Full paper

Recovery of Synthetic Dye Red 3BS from Simulated Wastewater using Supported Liquid Membrane Process Containing Immobilized Kerosene-tridodecylamine Liquid Membrane

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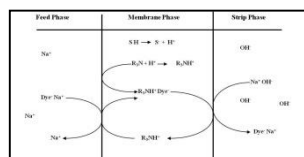[b]Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia
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Graphical abstract

Abstract

The discharge of reactive dyes into the environment has led to the toxicity problems especially to the aquatic organism. Therefore, there is a necessity for treatment of the reactive dyes from wastewater. In this work, Red 3BS reactive dye was separated using supported liquid membrane process. Commercial polypropylene (PP) membrane was used as a support of kerosene-tridodecylamine liquid membrane. Several important parameters such as flow rate, pH of feed phase, initial concentration of feed phase and stripping agent concentration were investigated. The result shows that for 50 ppm Red 3BS solution containing 0.00001M Na$_2$SiO$_3$ almost 100 and 89% of Red 3BS was removed and recovered respectively at the favorable condition of 0.1 M NaOH as a stripping agent, pH 3 of feed phase and 100 ml/min of flow rate.

Keywords: Red 3BS; supported liquid membrane; tridodecylamine; recovery; stability

■1.0 INTRODUCTION

Synthetic dyes have been widely used by most of the textile industries as main colorant instead of natural dyes in their manufacturing process owing to several advantages such as low cost of production, good fixation with the fabric, easiness in application and vibrant color choices. These synthetic dyes are manufactured out of number of chemicals, additives and solvents notably dioxin, formaldehyde, sulfuric acid, chromium, copper and other metallic elements. The existences of these chemicals on the dyes structure have caused this component to have high stability and resistance towards any degradation process. Moreover, the chemicals used to produce these dyes are highly toxic, carcinogenic, or even explosive.

Reactive dye is one of the synthetic dyes which is a colored substance and able to form covalent bond with fiber polymer resulting in strong adhesion between functional group of reactive dye and fiber. Generally, this component is considered very toxic and cannot be directly discharged to the environment without adequate treatment since their structure contains a lot of dangerous chemicals, which are harmful for the environment and human beings. The discharge of dye containing wastewater into the environment is unpleasant because of huge amount of toxic dyes are released and their breakdown products are carcinogenic and mutagenic to life form [1].

Hence, in order to avoid textile wastewater to impair the environment and health of human beings, the wastewater should be treated before it is discharged to the environment. Various de-colorization treatments are utilized such as coagulation and flocculation, oxidation, activated charcoal, electrochemical, biological refining method, photocatalyst, Fenton reagents and membrane separation technology [2-5]. However, all these treatments provide several advantages and disadvantages in terms of cost, efficiency of technology, environmental and practical consideration. Based on previous research, it is stated that the conventional treatment such as chemical precipitation, ion exchangers, reverse osmosis, ultra filtration and electro dialysis are not effective for the removal of dye stuff from wastewater [6-7]. Besides, these conventional methods also have certain limitation such as less efficiency, production of secondary sludge, sensitive operating condition and difficulty to oxidize dyestuff [8]. However, the adsorption of reactive dye by activated carbon is a powerful technology but high cost of activated carbon and its loss during the regeneration restricts its application [9].

Supported liquid membrane (SLM) process has been chosen as an alternative treatment of wastewater containing reactive dye due to a potential of removal and also recovery of reactive dyes [10-11]. SLM was reported to have high selectivity to the targeted solutes, minimum amount of expensive carrier usage, high separation factor, low energy requirement and low operation cost [12-14]. This process is widely used in many applications of separation and purification of desired solute. SLM is known as pre-concentration system by achieving a maximum separation by combining extraction and stripping processes in one single step. This single step process provides promising excellent removal and recovery performances and has great potential in reducing cost significantly [15].

To the best of our knowledge, no work has been reported on the separation of anionic reactive dye, Red 3BS using supported liquid membrane. In this study, an attempt was made to remove and recover Red 3BS from an aqueous phase by using SLM process. Several important parameters governing the separation of reactive dyes were studied in order to find the favorable condition for reactive dyes separation.

