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Dye Removal by Membrane Technology for Wastewater Treatment using a Cationic Carrier

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ABSTRACT

The removal efficiency of malachite green (MG) dye ions by using a bulk liquid membrane was investigated. The transport of MG dye ions was accomplished using a bulk liquid membrane, which contained salicylic acid as carrier, sodium hydroxide as extractant, and acetic acid as acceptor. Different factors were examined for removal efficiency, such as pH of the acceptor phase in the range of pH 3−7, initial dye concentration at 20−60 mg/L, and concentration of carrier in the range of 8−12 mg/L. Box-Wilson method for experimental design was adopted to establish the relationships between these operating variables attributed to affecting the treatment process, and the mechanism of dye transport from feeding to acceptor phase. The results indicated that the optimum conditions for dye extraction were achieved at pH 6, dye concentration of 20 mg/L, and carrier concentration of 12mg/L. The implementation of these parameters on the prepared dye solution revealed a relatively high removal efficiency of MG dye (98.4%). A Box-Wilson model was modified and found to fit the effect of variable response, with a correlation coefficient (R) = 0.977 and root-mean square error (S) = 1.8%. This work proved that liquid membrane was effectively useful for dye removal from the wastewater.

Keywords: BLM, malachite green, mathematical model, salicylic acid

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INTRODUCTION

One of the major environmental problems currently highlighted is the removal of dyes within the textile industries and wastewater prior to their discharge into natural water streams (Mohammad et al., 2017; Elumalai et al., 2015). Dyes are very toxic, carcinogenic, and risky towards aquatic living organisms. They can cause irritation to the skin and pose a serious threat to human beings and the environment alike (Soniya & Muthuraman, 2015). However, they are commonly used in many industries in products like paper, rubber, plastic, pharmaceutical items, textiles, and aquaculture (Abou-Gamra & Ahmed, 2015). Malachite green (MG) is a cationic dye (triphenylmethane) used in many fields such as color paper and fabric. It has also been used to treat protozoal and fungal infections in fish and fish eggs, it generally found in the form of crystal powder, revealing a metallic green luster and has high solubility in water and ethanol. The base dye is toxic and associated with harmful effects towards the kidney, gonads, reproductive system, brain and nervous system, the intestines, and pituitary gonadotropic cells. Due to its serious threat towards the aquatic life, MG is not one of the registered substances allowed for use in aquaculture. Therefore, MG should not be found in fish sold for human consumption. According to the latest studies, MG poses a significant threat to human health in concentrations of 0.1 mg/L−10 mg/L (Papinutti et al., 2006). The minimum requirement for performance limit to allow laboratories in carrying out surveillance for the sum of MG and leucomalachite green is 2µg/kg (Gavrilenko et al., 2019). There are many methods to treat dyes found in wastewater, such as sedimentation, crystallization, and gravity separation. Treatment methods like solvent extraction, reverse osmosis, ion exchange, electrodialysis, electrolysis, and adsorption may also be used (Muthuraman et al., 2009a; Muthuraman et al., 2009b).

Recently, the liquid membrane (LM) technique has become popular among to researchers in different fields of science, such as chemical engineering, biotechnology, biomedical engineering (Al-Hemiri & Noori, 2009; Rounaghi et al., 2016), and wastewater treatment. LM can be defined as the process of transferring a solution from the aqueous phase to another phase via an immiscible organic phase (Noble & Way, 1987; Zeng et al., 2019).

Extraction and recovery of MG ($C_{52}H_{54}N_4O_{12}$) can be explained by the following mechanism: NaOH reacts with dye in the feed phase, isolating the dye from water and causing it to become an ion (El-Ashtoukhy & Fouad, 2015). Ion dye encompassing transport from the feed phase through the liquid membrane at either feed membrane interface is associated with the presence of salicylic acid as the carrier in membrane, which reacts and forms an ion pair complex $[(R^- \ Dye^+]_{org}$ $[(C_7H_5O_3^-)\text{–}(C_{52}H_{53}N_4O_{11}^+)]$ (Equation 1) (Sathya et al., 2016). This complex dissolves completely in the liquid membrane, following which the (salicylic acid - dye$^+$ ion) pair complex reacts with acetic acid complex when it reaches the interface (membrane/acceptor). Then, the salicylic acid receives proton (H^+) from the acetic acid in the acceptor phase and diffuses back into the organic membrane as a neutral carrier to repeat the cycle (Elumalai & Muthuraman, 2013; Baylan & Çehreli, 2019). Next, the dye diffuses into the acceptor phase with the acetate (CH_3COO^-) ion, forming the safety solution (Naim et al., 2016). The proposed mechanism is shown in Figure 1.

