Bulk Liquid Membrane Process for The Transport and Kinetics Study of Malachite Green From Textile Wastewater

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A B S T R A C T

A bulk liquid membrane (BLM) system contained Di (2-ethyl hexyl) phosphoric acid (D2EHPA) as an extractant was used for transport of malachite green (MG) dye from textile wastewater. D2EHPA present in n-hexane is an effective, efficient and highly selective carrier for the transport of MG dye through BLM. Maximum transport 88% was observed at 0.24M concentration of D2EHPA in the membrane phase and 7 moles concentration of acetic acid in the receiving phase after 300 min. The effect of parameters influencing the transport of MG dye such as pH and concentration of dye in the donor solution, extractant concentration in the membrane phase, nature of the organic solvent, the composition of receiving phase, stirring speed and kinetics parameter were elucidated. First order irreversible reaction kinetics k_1 and k_2 were applied for the transport of MG dye from aqueous phase BLM phase and BLM to acceptor phase. The accumulation of MG in BLM phase and the rate controlling step under different experimental conditions were also discussed. Finally, the proposed liquid membrane was effectively applied for MG dye transport from textile wastewater.

INTRODUCTION

Removal of dye from wastewater released from various industries such as textile, paper, rubber, plastic, cosmetics etc., to the surface and ground water sources are most important and serious concern for the government regulatory bodies [1]. In general, dyes are classified as: anionic- acid, direct and reactive, cationic- basic and non-ionic disperse dyes [2]. A recent study estimated that more than 100,000 different dyes are manufactured and over 7×10^5 tons of dyes are annually produced for commercial purpose [3]. Among the various dyes, malachite green oxalate (MG basic dye), is one of the most widely used as colouring agent in the silk, wool, cotton, leather, paper, acrylic industries, food colouring and other purposes [4-5]. In addition, MG has been extensively used as antiseptic, antibacterial and antiprotozoa and other medical applications [6]. Furthermore, it is also used as a disinfectant in aquaculture and agriculture applications [7]. However, MG presents in wastewater is considered to be toxic, pose serious threat to aquatic life and has detrimental effects on liver, gill, kidney, nervous, reproductive system, brain intestine, gonads and pituitary gonadotropic cells [8-9]. In humans, MG causes skin irritation, contact with eye will lead to permanent injury and considered as carcinogen and mutagen [10]. The existing conventional treatment techniques are either expensive or inefficient to treat organic dyes present in water and wastewater. Hence, there is an urgent need to develop an efficient and economically viable treatment technique to remove dyes from wastewater [11]. Phtocatalytic degradation of MG dye with TiO_2/WO_3 composite from synthetic wastewater has been reported, but their long term stability and reusability of the catalytic is not discussed in detail [12]. Removal of MG from aqueous solutions by native and heat-treated anaerobic granular sludge has also been reported [13]. The use of biological process for removal of dye from wastewater is not successful and their large scale application is highly questionable.

Recently, liquid membrane (LM) process has emerged as an efficient and economically viable technique of removal of cationic and anionic dyes from

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industrial wastewater [14]. LM systems are being studied broadly by researchers in the field of inorganic, organic and analytical chemistry, chemical engineering, biotechnology and biomedical engineering and wastewater treatment [15]. LM has shown high potential for removal organic and inorganic pollutants, particularly against low concentration of pollutants, where other techniques cannot be applied efficiently [16]. The advantages of using LMs when compared to other techniques are that they are highly selective in nature, small amount of carrier is sufficient to continuously transport the dyes and metal ions. According to configuration definition, LMs can be categorized as bulk liquid membranes (BLM), supported liquid membranes (SLM), emulsion liquid membranes (ELM), polymer inclusion membranes (PIMs) and activated composite membranes (ACM) [17]. Among these, BLM is highly suitable for screening different carrier-mediated transport systems on a laboratory scale applications [18].

Liquid membranes have been successfully applied to treat heavy metal ions such as, thorium, copper, chromium, nickel, mercury, uranium, cadmium, cobalt etc., and cationic and anionic dyes such as methylene blue, rhodamin B, cibacron red FN-R [19-29]. The solvents, carriers and phase modifiers are in variably diluted to the diluents such as n-hexane, xylene, benzene, kerosene, chloroform and dichloromethane etc., [30-35]. Use of various carriers such as D2EHPA, salicylic acid, benzoic acid, Tri-n-octyl amine, Tetra butyl ammonium bromide, phenol have been extensively studied by various research groups [36-41]. D2EHPA is a well-known extractant when compared to other carriers due to its chemical stability, high complexion ability, stripping characteristics, exceptionally low solubility in aqueous acidic solutions and D2EHPA is a bidentate ligand and shows high removal efficiency for the removal of inorganic metal ions rather than organic pollutants [42-43]. Removal of various form of dyes from aqueous solution have been carried out using ELM and BLM [44, 45]. Removal and recovery of golden yellow and cibacron LSG dyes from aqueous solution by BLM technique was reported [46]. Similarly, calix [4] are ne-mediated uphill transport of methyl red through BLM and their kinetics of operational variables was studied [47, 48]. Recovery of acid red 10 B and acid pink BE silk dyes by BLM using tri-n-butyl phosphate as carrier was studied [49].