■2.0 TRANSPORT MECHANISM IN SLM PROCESS

In the SLM transport process, the diffusion of dye ions takes place via the following steps [16]:

(a) Basic carrier, TDA (R_3N) in the membrane phase is protonated with the salicyclic acid (SA) H^+ in the membrane phase and form ammonium salt ion (R_3NH^+). Hydrogen ion (H^+) is obtained from dissociation of SA will protonated the non-ionic tertiary amine which can promote the carrier to undergo the extraction process. The protonation reaction is shown in Equation 1.

$$R_3N|_m + H^+|_m \rightarrow R_3NH^+|_{f-m\ interface} \qquad (1)$$
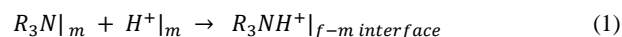
With m = membrane phase, f= feed phase,

(b) Diffusion of dye ions from the feed phase towards feed–membrane interface.
(c) Dye ion forms a complex with the protonated carrier at the feed–membrane interface. The complexation reaction between anionic dye ion and protonated carrier is shown in Equation 2.

$$Dye^-|_{f-m\ interface} + R_3NH^+|_{f-m\ interface} \rightarrow R_3NH^+Dye^-|_m \qquad (2)$$
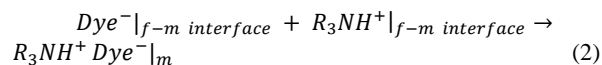
(d) Dye-carrier complex diffuses across the membrane to the membrane-strip interface.
(e) De-complexation of the dye-carrier complex of membrane-strip interface due to unstable conditions for complexation.
(f) The dye ions are stripped into the stripping phase via the reaction with the stripping agent, NaOH in the membrane-stripping interface as shown in Equation 3 below:

$$R_3NH^+Dye^-|_{f-m\ interface} + NaOH|_s \rightarrow Na^+Dye^-|_s + R_3NH^+|_m + OH^-|_s \qquad (3)$$
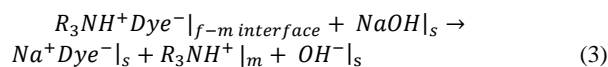
with s = strip phase

(g) Free carrier molecule will diffuse back towards the membrane-feed interface and cycle continues. The transport mechanism of separation of reactive dye is illustrated in Figure 1.
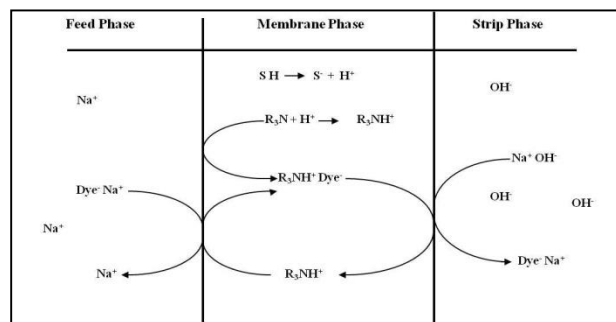

Figure 1 Transport mechanism of the separation of reactive dyes through SLM[2]

■3.0 MATERIALS AND METHODS

3.1 Materials

Red 3BS reactive dye was obtained from Batik industry in Malaysia in powdered form. The chemical structure of Red 3BS is shown in Table 1. Tridodecylamine (TDA) as a carrier was obtained from Merck (purity > 95%), salicyclic acid (SA) (purity > 99.99%) as a co-carrier and kerosene as organic diluent were obtained from Fisher Chemical and Fluka respectively. Sodium hydroxide as stripping agent was obtained from Merck and sodium silicate (Na_2SiO_3) was obtained from Bendosen Laboratory. The hydrophobic commercial polypropylene (PP) membrane was used as a solid support and supplied by Accurel Membrana. The physical characteristics of the membrane are porosity (71.9%), thickness (100 μm) and average pore size (0.1 μm).

Table 1 Chemical structure of Red 3BS [17-18]

Reactive Dye	Chemical Structure	Wavelength (nm)
Red 3BS (MW= 1085g/mol)		511

3.2 Analytical Method

The concentration of dye ions in the feed and strip phase was analysed using an ultraviolet-visible spectrophotometer Jenway model whereas pH of feed phase was measured using portable smart pH meter (Milwaukee Model).

