCUSSION

3.1 Effect of Carrier Concentration

Figure 4 shows the effect of carrier concentration on the percentage of extraction and breakage. The concentration of carrier was varied from 0.01 M to 0.1 M. Rate of facilitated transport of the solutes are directly affected by the amount of carrier that is presented in the liquid membrane [16]. Therefore the increase in carrier concentration will increase the ability of the membrane phase for extraction. As the concentration increased to 0.07 M, more dye solutes can be reacted with the carrier as they being transferred from external to internal phase.

However, at 0.1 M of carrier concentration, the percentage of extraction decreases rapidly. This is due to the interfacial properties of the carrier resulting in increasing in viscosity of the membrane. There are also the factors of swelling as mentioned by Othman *et al.* [17]. At high concentration of carrier in the membrane phase, high osmotic swelling and membrane breakdown occurred. It means that the water in external phase will be transferred into internal phase and resulting to higher concentration in the external phase.

From Figure 4, it was observed that the extraction efficiency increased with the increase

in the concentration of carrier from 0.01 M to 0.07 M. Increase of TDA concentration accelerates the migration of the dye ions towards the oil phase interface towards an extraction process [18]. Further increase the amount of carrier higher than 0.07 M decrease the degree of dye extraction. However, very high carrier contains in the membrane does not result in a benefit due to respective increase in viscosity, which leads to larger globules [11].

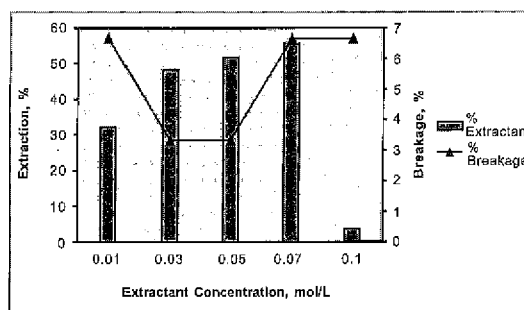


Figure 4 Percentage of extraction and breakage at the various carrier/extractant, Tridodecylamine (TDA) concentration [Span 80: 5%, NaOH: 1 M, Thiourea: 0.5 M, agitation speed: 250 rpm, contact time: 10 min, emulsifying speed: 12 000 rpm, Initial concentration of dye: 50 ppm, treat ratio, 1:3]

3.2 Effect of Surfactant Concentration

The surfactant concentration in membrane phase is most important to any ELM system. While it ensures the stability of membrane during the extraction, it also changes the viscosity of the membrane so as to change the mass transfer resistance [19]. The effect of this factor to the percentage of extraction and breakage are presented in Figure 5. The concentration of surfactant was varied from 1 %w/v to 5 %w/v.

At 1%w/v and 3%w/v surfactant concentration, the percent of extraction is still considerably low. This is because low surfactant concentration destabilizes the membrane [19]. Therefore even the solutes transfer into the internal phase is actually increased; the amount of leakage due to membrane breakage also increases resulting to low net transport. As the surfactant concentration increased to 5%w/v, the membrane becomes stronger. It was reported by Mortaheb *et al.* [20], higher concentration of surfactant will lower the surface tension of emulsion. This will lead to smaller globules and higher contact area between external phase and internal phase. This phenomenon also described by Othman *et al.* [17] where stability of the membrane increased due to an increasing adsorption of the surfactant in the interface by an increase in the interface film force of surfactant molecules.

However when the surfactant concentration continues to increase to 8 %w/v, the extraction rate starts to decelerate. Although the emulsion was expected to be stabilized with increasing surfactant concentration [21], beyond the critical surfactant concentration the degree of stability becomes approximately constant due to the saturation of surfactants at the oil/water interface. But even though high degree of stability results in stronger membrane, it also leads to thicker globules wall. Therefore it cause higher mass transfer resistance and inversely decrease the removal efficiency. Mortaheb *et al.* [20] also described that excessive surfactant concentration lead to increase in swelling due to secondary emulsification of the entrained solvent by excess surfactant in primary emulsion.