$$(\text{Carrier})_{org} + (\text{Dye})_{ion} = \text{complex} + \text{water}$$

$$(C_7H_6O_3)_{org} + [C_{52}H_{54}N_4O_{12}^{+}]_{ion} = [C_7H_5O_3^{-} - C_{52}H_{53}N_4O_{11}^{+}]_{org} + H_2O \quad (1)$$

The 2nd reaction in the inter phase of (membrane/acceptor) can be explained using the following Equation 2:

$$[C_7H_5O_3^{-} - C_{52}H_{53}N_4O_{11}^{+}]_{org} + (CH_3COOH)_{aq} = (C_7H_6O_3)_{org} + [CH_3COO^{-} - C_{52}H_{53}N_4O_{11}^{+}]_{aq} \quad (2)$$

LM offers many advantages compared to other separation methods, such as high selectivity, efficient high fluxes, high potential of removing cationic and anionic dyes, reusability, and low energy consumption (Marchetti et al., 2014; Han et al., 2017). According to configurative definition, it is very actively utilised in water treatment for the removal of cationic and anionic dyes from industrial water (Joshi et al., 2004). LM can be categorised as bulk liquid membrane (BLM), emulsion liquid membrane (ELM), and supported liquid membrane (SLM) (Bahram & Pourabdollah, 2015; Chang et al., 2011a; Hernandez et al., 1986). The main technological problems of using ELM and SLM are the irreversibility of the operation and their instability in terms of long-term performance (Saeed et al., 2016). Furthermore, BLM is a simple design for liquid membrane processes and associated with many advantages, such as simple equipment, high separation and uses less amounts of organic solvent and carrier (extractant) (Chang et al., 2011b). The BLM technique has been successfully employed in the treatment of metal ions and hydrocarbons (Laki & Kargari, 2016; Candela et al., 2013) and cationic and anionic dyes, such as methylene blue (Soniya & Muthuraman, 2015) and rhodamin B (Elumalai & Muthuraman, 2013). The objective of the present study was to eliminate MG (oxalate) dye by using BLM via hexane utilisation as the membrane. Furthermore, parameters, such as pH, carrier concentration, dye concentration, and the mechanism of dye transport from feed to acceptor phase via LM were investigated. In the recent years, a remarkable increase of LM applications in separation processes has been observed. In the present work, BLM was used as a low cost process with the Box-Wilson rotatable central composite design to maximize dye removal efficiency from waste water. It can also optimize pH acceptor phase, the concentration of dye, and the concentration of carrier.

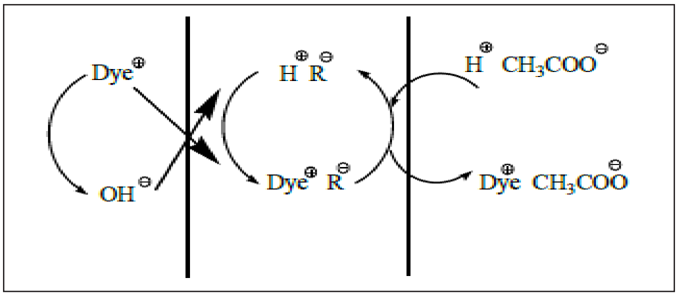

Figure 1. A schematic shows mechanism transport of dye in liquid membrane

MATERIALS AND METHODS

Materials

Hexane (95%, Merck), salicylic acid ($C_7H_6O_3$, 99.8%, Merck), sodium hydroxide (NaOH, Merck, ≥ 97% purity), acetic acid (CH_3COOH, Thomas Baker, ≥ 98% purity), and malachite green oxalate ($C_{52}H_{54}N_4O_{12}$ ≥ 80% purity) were supplied by HiMedia.