3.3 Supported Liquid Membrane Process

Supported liquid membrane was prepared by submerging the membrane support in formulated organic liquid membrane solution for almost 24 hours. The organic liquid membrane was prepared by dissolving TDA and SA in kerosene. It was assumed that all the empty voids were filled with the liquid membrane phase. Filter paper was used to remove the excess liquid on the membrane surface. Once the SLM support was prepared, it was placed in between two compartments of membrane cell as shown in Figure 2. 150 ml of feed and strip solution was added into cell 1 and cell 2 respectively. All experiments were performed at ambient temperature. An overview of the experimental series is given in Table 2.
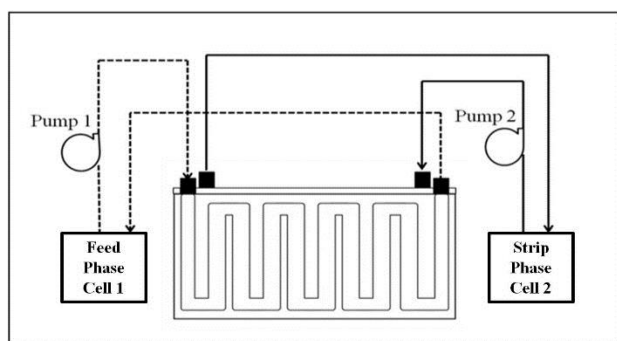

Figure 2 Schematic diagram of supported liquid membrane process

Table 2 Experimental condition for transport of dye

Parameter	Range of study
Flow rate of feed phase (ml/min)	50, 100, 125, 150
pH of feed phase	pH 1, 2, 3, 4, unmodified pH
Concentration of stripping agent, NaOH (M)	0.025,0.05,0.1,0.2
Initial concentration of feed phase (ppm)	10,30,50,70
Concentration of sodium silicate Na$_2$SO$_{3,}$ (M)	0.00001,0.001,0.01, 1.0

3.4 Determination and Calculation

The percentage of removal and recovery of reactive dye ions during the extraction process was calculated using Equation 4 and 5:

$$Removal\ (\%) = \frac{[Dye]_{fi}-[Dye]_{fo}}{[Dye]_{fi}}\ x100\% \qquad (4)$$

$$Recovery(\%) = \frac{[Dye]_s}{[Dye]_{fi}}\ x\ 100\% \qquad (5)$$

where,

[Dye]$_{fi}$ is the initial concentration of dye ions in the feed phase, [Dye]$_{fo}$ is the final concentration of dye ions in feed phase and

[Dye]$_s$ in the concentration of dye ions in the strip phase at given time.

The concentration of reactive dye was measured using UV spectrometer with wavelength 511 nm for Red 3BS.

■4.0 RESULTS AND DISCUSSION

4.1 Selection of Support Material for SLM

A blank experiment has been carried out in order to find the possibility of commercial polypropylene (PP) as a membrane support. In this experiment, no transportation of Red 3BS was observed, which indicates the possibility of using PP membrane as a support liquid membrane as it did not assist the transportation process. Therefore, in order to assist the transportation of dyes, commercial membrane support was impregnated in liquid membrane. Liquid membrane contained TDA and SA in kerosene with the concentration stated by Othman *et al.* [17].