In the present study, removal of MG (oxalate) has been carried out by BLM using hexane in D2EHPA as carrier. The controlling parameters such as pH, carrier concentration, nature of diluents, stirring rate and time have been evaluated at ambient temperature and pressure. The mechanism of the dye transport from feed to strip phase through BLM has been discussed. The structural modification of MG has been monitored using UV-Visible and Fourier Transform Infrared Spectrophotometer (FTIR) analysis.

MATERIAL AND METHODS

Regents
Hexane, Di (2-ethyl hexyl) phosphoric acid, MG were obtained from qualigens fine chemical, India and used without further purification. The following inorganic bases and organic solvents such as glacial acidic acid ($\geq$ 99.5%), malachite green (oxalate) (80%), sodium carbonate (99%), benzene ($\geq$ 99%), toluene (98%), hexane (95%), and xylene (99%) were also used without further purification. All chemicals used were analytical grade and reagents were prepared in double distilled water.

Stock solution preparation
Malachite green (oxalate) is a cationic dye. Its IUPAC name is N, N, N, N-Tetramethyl-4,4 diamino triphenyl carbinium oxalate. It has been classified as CI Basic green 4, CI, CI 42000. It has a molecular formula $C_{52}H_{54}N_4O_{12}$ and molecular weight of 927.03 g/mol. The maximum wavelength of this dye is (λ_{max}) 618 nm. The stock solution of 1000 mg/L was prepared by dissolving an appropriate quantity of MG using double distilled water. The working solutions were prepared by diluting the stock solution with double distilled water to give the appropriate concentration. pH meter (Elico Li 120, India) was used to measure pH of aqueous solutions. For agitation of solution a shaker and magnetic stirrer was used (IKD-KS 50, India).

Electrophoresis study
The applications oriented of this study very important and a known concentration of mixing of textile wastewater MG dye solution was filled into the electrophoresis chamber (Systronics Electrophoresis 606) and constant current at 20 V was run for 1 h. At the end of the first hour the sample was taken from cationic and anionic compartments and UV spectroscopy analysis absorption measured to qualitative decision find out whether the known dye solution is measured cationic or anionic.

BLM Procedure
BLM is the simplest design to perform LM process. The H-type BLM apparatus contains three phases, Aqueous solution was placed in two phases , namely donor and strip phase and third phase is organic membrane phase as shown in Fig. 1. The inner dimension of transport cell is 70 mm diameter × 195 mm depth for H-type. A bridge with 45 mm height (from the bottom) divides the cell into two compartments. The diameter of the bridge is 30 mm and its length is 120 mm. Experiments were carried out at ambient temperature (300 K), and the aqueous feed

phase containing dye solution (50 mg/L, 260 mL) and strip phase containing glacial acetic acid (7M, 260 mL) were taken in the BLM apparatus. The solutions stirred at 300 rpm. The third phase containing hexane solution (520 mL) with Di (2-ethyl hexyl) phosphoric acid (0.21 mol/ L). Both interfaces (feed/membrane and membrane/strip) were at the same level and were separated by the barrier [50]. Samples were taken out from the feed and strip phases at regular intervals of time and the concentration of dye was measured using spectrophotometer λ_{max} = 618 nm.
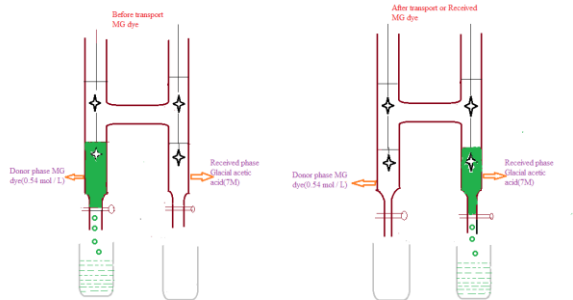

Figure 1. Schematic experimental setup for bulk liquid membrane for before transport of MG dye and after transport of MG dye.