Equipment

The feed, acceptor, and membrane phases were stirred using a magnetic stirrer (Fisher Scientific, JENWAY, 1000, UK(. The absorbance of dye sample was determined using UV visible spectrophotometer (GBC Cintra 6 series V-3656), while the pH of the feed phase (dye solutions) and acceptor phase were determined by using pH meter (pH7110 WTW, Germany).

Procedure

The experiments of MG removal by implementing BLM were carried out in two beakers that were concentric at the bottom portion. The outer beaker (ID=11.5 mm, V=1000 ml) is bigger than the inner beaker (ID=9 mm, V=500 ml) as shown in Figure 2 (Noori et al., 2018). In this design, the outer beaker contained feed aqueous solution comprised of dye in different quantities, 400 mL distilled water, and drops of NaOH to yield pH of 9. It was placed in a magnetic stirrer set up. Meanwhile, the inner beaker contained the acceptor aqueous solution (CH_3COOH and 200 mL of distilled water) that was fixed by two stands inside the outer beaker. Both aqueous solutions were above the liquid membrane (i.e. 300 ml hexane

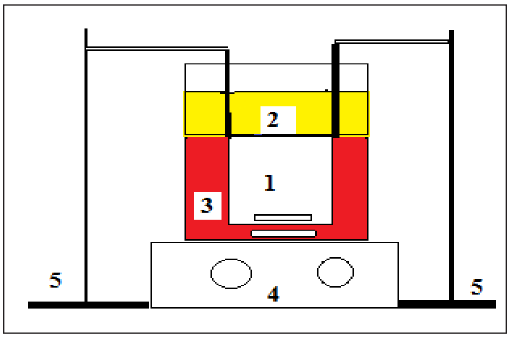

Figure 2. BLM (1-acceptor phase, 2-membrane phase, 3-feed phase, 4-magnetic stirrer, 5-a stand)

and salicylic acid as the carrier in different quantities), whereby the liquid membrane was poured above the two layers of previous aqueous phases using a mechanical pipette for the measurement of dye absorbance and concentration ,while reaction time takes (15-20) min. The measurements were obtained using the UV-spectrophotometer at a wavelength of 618 nm. Similarly, the corresponding concentration of MG was calculated from the calibration curve (Sathya et al., 2016). The controlled temperature was also varied from 25°C to 27°C to study its effect on the removal of MG dye.

Most importantly, different densities were maintained to keep the three phases immiscible with each other. The operating parameter used for the Box-Wilson method of experimental design was feed phase containing dye (i.e. 20−60 mg/L, V=250 mL). The same volume of the acceptor solution (pH=3−7, V=250 mL) was adjusted by using NaOH and acetic acid solution, while the organic phase was undertaken using salicylic acid (8−12 mg/L, V=300mL). Experiments were performed by using the magnetic stirrer set up, which was speed-adjusted to ensure the contents did not mix with each other. Then, samples were taken every 30 min from the feed and acceptor solutions (Eljaddi et al., 2017).

Mathematical Model

With the aim of establishing the phenomenon of dye removal, a standard Response Surface Methodology (RSM) design known as the Box-Wilson central composite design was adopted and using the statistical software version 10. This design can reduce the number of experimental trails needed to evaluate multiple parameters and their interactions (Majeed et al., 2017). From the preliminary experiments, independent variables were determined to be pH of the acceptor phase (x_1), concentration of the dye (x_2), and concentration of the carrier (x_3). The response of the experiments was determined according to the Box-Wilson method (Box & Wilson, 1951). It comprised of a linear equation with four parameters (Equation 3), whereby the result was used as an initial approximation for the second model (Equation 4).

Simple linear multi-variable model:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 \tag{3}$$

Where,

y is the dependent variable or response

x_i is the independent variable

b_0, b_1, b_2 and b_3 are four parameters to be obtained by curve-fitting from the observed results.

Second polynomial model:

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_4x_1x_2 + b_5x_1x_3 + b_6x_2x_3 + b_7x_1^2 + b_8x_2^2 + b_9x_3^2 \tag{4}$$

Thus, for a three-variable process, the number of experiments needed were according to the following Equation 5:

$$N_0 = 2^P + 2P + 1 \tag{5}$$

Where, N is the number of optimization processes(experiments) and P is the number of factor.