4.2 Effect of Flow Rate at the Feed Phase

Figure 3 illustrates the effect of feed flow rate on the removal of Red 3BS from an aqueous phase. It can be observed that at the first 60 minutes, there was high percentage of removal with increasing flow rate of up to 100 ml/min. At this stage, this flow rate was sufficient for thinning the boundary layer near feed-membrane interface. As a result, the dye ions were easily diffused through the aqueous boundary layer hence leading to the high permeation rate of dye ions through the membrane phase which is in agreement with Rovira and Sastre [19]. However, the percentage of extraction slowly decreased at flow rate beyond 100 ml/min due to high turbulence which caused the loss of liquid membrane from the membrane. This is in line with Surucu *et al.* [20] and Amiri *et al.*, [21] who stated that high level of flow rate decreases the dye transport efficiency due to high turbulence which causes the instability of SLM process. After 60 minutes, the percentage of extraction at flow rates from 100 to 150 ml/min gradually increased and started to plateau after 300 minutes of extractions, indicating that 100% of dye ions had been completely extracted. Nevertheless at 50 ml/min, the rate of diffusion of dye ions occurred continuously within 360 minutes because the range of time studied is inadequate to completely remove all dye ions.
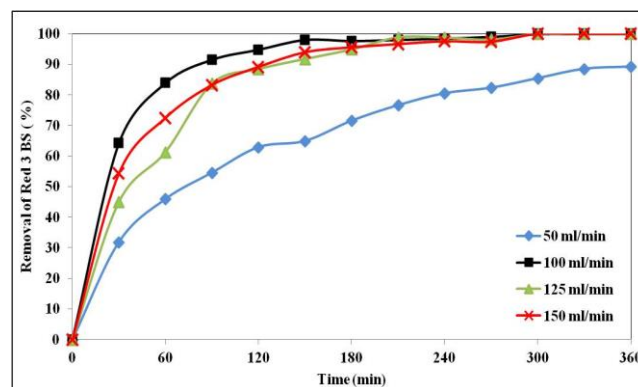

Figure 3 Removal of Red 3BS by varying flow rate of feed phase (Experimental condition: Red 3BS: 50 ppm (pH: 3), Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M)

At the same time, the recovery efficiency was tested and is shown in Figure 4. After 360 minutes, the lowest percentage of recovery was attained at the flow rate of 50 ml/min. This can be attributed to the low performance of extraction resulting in low recovery efficiency due to one single step of SLM process in which removal and recovery occurred simultaneously. Meanwhile, the highest recovery percentage was obtained at the flow rate of 100 ml/min with almost 88% of Red 3BS recovered. This flow rate is found sufficient to enhance the diffusion flux of Red 3BS ions through the membrane interface thus increasing the recovery rate. However, further increase in the flow rate of up to 150 ml/min decreased the recovery percentage to 73%. This can be explained by the fact that high flow rate generates the turbulence which induces the possibility of loss of carrier in pore of membrane, causing an interference in the transfer of dye ion from the membrane to strip phase. Similar finding was obtained by Marchese *et al.* [22] and Mittiche *et al.*, [23] who found that the flux of solute across SLM diminished at high flow rate due to the displacement of carrier from the membrane phase. Therefore, it can be concluded that the favorable feed flow rate for extraction of Red 3BS is 100 ml/min and therefore has been used throughout the experiment.
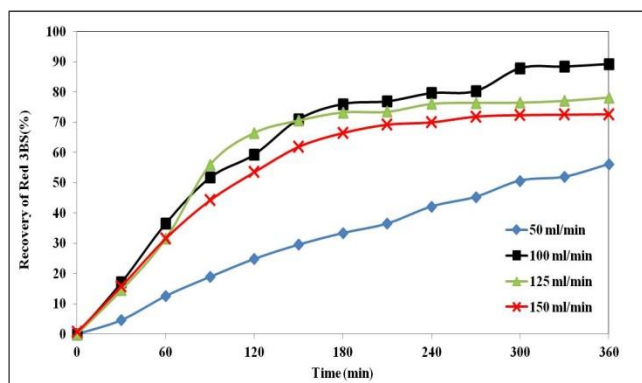

Figure 4 Recovery of Red 3BS by varying flow rate of feed phase (Experimental condition: Red 3BS: 50 ppm (pH: 3), Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M)