The proportion of surfactant in organic phase is an important factor as it directly affects the

stability, swelling, breaks up of ELM [20] and viscosity of ELM [21]. Figure 5 represents the variation of percentage extraction of TB and percentage swelling of membrane for various SPAN 80 concentrations.

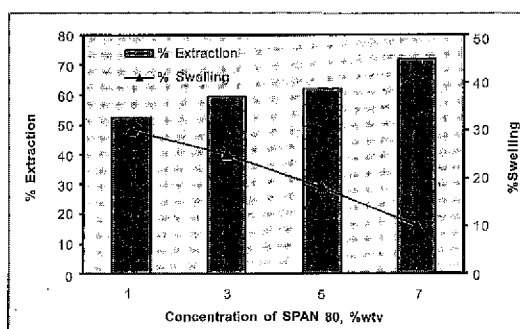


Figure 5 Variation of % extraction of TB and % swelling of membrane for different SPAN 80 concentrations uses 0.07 M TDA concentration, 0.5 M Tu in 1 M NaOH concentration, 5 minutes emulsifying time at 12000 rpm and 10 minutes extraction time at 250 rpm

The results presented in Figure 5 show that an increase in the concentration of SPAN 80 increased the stability of emulsion. At lower SPAN 80 concentration (less than 5% w/v), emulsion break easily leading to poor extraction of TB because the less emulsion interfacial surface areas between internal phase and membrane phase plus less dispersion interfacial surface areas between external continuous phase (dye solution) and membrane phase [22].

These findings also indicate that the percentage swelling of membrane was very obvious even the SPAN 80 concentration was increased to 7 w/v%. It is because SPAN 80 which molecular weight 428.61 g/mol has a large hydrophilic group mainly

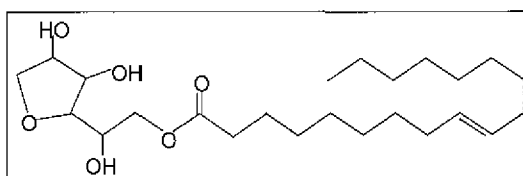


Figure 6 Chemical structure of SPAN 80

composed of oxygen with high electronegativity thus may have the highest hydration capacity and largest diffusivity [23]. Figure 6 shows the chemical structure of SPAN 80.

3.3 Effect of Stripping Agent Concentration

The effect of Tu concentration in NaOH in the internal phase on both extraction of TB and swelling of membrane is shown in Figure 7. Different Tu concentration ranging from 0.1 M – 0.7 M were used. It is observed that the maximum extraction (71.74%) occur at Tu concentration of 0.5 M. The extraction of dye increases with increasing the Tu concentration from 0.1 M – 0.5 M. This may be due to the increase in the capacity of the internal phase by increase its concentration, which delay the accumulation of the carrier complex in the peripheral oil layer [24]. Further increase of Tu concentration up to 0.7 M cause decreased the extraction rate since the excess Tu causes swelling of emulsion leading to destabilization of liquid membrane system causing reducing in percentage extraction. At lower concentration (below 0.5 M) of Tu, in NaOH, almost of reactant is consumed in the internal phase resulting in lower efficiency [25]. Based on the result has shown, the optimum Tu concentration in NaOH as stripping agent is found to be 0.5 M.