There were 15 experiments applied to Equation 5 in finding the optimum operating conditions, whereby the results indicated the following conditions (Alalayah et al., 2010).

x_1 = pH acceptor phase = 3−7

x_2 = Concentration of dye = 20−60 mg/L

x_3 = Concentration of carrier = 8−12 mg/L

More precise model of the following form can be obtained:

$$\sum \frac{x_1}{n} = \sum \frac{x_2}{n} = \sum \frac{x_3}{n} = \sum \frac{x_1 x_2}{n} = \sum \frac{x_1 x_3}{n} = \sum \frac{x_2 x_3}{n} = 0, \text{ and}$$

$$\sum \frac{x_1^2}{n} = \sum \frac{x_2^2}{n} = \sum \frac{x_3^2}{n} = 0.933$$

The model can be used to reach even more precise regression following Equation 6:

$$y = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_1 x_2 + b_5 x_1 x_3 + b_6 x_2 x_3 + b_7 (x_1^2 - 0.933) + b_8 (x_2^2 - 0.933) + b_9 (x_3^2 - 0.933) + b_{10} x_1^3 + b_{11} x_2^3 + b_{12} x_3^3 + b_{13} x_1 x_2 x_3 \tag{6}$$

Substituting the parameters obtained by minimizing the sum of squared errors, Equation 6 became Equation 7:

$$y = 325.4675 + 9.514032 x_1 + 1.77026 x_2 - 68.4625 x_3 + 0.280709 x_1 x_2 + 1.590699 x_1 x_3 + 0.123205 x_2 x_3 - 4.79326 ({x_1}^2 - 0.933) + 0018892 ({x_2}^2 - 0.933) + 6.360562 ({x_3}^2 - 0.933) + 0.303146 {x_1}^3 - 0.000155 {x_2}^3 - 0.214358 {x_3}^3 - 0.031284 x_1 x_2 x_3 \tag{7}$$

The above equations were used to obtain a correlation factor nearer to one. Meanwhile, the percentage of dye removal was obtained following Equation 8:

$$Dye\ removal\ (\%) = \frac{Initial\ concentration\ of\ dye - Final\ concentration\ of\ dye}{Initial\ concentration\ of\ dye} \times 100 \quad (8)$$

RESULTS AND DISCUSSION

Effect of Acceptor Phase pH Value on Removal Percentage of Dye

The effect of acceptor phase PH in the percentage of dye removal is shown in Figure 3 and Figure 4.

Feed aqueous solutions prepared using a constant dye concentration of 20 mg/L at different pH values of the acceptor phase varying from 3 to 7 were used and carrier concentration was changed from 8 to12mg/L .In Figure 3 ,the removal of dye changed alongside increasing pH from 3 to6, then it decreased when pH increased to 7. The results were observed in all carrier concentrations.

The highest dye removal was 100% obtained at the pH of 6 and S of 12 mg/L, which were considered the optimum operating conditions and the lowest dye removal was obtained at pH of 7 (93.28%, S=8 mg/L acetic acid). The weak aliphatic acid was used as an acceptor phase to react with the compound of (dye-salicylic acid) at the interphase of the (membrane/acceptor) to form (dye –acetic acid) ion pair compound (Sathya et al., 2016).

Furthermore, Figure 4 shows the effect of pH on dye removal at different initial dye concentrations and fixed initial carrier concentration of 12 mg/L.

It was observed that the change of pH for the acceptor phases yielded the best results when the pH value was 6. When the concentration of dye increased from 20 mg/L to 50 mg/L, the percentage of dye removal decreased and the compound formed was reverted to the acceptor phase solution. At a high pH value, the ionized group present in the carrier