Kinetics MG transport process

A BLM transports component of interest between two aqueous donor and receiving phase. The transport of MG as depends on the concentration of carrier present in BLM, pH of the aqueous phases, nature of the solvent and stirring rate and nature of the acceptor present in receiving phase. The kinetic behaviour of the MG dye transport with time was directly measured both donor (C_d) and receiving (C_r) phases. Experiments were performed for the fixed time of 300 min and sample was collected from both donor and acceptor phases for every 60 min. The reduced dimensionless concentrations were used for experimental purpose;

$$R_{d=\frac{c_d}{c_{do}}} \quad , \quad R_{m=\frac{c_m}{c_{do}}} \quad , \quad R_{r=\frac{c_r}{c_{do}}} \tag{1}$$

Where C_{do} is the initial MG concentration of the donor phase, while C_d, C_{LM}, C_r represented the MG dye concentration in donor phase, membrane phase, receiving phase respectively. The material balance with respect to the reduced concentrations can be expressed as

$$R_d + R_m + R_r = 1$$

From this expression the kinetic behaviour of the consecutive irreversible first order reactions can be described as follows;

$$[MG\ dye]_d \overset{k_1}{\to} [MG\ dye]_m \overset{k_2}{\to} [MG\ dye]_r \tag{2}$$
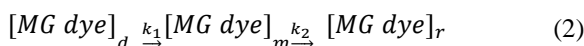
Where k_1 and k_2 are the apparent membrane entrance and

departure rate constant respectively.

Both the values of k_1 and k_2 are related with each other, there are three possibilities
(i)If values of k_1 and k_2 are comparable, i.e. $k_1 \approx k_2$, it means rate of transport at both donor– membrane and membrane–acceptor interfaces are equal.(ii)$k_1 \gg k_2$ shows that rate at donor–membrane interface is high as compared to membrane–acceptor interface; in this case organic membrane phase carries high MG dye content. (iii) In $k_1 \ll k_2$ there is reverse of above stated condition; organic membrane phase here carries a little MG dye quantity. Hence, the system in this study worked on third condition.

The kinetic scheme for consecutive reaction systems can be described by following rate equations [51].

$$\frac{dR_d}{dt} = -k_1 R_d = -J_d \tag{3}$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \tag{4}$$

$$\frac{dR_r}{dt} = k_2 R_m = J_r \tag{5}$$

where J is the flux. When $k_1 \neq k_2$; and integrating the above differential equations gives

$$R_d = \exp(-k_1 t) \tag{6}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \tag{7}$$

$$R_r = 1 - \frac{k_1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \tag{8}$$

while the maximum values of R_m and t_{max}(when $dR_m/dt=0$) can be written as;

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{-k_2/k_1 - k_2} \tag{9}$$

$$t_{max} = \left(\frac{1}{k_1 - k_2}\right)\ln\frac{k_1}{k_2} \tag{10}$$

By combining equ (9) and (10) the following relationship can be obtained [52].

$$k_2 = \frac{\ln\left(\frac{1}{R_m^{max}}\right)}{t_{max}} \tag{11}$$

Numerical analysis by non-linear curve fitting permits the rate constants to be determined, the value of k_1 is directly obtained by iteration from Eq. (6). This value is introduced as a constant value in Eqs. (7) and (8). An initial value of k_2 is obtained from Eq. (11) that was introduced in Eqs. (7) and (8) and iterated. By considering the first order time differentiation Eqs. (6–8) at t_{max}, one obtains the following equations:

$$\frac{dR_d}{dt}\bigg| \max = -k_1 \left(\frac{k_1}{k_2}\right)^{-k_1/k_1-k_2} \equiv J_d^{max} \qquad (12)$$

$$\frac{dR_r}{dt}\bigg| \max = k_2 \left(\frac{k_1}{k_2}\right)^{-k_1/k_1-k_2} \equiv J_r^{max} \qquad (13)$$

$$\frac{dR_m}{dt}\bigg| \max = 0 \qquad (14)$$

$$-J_d^{max} = J_r^{max} \qquad (15)$$

It was noted that at t = t_max, the system may be in quasi steady state approximation because the concentration of MG dye in the membrane does not change with time (Eq. 14). As a result of this the departure and entrance fluxes are equal and have opposite signs (Eq. 15). It can be seen that R_d versus t yields a decreasing mono-exponential curve whereas the time variation of both R_m and R_r is bi-exponential. The actual numerical analysis was carried out by non-linear curve fitting. The variation of R_d, R_m and R_r with time through BLM is shown in Fig. 2.
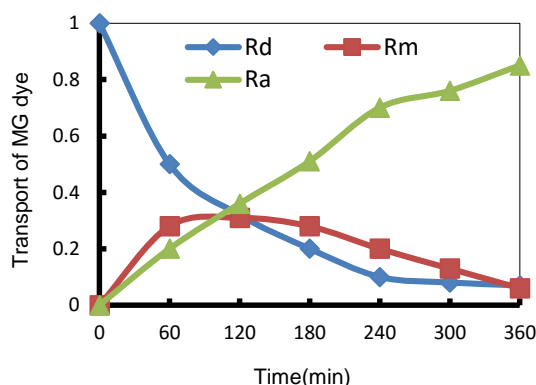

Figure 2. Time dependence of R_d, R_m, R_r for the transport of dye theoretical curves calculated from Eqs (6)-(8) (Experimental conditions: donor phase = 0.54×10^{-4}mol/L dye at pH 9 ± 0.1,receiving phase: 7M Acetic acid (AcOH) solution, membrane organic phase : 0.21mol/L carrier in n-hexane stirring speed: 300 rpm,5h.