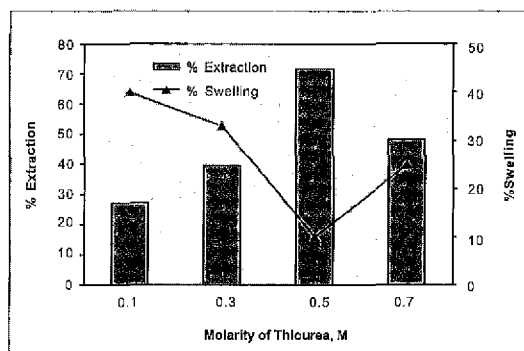


Figure 7 Variation of % extraction of TB and % swelling of membrane for different Tu concentrations using 0.07 M TDA concentration, 1 M NaOH concentration, 7 w/v % SPAN 80, 5 minutes emulsifying time at 12000 rpm and 10 minutes extraction time at 250 rpm

3.4 Effect of Stirring Speed

The effect of agitation speed during extraction on percentage of extraction and breakage is shown in Figure 8. The agitation speed was varied at 150 rpm to 450 rpm. At 150 rpm, it was observed that most emulsion globules are not properly dispersed in the external phase due to the low agitation speed. The emulsion only spread at certain part of the external phase and mostly at the water surface resulting in low percentage of extraction.

As the agitation speed increased to 250 rpm, the emulsions started to disperse uniformly and the globules will become smaller due to the fluid shear. There will be large surface area for mass transfer of solutes to the internal phase. The increases in agitation speed also reduce the thickness of boundary layer at interface of emulsion globules and internal phase. Both of these factors lead to higher percentage of extraction since there are more chances on mass transfer. However at 350 rpm and 450 rpm, percent of extraction decrease. This observation indicates that dye concentration in external phase increased back after the minimum concentration was reached. This increase in concentrations during later phase of extraction resulted due to emulsion rupture by fluid shear is greater than the rate of extraction. This was also described by Mok *et al.* [26] as

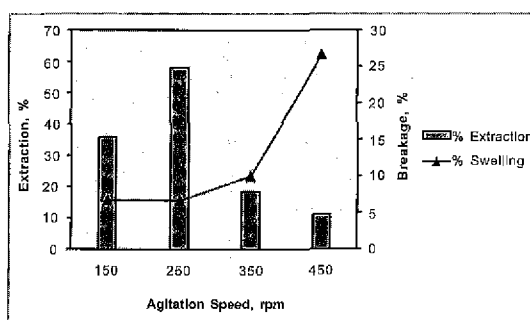


Figure 8 Percentage of extraction and breakage at the various agitation speeds during extraction [TDA: 0.07 M, Span 80: 5%, NaOH: 1 M, Thiourea: 0.5 M, contact time: 10 min, emulsifying speed: 12 000 rpm, Initial concentration of dye: 50 ppm, treat ration: 1:3]

agitation speed increasing, membrane breakage will increase due to fluid shear and feed phase entrainment. Instability of emulsion due to fluid shear is also mentioned by Park *et al.* [27].

The effect of agitation speed on both extraction of TB and swelling of membrane is shown in Figure 8. The optimum stirring speed was at 250 rpm because gives the maximum extraction of TB and minimum swelling of membrane. At high agitation rate hydrodynamic shear and swelling work together causing lower extraction [17]. Increasing the stirring speed above 250 rpm not only decreases the extraction efficiency but also affects the stability of membrane.

For lower stirring speed (below 250 rpm), the extraction efficiency decrease because of formation of larger emulsion globules hindrance for the mass transfer. Higher stirring speed and larger mass transfer area bring faster mass transfer rate, and vice versa [18]. Unfortunately, too fast speed will result the membrane break easily and lower the extraction percentage of TB as well.

4.0 CONCLUSIONS

All the parameters studied such as concentration of Tu in NaOH, concentration of SPAN 80, concentration of carrier and agitation speed were affected the percentage of extraction of TB reactive dye and swelling of membrane. The maximum percentage of extraction of TB was found to be higher than 70% at the optimum working conditions of 0.07 M TDA, 0.05 M Tu in 1 M NaOH, 250 rpm agitation speed for 10 minutes, 7 w/v% SPAN 80 and 12000 rpm emulsifying speed for 5 minutes. The ELM technique was shown to be of interest for the treatment of TB reactive dye from simulated batik industry wastewater.

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