4.3 pH Effect of Feed Phase

The effect of pH on the removal of Red 3 BS is illustrated in Figure 5. During the first 60 minutes, low performances of removal were observed at pH 1, 4 and 7. It was found that at too acidic condition medium will enhance the dissociation of dye ion thus leading to saturation of dye-carrier complex on feed-membrane interface while non-acidic medium provides unfavorable condition for ionic formations of dye hence reducing the complexation reaction with the carrier as explained by previous researchers, Drapala and Wieczorek [24]. In contrast, the highest performance was obtained at pH 3 with 84% removal. This shows that pH 3 is adequate enough for the formation of anionic Red 3BS and complexation between carrier and Red 3BS thus increasing the extraction efficiency as reported by Muthuraman and Palanivelu [25]. After 150 minutes, the removal performance at pH 3 started to plateau which indicates all of dye ion has been successfully removed from feed phase. Meanwhile, the removal performances for other pH gradually increased and continuously occurred until 360 minutes of extraction.
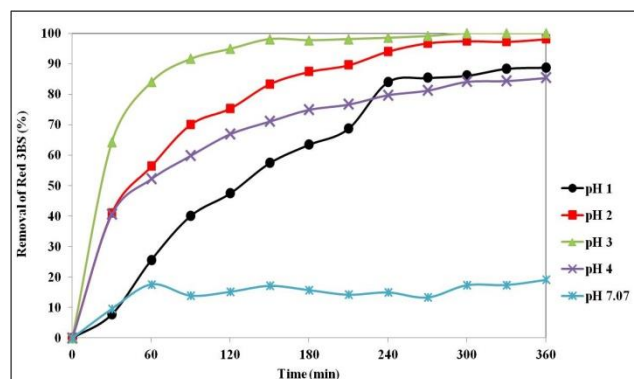

Figure 5 Removal of Red 3BS by varying pH of feed phase (Experimental condition: Red 3BS= 50 ppm, Tridodecylamine= 0.1 M, Salicyclic Acid= 0.1 M, Sodium Hydroxide = 0.1 M, Flow rate= 100ml/min)

The effect of pH on the recovery of Red 3BS is presented in Figure 6. It can be observed that high recovery performances have been obtained at pH 1 and pH 3. The highest recovery percentage was obtained at pH 3 with almost 89% of Red 3BS recovered within 360 minute of extraction. This can be due to one single step of the SLM process where extraction and recovery occur simultaneously. High percentage of dye removal leads to high possibility of dye being recovered in strip phase. Therefore, the recovery performance is dependent on extraction performance. Further increase beyond pH 3, decreased the recovery efficiency. In addition, no recovery of dye ions was observed at pH 7. This is due to the unfavorable condition for the ion formation of Red 3BS. Hence, dye is unable to form complexation with carrier and failed to diffuse through the membrane. This circumstance leads to low extraction and recovery simultaneously. In overall, pH 3 is decided as an optimum condition and was fixed for further experiment.
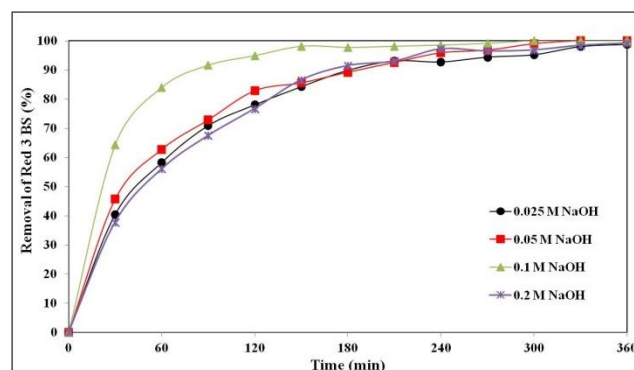

Figure 6 Recovery of Red 3BS by varying pH of feed phase (Experimental condition: Red 3BS: 50 ppm, Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M, Flow rate=100ml/min)

4.4 Effect of Stripping Agent Concentration

Figure 7 shows the removal percentage of Red 3BS by varying NaOH concentration. During the first 60 minutes, the removal efficiency for concentration of 0.025, 0.05 and 0.2M was gradually increased with an average percentage of 59%. There are several reasons that lead to the results obtained. At

concentration of 0.025 and 0.05 M, extraction efficiencies were slightly low due to the insufficient concentrations of NaOH in the stripping phase. As a result, a lot of dye ions are unable to strip out from the membrane phase due to lack of Na^+ ions and cause an accumulation in the membrane-strip interface. However by increasing the concentration up to 0.1 M NaOH, the percentage of removal was drastically increased up to 84%. It can be due to the concentration of 0.1 M NaOH in the strip phase is adequate to strip out dye ion from the membrane-strip interface. This result was consistent with previous finding by Muthuraman and Palanivelu [26] who examined that the extraction of dyes ion increased by increasing the stripping agent concentration until reached a maximum point. However, further increased the concentration of NaOH to 0.2 M, the performance of extraction was slowly decreased due to the possibility of strip phase reached a saturation limit and existense of osmotic pressure between feed and strip phases resulted in decreasing of mass flux as been reviewed by Chakrabarty *et al.* [23]. Beyond 60 minutes, the removal rate gradually increased for all concentration of stripping agent. At concentration of 0.1 M NaOH, the removal percentage nearly reached plateau starting at 150 minutes meanwhile other concentrations exhibit similar efficiency of removal and reached plateau at 330 minutes.