UV Spectroscopy study
A UV visible spectrophotometer in double beam (Elico Sl 159, India) was used to find out λ_{max} and measure dye concentration in the transport feed (donor) phase and strip (acceptor) phase solution.

FTIR study
The Structural modification and quality and consistency of the transported MG from donor phase, LM and acceptor phase were determined by Fourier Transform Infrared (FT-IR) Spectrophotometer thermo scientific NICOLET iS5 model iD using potassium bromide (KBr coated Germanium is used for beam splitting in mid infra-red and polyethylene terphthalate in far infrared

region) disc method, within the range 400-5000 cm⁻¹. The analysis of FT-IR was carried out for the samples taken from organic and aqueous phase of after extraction and stripping, respectively.

RESULT AND DISCUSSION

Effect of pH of donor phase
The effect of pH of donor phase on the transport efficiency of MG and kinetic parameters are shown in Fig. 3. Aqueous solutions containing fixed concentrations of MG dye was used in the pH ranges of 7-10±0.1 to study the transport efficiency. The transport of MG dye increased with increasing pH and research maximum at pH 9±0.1 was observed. Further increase in pH did not make any significant change. In basic condition(more than pH 9.0), nitrogen functional groups presents in the (P_{ka} 10.3) MG readily accept electron and form leuco malachite green (LMG) The electro positively of MG decreases when the pH increases beyond pH 9.0. The positive charge existing on the tertiary nitrogen ions present in MG readily move towards the negatively charged D2EHPA present in LM (P_{ka} 3.95) from a MG-D2EHPA ion pair complex. Marginal increase in flux was observed up to pH 9.0 and the flux value started decreasing beyond pH 9.0. At higher pH, passivation of OH ions on the surface of MG restricts the mobility of MG and reduces the transport rate. The maximum transport efficiency was achieved LLE at pH 9.0±0.1 [53].
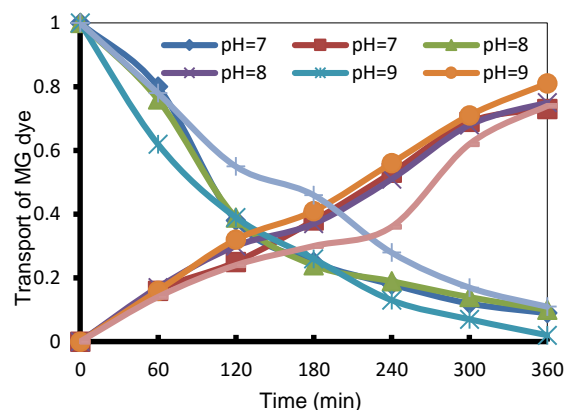

Figure 3. Effect of pH of donor phase (Experimental conditions: donor phase = 0.54×10^{-4}mol/L dye at pH 7-10±0.1, receiving phase: 7M AcOH solution, membrane organic phase : 0.21mol/L carrier in n-hexane stirring speed: 300 rpm, 5h.

Effect of dye concentration in the donor phase
The influence of MG concentration in the donor phase on the kinetics parameter and transport efficiency is presented in Table.1 and Fig 4. The dye concentration

(0.54-1.62×10⁻⁴ mol/L) in the donor phase was investigated with fixed times intervals. The feed phase concentration increases from 0.54 to 1.62×10⁻⁴ mol/L, the transport flux value decreased from ±10.80×10⁻⁴ to 2.95×10⁻⁴ min⁻¹, respectively. The similar results were obtained in BLM for the removal of metals [54]. At low concentration, the MG interacts well with D2EHPA at the donor membrane interface: hence, the transport of MG increased. Further increase in MG concentration decreases flux of MG. The first part is due to an enhancement in the influence contact between MG and D2EHPA. In addition, MG concentration in the feed phase produces higher ionic strength of the solution and molecular geometry in the donor to LM interface. This results a lower activity coefficient for MG and reduces less activity of MG⁺ to form the MG-D2EHPA ion- pair complex formed.

TABLE 1. Dye concentrations of donor phase and its kinetic parameters.