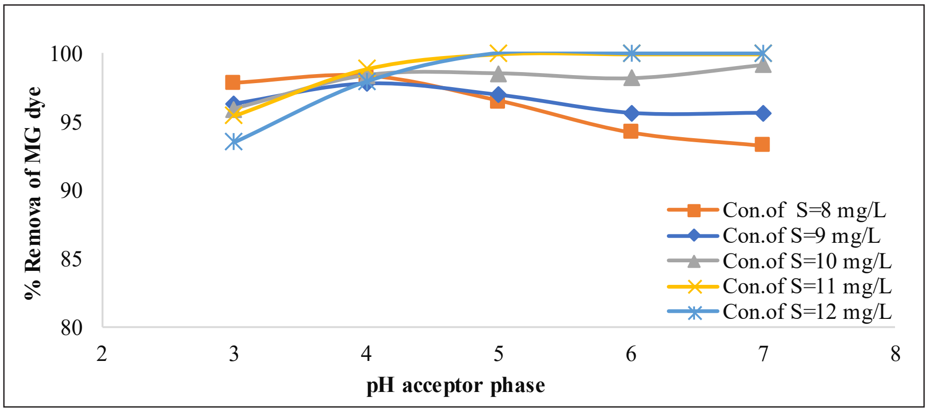

Figure 3. Effect of initial pH of acceptor phase at different initial carrier concentration) and fixed dye concentration =20mg/L, here (S: Initial carrier concentration & d ;dye concentration)

salicylic acid can attract more dye and lead to the formation of compounds capable of enhancing dye transport processes. The maximum removal rate was found to be 99.96% at the pH of 6 and initial dye concentrations of 20 mg/L. Hence these were considered the optimum operating conditions (Patro, 2016).

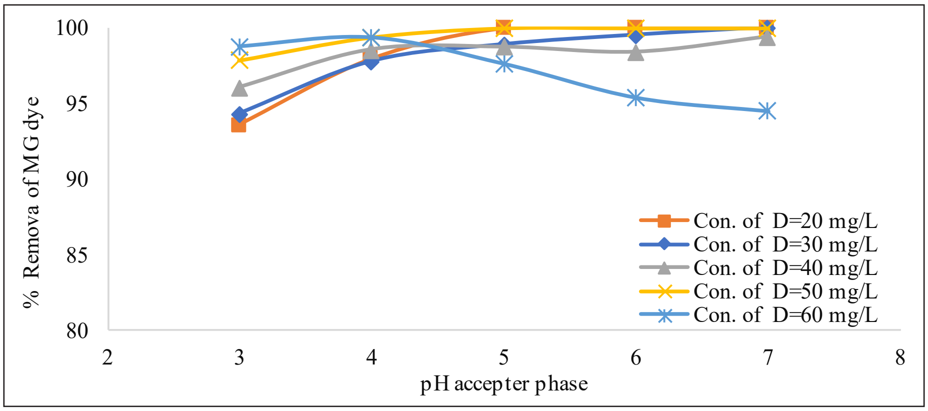

Figure 4. Effect of initial pH of acceptor phase at different dye concentration and fixed initial carrier concentration=12mg/L

Effect of Dye Concentration

The effect of MG concentration in the feed phase towards the percentage of dye removal is presented in Figure 5 and Figure 6. The experimental dye ranging between the concentration of 20 mg/L and 60 mg/L in the feed phase was investigated by fixing the optimum operating conditions. They were utilized per the first study on the previous effects, namely S of 12 mg/L and pH of 6.

Figure 5 shows the effect of dye concentration on the percentage of dye removal at different pH values at a constant initial carrier concentration of 12 mg/L (i.e. optimum operating conditions). It was clearly revealed that the percentage of dye removal decreased with increasing concentration of dye from 20 mg/L to 60 mg/L. The maximum removal of 100% was observed at the pH of 6 and D of 20 mg/L, which were considered the optimum operating conditions. The reasons behind these results were due to the low MG concentration in the feed phase that leads to enough amount of carrier covering all present dye molecules ,consequently the area of ionic attraction (electrostatic attraction) leading to increase the ionic strength of the feed solution, as well as molecular geometry in the (feed/liquid membrane) interface. It can also be explained by the fact that at higher dye concentrations and limited carrier in the LM, inability of salicylic acid to react with the excess dye can be seen. Similar results were obtained in BLM for the removal of metals (Elumalai et al., 2014).