Figure 8 exhibits the recovery efficiency of Red 3BS at different concentration of stripping agent. As can be seen, the recovery performance experienced a stable increment throughout the time. High recovery of Red 3BS were obtained at the concentrations of 0.025 and 0.1 M with almost 91 and 89% of dye ions were succesfully recovered. This can be attributed to adequate concentration of NaOH in the strip phase enhance the complexation reaction between Na^+ ions and anionic dye in the membrane-strip interface. In contrast, lower recovery efficiency were obtained at a concentration of 0.05 and 0.2 M. This is due to insufficient amount of Na^+ present at concentration of 0.05 M NaOH which restricts the recovery process. As a consequence, dye ions fail to get stripped into the strip phase and stucked inside the pore near membrane-strip interface. In contrast for 0.2M NaOH, increase the stripping agent concentration facilitates recovery efficiency within short time. As a result, the strip phase reaches saturation limit and decreased the solubility. Similar findings have been obtained by Nowier *et al.* [27] and Rounaghi *et al.* [28]. Therefore, it is concluded that the favorable concentration for stripping agent would be 0.1 M NaOH due to high extraction and recovery efficiency.
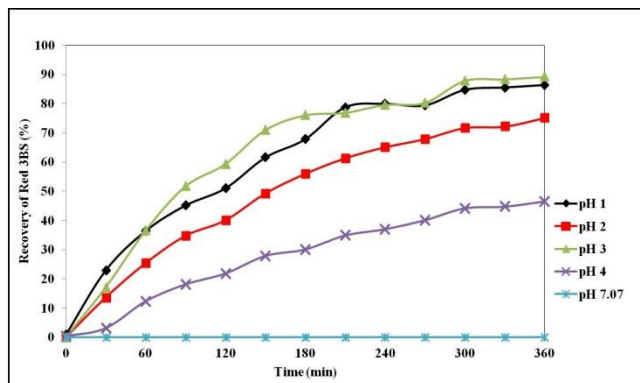

Figure 8 Recovery of Red 3BS by varying concentration of stripping agent, NaOH (Experimental condition: Black B: 50 ppm (pH: 3), Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Flow rate=100 ml/min
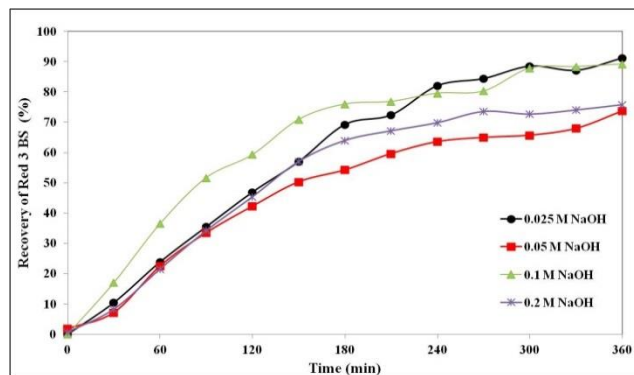
4.5 Effect of Initial Feed Phase Concentration

The effect of initial feed concentration on the removal Red 3BS is shown in Figure 9. During the first 60 minutes, it was observed that the removal performance at concentration of 50 ppm is very fast with 84% of dye was extracted. This finding can be related to the mass flux through membrane-feed interface. According to Rehman *et al.* [29] and Muthuraman and Teng [30] stated that the mass flux is directly proportional to the feed concentration where mass flux transfers from the medium of high concentration to low concentration. However, beyond the concentration of 50 ppm Red 3BS, the removal performance was reduced to 66%. This decrement is due to the saturation of dye ion on membrane interface and builds up the layer on the membrane which induces the retention of the separating constituent on the feed side. Similar result was obtained by Muthuraman and Teng [30] who found that flux value was increased by increasing initial feed concentration until reach the maximum point. After 60 minutes of extraction, the removal of dye was gradually increased until reach plateau. It was observed that the increase in concentration of feed phase lengthens the time required for removal of all dyes ion from feed phase.