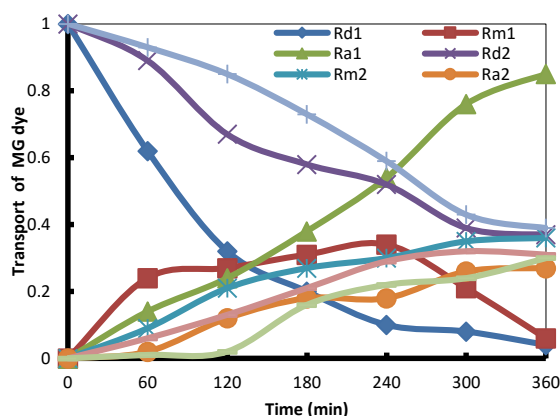| Dye concentration	$k_1 \times 10^{-3}$	$k_2 \times 10^{-3}$	R^m_{max}	max	$J_d^{max} \times 10^{-4}$	$J_a^{max} \times 10^{-4}$
(mol/L) ×10⁻⁴	(min⁻¹)	(min⁻¹)		(min)	(min⁻¹)	(min⁻¹)
0.54	2.08	4.70	0.23	307.6	−10.80	10.80
1.08	0.72	4..31	0.12	487.5	−5.00	5.000
1.62	0.41	2.63	0.13	829.9	-2.95	2.95

Figure 4. Effect of dye concentration in membrane phase (Experimental conditions: donor phase = 0.54×10⁻⁴ -1.62mol/L dye at pH 9±0.1, receiving phase: 7M AcOH solution, membrane organic phase: 0.24mol/L carrier in n-hexane stirring speed: 300 rpm, 5h.

Effect of carrier concentration in membrane phase

In the BLM transport, carrier D2EHPA plays the role of a phase transfer catalyst. It forms a transportable complex diffusing in the membrane and then releases the analyte into the receiving phase. The effect of the concentration of D2EHPA (P_{ka}=3.95, M=322.43(g/mol), density=0.976g/mL, solubility in water<0.01 at 27ºC in the membrane phase, kinetic parameters and transport efficiency of MG dye were studied at five different initial concentrations at fixed stirring speed of 300 rpm. The carrier concentration in organic (membrane) phase showed significant effect on the dye ion pair –complex transport across the liquid membrane. The results are predicted in Table 2. It is obvious equations 3 and 5 that the flux is oppositely signing values related to the carrier concentration. Transport of MG through bulk liquid membrane was improved with an increase in D2EHPA concentration up to 0.12-0.30 mol and further increase in concentration did not make any significant change. At lower carrier concentration, the interface between the feed and membrane is not saturated by the carrier. Similar results were also reported [55]. Therefore, the transport of dye increases with increases the carrier concentration. Hence, 0.24 mol/L of D2EHPA in hexane was fixed for further studies.

TABLE 2. D2EHPA carrier concentrations of organic membrane phase and it's kinetic parameters.

D2EHPA concen×10⁻¹	$k_1 \times 10^{-3}$	$k_2 \times 10^{-3}$	R^m_{max}	t_{max}	$J_d^{max} \times 10^4$	$J_a^{max} \times 10^4$
(M)	(min⁻¹)	(min⁻¹)		(min)	(min⁻¹)	(min⁻¹)
1.2	0.97	2.39	0.22	632.19	−5.34	5.34
1.5	1.41	3.20	0.23	463.17	−7.05	7.05
1.8	1.85	3.83	0.25	372.19	−9.25	9.25
2.1	1.99	3.87	0.23	367.50	−9.15	9.15
2.4	2.08	4.70	0.23	308	−10.8	10.80

Effect of nature of diluents in organic membrane phase

The nature of organic solvents such as n-hexane, toluene, xylene and benzene on the MG transport efficiency and kinetics was studied detail. The results for the transport

of MG through the BLM in different low density solvents and kinetic parameters are presented Fig. 5 and Table 3. The polarity and density of the solvents are important parameters for the stability and transport property of BLM. The characteristics of the diluents are predominantly responsible for the solubility of the complex formed and diffusion co-efficient of solvent. The MG transport and kinetic parameters in different solvents depends on many factors such as distribution coefficient of the complex and physicochemical properties Table.4. The maximum transport of MG was observed in the presence of hexane when compared to toluene, xylene and benzene. The MG transport efficiency decreased in the order of hexane > toluene > xylene > benzene.
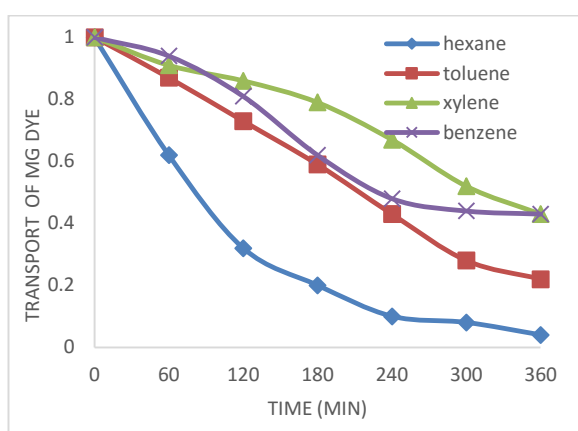