Figure 6 depicts the removal percentage of dye studied using four different initial salicylic acid concentration values at a constant initial pH of acceptor phase (pH=6). It can be observed that the increasing values of the salicylic acid concentration will increase the removal percentage. The maximum removal was at 100% for S of 12 mg/L and D of 20 mg/L, which were considered the optimum operating conditions. These results were attributable to the high concentration of salicylic acid that interacted well with the MG dye at the (feed/membrane) interface. Hence, the transport of MG increased. Furthermore, the increase of the salicylic acid concentration resulted in the increase of the MG influx. The first part was due to the enhancement of contact influence between MG and salicylic acid, along with the increasing dye concentration (Othman et al., 2014).

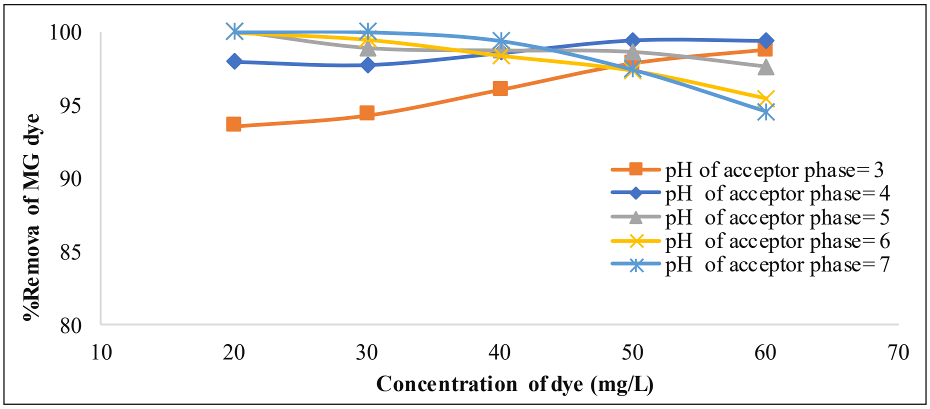

Figure 5. Effect of initial dye concentration at different initial pH of acceptor phase and fixed initial carrier concentration =12mg/L

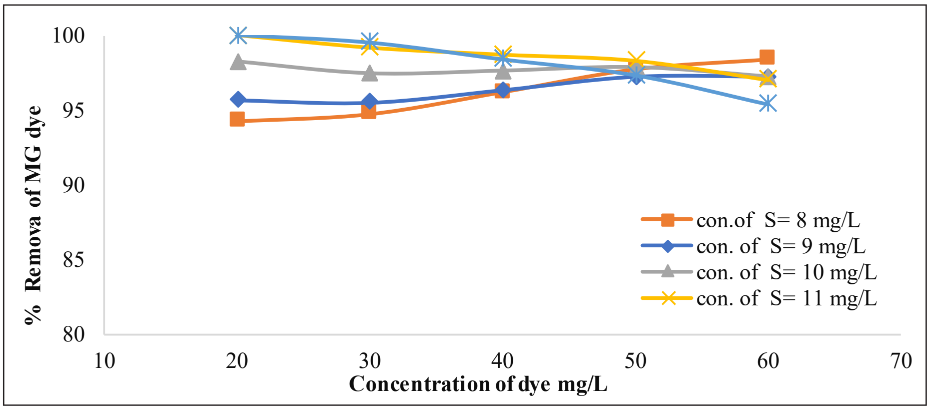

Figure 6. The effect of initial dye concentrations at different initial carrier concentrations s and fixe initial pH of acceptor phase =6

Effect of Carrier Concentration on Removal Percentage of Dye

The amount of carrier (salicylic acid) plays an important role in dye transfer and removal. In this work, the concentration range between 8 mg/L and 12 mg/L was maintained throughout.