Meanwhile at 70 ppm of feed phase, thick red precipitation of dye was observed on membrane surface after 360 minutes of extraction. High concentrations of dye induce to accumulation and saturation of dye ion in the pore of the membrane, hence distracting the stripping performance. Alguacil and Alfonso [32] demonstrated that initial flux is less dependent on higher concentration of solutes due to membrane saturation with solute-carrier species and lower effective membrane area which assists the retention of the complexes on the feed side. Based on the result obtained, 50 ppm of Red 3BS was selected as the most stable concentration with maximum removal and recovery of Red 3BS.
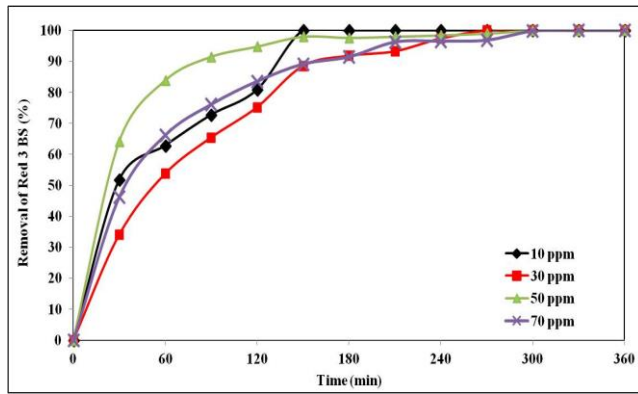

Figure 7 Removal of Red 3BS by varying concentration of stripping agent, NaOH (Experimental condition: Black B: 50 ppm (pH: 3), Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Flow rate=100 ml/min)

Figure 9 Removal of Red 3BS by varying initial concentration of feed phase (Experimental condition:, Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M, Flow rate=100 ml/min)

Meanwhile, the results of recovery efficiency of Red 3BS was shown in Figure 10. As can be seen, the recovery performance for all concentrations were markedly increased within 120 minutes of extraction. However after 120 minutes, the rate of recovery slightly decreased due to the accumulation of dye ion on membrane-strip interface which limits the membrane area for complexation between dye and stripping agent. The highest percentage of recovery was obtained at 50 ppm of feed phase. High mass flux in feed phase enhance the complexation rate in feed-membrane interface, and then increase the decomplexation rate in the membrane-strip interface as reported by Kaya *et al*.[31] In contrast, low percentages of recovery were obtained at 10 and 70 ppm with an average value of 62% dye recovered. Low concentration of feed phase resulted in low mass flux in the extraction process, thus affecting the recovery efficiency.
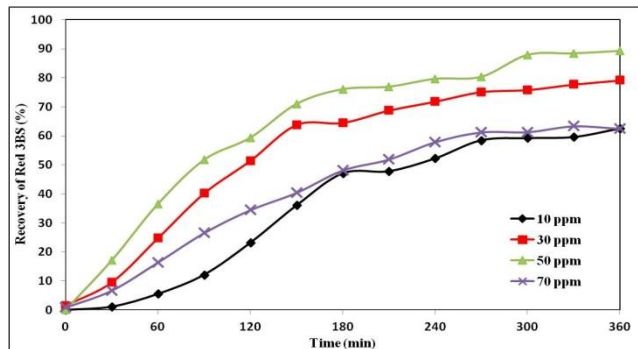

Figure 10 Recovery of Red 3BS by varying initial concentration of feed phase (Experimental condition:, Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M, Flow rate=100 ml/min)