Figure 5. Effect of the nature of diluents in organic membrane phase (Experimental conditions: donor phase = 0.54×10^{-4} mol/L dye at pH 9 ± 0.1, receiving phase: 7M AcOH solution, membrane organic phase: 0.21mol/L carrier in n-hexane, xylene, benzene, toluene, stirring speed: 300 rpm, 5h.

TABLE 3. Effect of different solvents in the transport of MG dye and its kinetic parameters.

Type of solvent	$k_1 \times 10^{-3}$	$k_2 \times 10^{-3}$	R^m_{max}	t_{max}	$J_d^{max} \times 10^{-4}$	$J_a^{max} \times 10^{-4}$
	(min^{-1})	(min^{-1})		(min)	(min^{-1})	(min^{-1})
Benzene	0.70	2.92	0.16	642.9	-4.4	4.48
Xylene	1.00	4.59	0.14	423.1	-6.5	6.54
Toluene	1.68	4.62	0.20	344.6	-9.4	9.41
Hexane	2.08	4.70	0.23	307.6	-10.8	10.80

Benzene displayed least transport efficiency even at extended transport time due to high solubility in water and dielectric constant. Similarly, the transport of MG using xylene and toluene showed less transport property when compared to hexane. The latter is a general basic property of solvent and mainly depends on the viscosity of solvent [56]. Hexane showed remarkable transport efficiency due to its low viscosity of hexane ($\eta = 0.31$),

which leads to increase in the rate of MG transport donor to LM and LM to acceptor phase. Hence, hexane was chosen as diluent for the studies.

TABLE 4. Characteristics of different solvents and physic- chemical properties.

Types of Solvent	ϵ_0	μ(D)	η(cP)	B.P. (LC)	d (g/mL)	Solubility in water
Hexane	2.02	0.08	0.31	068.7	0.655	0.001
Toluene	2..24	0.36	0.59	111.0	0.870	0.051
Xylene	2.26	0.00	0.81	138.5	0.864	0.018
Benzene	2.28	0.00	0.61	080.1	0.877	0.430

ϵ_0=Dielectric constant; μ= Dipole moment; η=Viscosity (cP at 20ºC); d= density (mg/L)

Effect of nature and concentration of the receiving phase

The transport of dye across a hexane-D2EHPA membrane phase strongly depends on the nature and concentration of stripping phase present on the receiving side of the membrane. It is apparent that many aqueous stripping solutions such as CH_3COOH, $C_2H_2O_4$, HNO_3, H_2SO_4 and HCl were tested for the transport of dyes. Among these, 7M acetic acid has shown to be the most efficient for stripping solution when compared to $C_2H_2O_4$, HNO_3, H_2SO_4 and HCl. The effect of acetic acid concentration on the flux was also studied and it was found that flux remained practically unchanged to 10.80×10^{-4} min^{-1} on keeping the donor basicity at 1×10^{-2} M $NaHCO_3$ and 0.54×10^{-4} mol/L initial concentration of MG dye solution as given in Table 5. A range of acetic acid concentration (4-7M) was studied indicated an increase in stripping efficiency with increasing molar concentration of acetic acid. The maximum efficiency was observed at 7 M concentration and beyond this there was no significant change observed.

TABLE 5. Effect of acetic acid concentrations of receiving phase and its kinetic parameters.

AcOH (M)	$k_1 \times 10^{-3}$	$k_2 \times 10^{-3}$	R^m_{max}	t_{max}	$J_d^{max} \times 10^{-4}$	$J_a^{max} \times 10^{-4}$
	(min^{-1})	(min^{-1})		(min)	(min^{-1})	(min^{-1})
4	1.10	3.21	0.19	512.99	-6.27	6.27
5	1.32	3.83	0.19	431.23	-7.52	7.52
6	1.92	3.87	0.24	354.30	-9.79	9.79
7	2.08	4.70	0.23	307.65	-10.80	10.80

Effect of stirring rate and time

Gentle agitation or stirring in donor and acceptor phases can facilitate the transport of MG dye through BLM. The effect of stirring speed of aqueous and organic phase in the range of 100-300 rpm on the MG dye transport efficiency and kinetic parameters were studied. Maximum efficiency of MG transport leads to higher values of entrance and exit flux. Accordingly, the rate of

transport of MG from donor phase to LM phase and LM phase to acceptor phase increased with increasing stirring rate. Stirring of feed and strip is necessary to minimize concentration polarization in the donor side and provide better penetration of MG in to the strip. At low stirring rates the transport of MG decreased. There was no significant change in transport efficiency beyond at 300 rpm (Table 6). Hence, 300 rpm was maintained for all the experiments. At high stirring rates, mixing of donor and receiving phase occurs.