Figure 7 shows the effect of increasing the carrier concentration on MG removal percentage. The concentration of the carrier in the membrane showed a clear effect on the compound transfer, which was formed between the dye and carrier through the membrane. It was found that increasing the carrier concentration would increase the MG removal efficiency, whereby the MG dye removal percentages and the variation of carrier concentration were studied using five different initial concentrations of dye. The acceptor pH of 6 was kept constant as shown in Figure 8. The maximum removal was

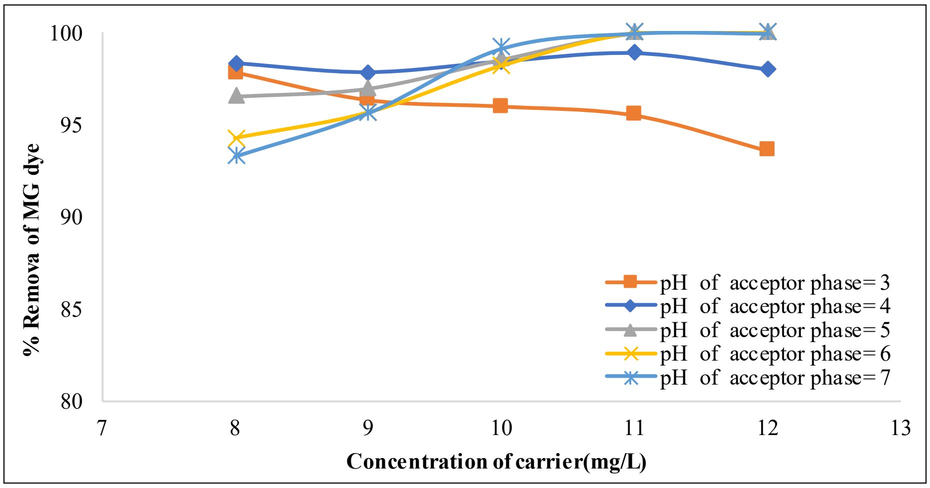

Figure 7. Relations between removal of dye with initial carrier concentration at different initial pH of acceptor phase and fixed initial carrier concentration

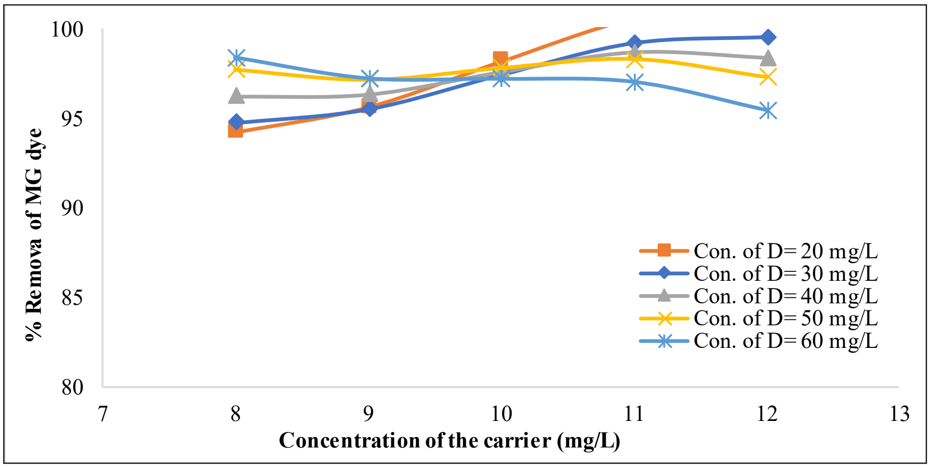

Figure 8. Effect of initial carrier concentration at different initial dye concentration and fixed initial pH of acceptor phase

observed at 98.4% at the perimeters of S (12 mg/L) and D (20 mg/L), thus considered as the optimum operating conditions. The carrier forms a transportable compound diffusing in the membrane, which then releases carrier into the acceptor phase. The carrier enables and provides the opportunity for its movement in the system using two ways, namely chemical reaction with the dye or diffusion. In the selected system, the dye first reacts with the carrier to form a dye-carrier compound that spreads through the liquid membrane and releases the solute in the acceptor phase. In this study, the effect of increasing the concentration of salicylic acid resulted in it being chosen as an appropriate carrier in the liquid membrane for the process of dye removal. Similar results were also reported by Ng et al. (2011).

Mathematical Model Calculations

Table 1 shows the values of the independent variables corresponding to the final form of the dye removal equation. To find the best condition, the variable that achieved maximum dye removal was studied. Table 2 shows the values from each variable, which are dependent on Equation 7. It was found that the optimum operating conditions consisted of the acceptor phase pH between 5 and 7, dye concentration of 20 mg/L, and carrier concentration of 12 mg/L. Further accuracy was ensured using the last process performed using the optimization conditions, whereby all processes became 28 (as show in Table 2) and the optimum pH was 6. The final result obtained yielded the correlation coefficient (R) = 0.977 and root mean square error (S) = 1.8%.