4.6 Effect of Sodium Silicate

Figure 11 shows the effect of Na_2SiO_3 on the removal percentage of Red 3BS. It can be observed that the percentage of removal Red 3BS decreased with increasing the concentration of Na_2SiO_3. During the first 60 minutes, high percentage of removal with 67% of dye was extracted at 0.00001 M Na_2SiO_3 compared to other concentrations of Na_2SiO_3. However after 360 minutes of extraction, 92 and 89% of removal were observed at 0.00001 and 1 M of Na_2SiO_3 respectively. The differences of removal percentage between

them are small. This is due to the presence of high content of ionic substances. According to Harman [33], the presence of Na_2SiO_3 in reactive dye solution can dissociate this component into NaOH and hydrogen silicate, H_2SiO_3 in reaction with distilled water. Therefore, there are four different compounds that exist in the feed phase which are anionic reactive dyes, Na_2SiO_3, NaOH, H_2SiO_3 and H_2O. The existence of the high amount of ionic substances increases the value of ion balance (χ) in the system, which in turn decreases the removal rate across the SLM process [34-35]. Besides, addition of Na_2SiO_3 decreased the solubility of analyte thus enhancing their partitioning into the organic phase as reported by Eskandari *et al*. [36]. However, this finding was in contrast with Muthuraman and Palanivelu [25], who found that the percentage transports of reactive dyes were not affected by the presence of inorganic salt at high concentration.

Meanwhile, Figure 12 shows the percentage of recovery of Red 3BS from the aqueous phase. It can be observed that the recovery performance for all concentrations of Na_2SiO_3 were almost similar and not much influenced by presence of Na_2SiO_3. The result showed that around 92% of Red 3BS was recovered at 0.00001 M Na_2SiO_3 However, further extending the concentration of Na_2SiO_3 up to 1 M, the recovery efficiency was reduced to 89%, which is not really significant. However, there were slightly differences in recovery value due to the low percentage of extraction. It can be concluded that the presence of Na_2SiO_3 in the feed phase does not influence much on the performance separation of reactive dyes.
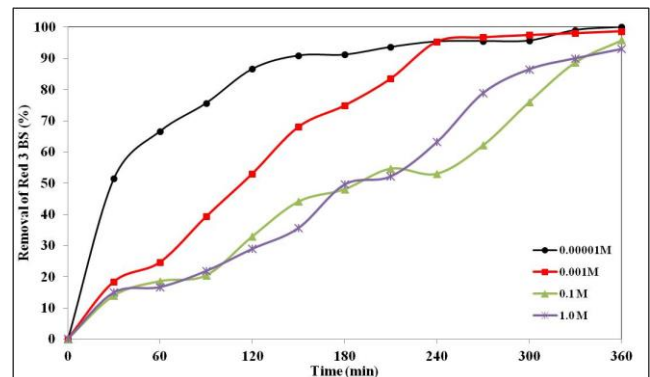

Figure 11 Removal of Red 3BS by varying concentration of sodium silicate, Na_2SiO_3 (Experimental condition: Red 3BS: 50 ppm (pH: 3), Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M, Flow rate=100 ml/min)

Figure 12 Recovery of Red 3BS by varying concentration of sodium silicate, Na_2SiO_3 (Experimental condition: Red 3BS: 50 ppm (pH: 3), Tridodecylamine = 0.1 M, Salicyclic Acid = 0.1 M, Sodium Hydroxide = 0.1 M, Flow rate=100 ml/min)
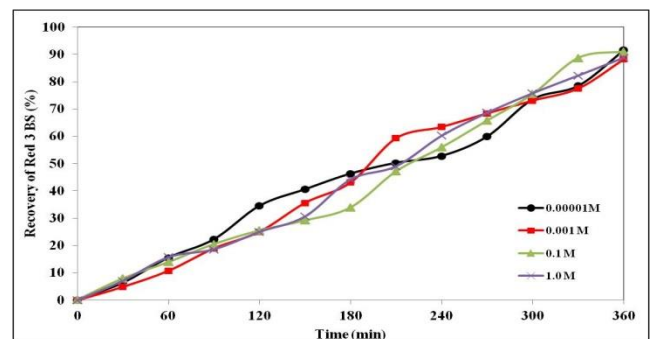
■5.0 CONCLUSION

As a conclusion, Red 3BS was efficiently removed and recovered using SLM process assisted by TDA as carrier. Under favorable condition, 100 and 89% of Red 3BS was successfully removed and recovered from an aqueous phase. The effect of fixing agent in the wastewater also studied and the results prove that the formulation of the liquid membrane and PP membrane support exhibit high stability toward any degradation during SLM process, hence feasible to be applied in industrial scale.

Acknowledgement.

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