Mechanism of uphill transport
The mechanism of extraction and stripping of dye has been described by Eqs. 16 and 17 as follows:
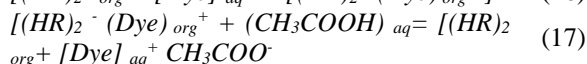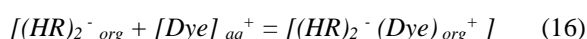
$$[(HR)_2^-{}_{org} + [Dye]_{aq}^+ = [(HR)_2^- (Dye)_{org}^+] \quad (16)$$

$$[(HR)_2^- (Dye)_{org}^+ + (CH_3COOH)_{aq} = [(HR)_2_{org} + [Dye]_{aq}^+ CH_3COO^- \quad (17)$$

TABLE 6. Effect of stirring rate in the transport of MG dye and its kinetic parameters.

Stirring Rate (rpm)	$k_1 \times 10^{-3}$ (min^{-1})	$k_2 \times 10^{-3}$ (min^{-1})	$R_m max$	t_{max} (min)	$J_d^{max} \times 10^4$ (min^{-1})	$J_a^{max} \times 10^4$ (min^{-1})
100	1.02	2.40	0.23	617.5	-5.5	5.5
200	1.42	2.86	0.24	479.8	-7.1	7.1
300	2.08	4.70	0.23	307.7	-10.8	10.8

Based on the results obtained dye transported across the Di (2-ethyl hexyl phosphoric acid - BLM system can be explained as follows: (i) The transport of donor phase to LM phase: cationic MG dye transport through organic membrane is facilitated by the presence of D2EHPA, which forms dimeric anionic carrier and under goes cation exchange reaction leading to formation of ion pair complex $[(HR)_2^- (Dye)_{org}^+]$. (ii)It has been observed that MG cationic dye can form an ion-associate by the electrostatic attraction of oppositely charged D2EHPA anionic carrier is very fast.(iii) The resulting neutral ion paired complex is favourably distributed into the LM phase. (iv) At the LM phase-strip interface in basic condition, the anionic carrier is distorted into neutral Di (2-ethyl hexyl) phosphoric acid. (v) The anionic carrier D2EHPA diffuses back across the membrane to the feed solution membrane interface where the cycle starts again.

UV Spectral studies
The UV absorbance spectrum of MG showed a strong absorption band maximum at 618 nm in the blue and green region of the visible spectrum and transmits wavelength below 618 nm, bestowing dark blue green color λ_{max} value of MG basic medium of donor, membrane phase, acidic medium of receiving phase were observed at 618, 626 and 617 nm. Only slight change in absorption was observed for MG analysed in the three phases clearly indicating that the structure of MG molecule is intact. An increase in absorbance with bathochromic shift (red shift) spectral shift was observed in donor phase to membrane phase increasing polarity intense of hexane in D2EHPA fully occupied in organic membrane phase of MG dye solution due to the solvent effect. A reduction in the absorbance with hypsochromic shift (blue shift) spectral shift was observed in membrane phase to receiving phase decreasing acetic acid phase. This blue shift results from hydrogen bonding which lowers the energy of the n orbital. This spectral study shows that the MG dye was recovered can be reused [57].

Spectral studies of FTIR technique
The FTIR spectra of MG dye presents several bands in the region 600-4200 cm^{-1}, which can be ascribed to donor, LM and received phase as shown in Fig. 6. The donor MG dye showed the specific peaks for the mono substituted benzene rings and para-substituted benzene rings which supporting to the peak at 1589 cm^{-1} for C=C stretching of aromatic skeletal vibration. The band at 1720 cm^{-1} corresponds to the carbonyl(C=O) stretching vibrations in carboxylic acids and peaks at 920 , 825 and
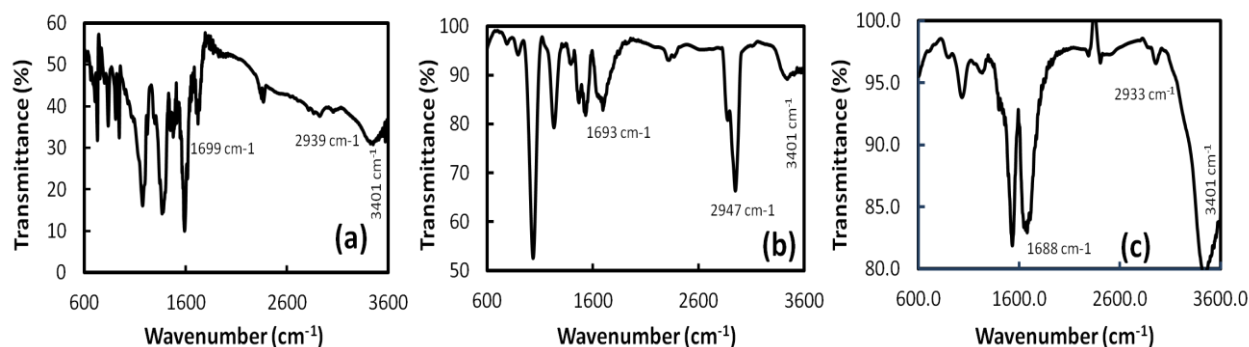