Table 1
The initial guess and values of real variables for the calculations of dye removal using the BLM method

Run No.	Initial values			Final converged values			%Removal (y)	%Real removal (Y)	Residual
	x_1	x_2	x_3	x_1	x_2	x_3			
1	-1	-1	-1	3.845	28.452	8.845	96.728	96.596	**0.133**
2	1	-1	-1	6.155	28.452	8.845	94.201	94.942	**-0.741**
3	-1	1	-1	3.845	51.547	8.845	98.623	99.404	**-0.780**
4	1	1	-1	6.155	51.547	8.845	96.309	96.706	**-0.3972**
5	-1	-1	1	3.845	28.452	11.155	97.548	96.53	**1.019**
6	1	-1	1	6.155	28.452	11.155	98.757	97.362	**1.395**
7	-1	1	1	3.845	51.547	11.155	99.599	98.294	**1.305**
8	1	1	1	6.155	51.547	11.155	97.168	96.73	**0.438**
9	-1.732	0	0	3.00	40	10	98.419	99.188	**-0.769**
10	1.732	0	0	6.99	40	10	99.026	99.423	**-0.398**
11	0	-1.732	0	5	20.000	10	99.687	100.632	**-0.944**
12	0	1.732	0	5	59.999	10	99.968	100.209	**-0.241**
13	0	0	-1.732	5	40	8.000	99.008	97.871	**1.137**
14	0	0	1.732	5	40	11.999	99.844	102.128	**-2.284**
15	0	0	0	5	40	10	98.587	98.642	**-0.055**

Table 2
Studying best variable that achieve maximums dye removal

No.	Constant variable	Best variables in constant certain variable		Maximum dye removal
	pH=3			
	pH of acceptor phase	Concentration of the dye (mg/L)	Concentration of the carrier (mg/L)	**(%)Maximum dye removal**
1	3	20	8	**97.827**
2	3	40	8	**97.951**
3	3	60	8	**98.309**
4	3	20	10	**95.994**
5	3	40	10	**97.292**
6	3	60	10	**98.824**
7	3	20	12	**93.6**
8	3	40	12	**96.072**
9	3	60	12	**98.778**
	pH=5			
	pH of acceptor phase	Concentration of the dye (mg/L)	Concentration of the carrier (mg/L)	**(%)Maximum dye removal**
10	5	20	8	**96.540**
11	5	40	8	**97.881**
12	5	60	8	**99.457**
13	5	20	10	**98.567**
14	5	40	10	**98.580**
15	5	60	10	**98.827**
16	5	20	12	**99.92**
17	5	40	12	**98.717**
18	5	60	12	**97.635**
	pH=7			
	pH of acceptor phase	Concentration of the dye (mg/L)	Concentration of the carrier (mg/L)	**(%)Maximum dye removal**
19	7	20	8	**93.285**
20	7	40	8	**95.844**
21	7	60	8	**98.637**
22	7	20	10	**99.172**
23	7	40	10	**97.899**
24	7	60	10	**96.861**
25	7	20	12	**99.97**
26	7	40	12	**99.393**
27	7	60	12	**94.524**
	pH=6			
	pH of acceptor phase	Concentration of the dye (mg/L)	Concentration of the carrier (mg/L)	**(%)Maximum dye removal**
28	6	20	12	**100**

CONCLUSION

Malachite green (MG) dye was transported by means of a liquid membrane. The efficiency of the system was dependent upon the principal parameters, such as the acceptor phase pH, dye concentration, and carrier concentration. The most suitable conditions were confirmed to be at the pH of 6, dye concentration of 20 mg/L, and carrier concentration of 12mg/L. Using these optimal conditions, the maximum removal efficiency of MG dye was found to be 99.7%. The Box-Wilson model was established accordingly, which further correlated the effect of such variables towards the responses with the correlation coefficient R = 0.977 and root mean square error(s)=1.8%.

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