Figure 6. a= MG in donor phase, b =MG in membrane phase, c = MG in received phase

704 cm^{-1} are characteristics of C-H bond located close to N in the aromatic ring . The located at 1375 cm^{-1}could be described to C-H bonding in the CH$_3$-N and peak at 1172 cm^{-1} attributed to the presence of the C-N bond.   The specific intense bond at 3435 cm^{-1} can be assigned to the N-H bond.

Characteristic changes were observed in the FTIR spectrum of MG dye after transport. The results indicated that some peaks were shifted or disappeared, and new peaks were also detected. A specific new band appears at 1350 cm^{-1} which can be assigned to the stretching vibration of P=O bond in organic membrane phase and other band at 1029 cm^{-1} can be assigned to the aromatic stretching vibration of P-O-C bond in organic membrane phase. These changes observed in the spectra clearly indicated that at the end of the reaction, structure of MG was not affected by the transport of different phases. These results further support the observation made in UV-Visible absorbance spectrum analysis.

TABLE7. Physical and chemical properties MG present in textile effluent

Parameters	Synthetic dye bath	Textile dye bath
pH	7.0-9.0	7.0-9.0
λ_{max}(nm)	618	617-620
Color	Deep blue green	Deep blue green
Nature of dye	basic dye	basic dye
Chloride(mg/L)	1400	1020
Biochemical Oxygen Demand (mg/L)	538	325
Chemical Oxygen Demand (mg/L)	836	450
Total Suspended Solids (mg/L)	120	109
Total Dissolved Solids (mg/L)	3100	2689
Total Kjeldahl Nitrogen (mg/L)	89	79

Application of developed BLM for textile waste water
The wastewater from local industry was selected for testing the applicability of the developed BLM system. Dye wastewater, containing mixed of MG obtained from a small scale dyeing local industry was used in the study. The assay of wastewater is presented in Table 7. The dye wastewater was diluted by 10 times to obtain a similar concentration of synthetic dye used for the screening studies and almost identical transport efficiency was for industrial wastewater too.

CONCLUSION

The present study demonstrates the transport of MG through BLM using D2EHPA in hexane from textile aqueous solution. The results reveal that D2EHPA as an excellent carrier for the transport of MG through BLM. The rate constants such as transport (k1), and receiving (k2) were determined using two consecutive first order irreversible reactions. The kinetic parameters such as R$_m^{max}$, t$_{max}$, J$_d^{max}$, and J$_r^{max}$ were calculated on the basis of transport and receiving rate constant. The maximum

transport flux value of 10.80×10^{-4} min-1 was observed using 0.24 mol/L D2EHPA concentration in the donor phase and 7mol/L acetic acid in the receiving phase. Optimized parameter such as pH 9.0, stirring rate 300 rpm and the transport time at 300 min were maintained for all the reactions. The UV-visible and FTIR spectrometer studies confirm that functional groups were not changed in the recovered dye.

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Persian Abstract

چکیده

سیستم غشا تودی ای (BLM) ، شامل دی) -۲اتیل هکسیل (اسید فسفریک (D2EHPA)) به عنوان یک استخراج کننده برای انتقال رنگ malachite سبز (MG) از پساب نساجی مورد استفاده قرار گرفت. D2EHPA موجود در n-hexane یک حامل موثر، کارامد و با گزینش پذیری بسیار بالا برای انتقال رنگ (MG) ازسیستم غشا توده ای است. بیشترین انتقال ۸۸ درصد در غلظت ۰،۲۴ مولار D2EHPA در فازغشا و غلظت ۷ مول از اسید استیک در فاز دریافت کننده پس از ۳۰۰ دقیقه مشاهده شد. تاثیر پارامترهای موثر بر انتقال رنگ MG مانند pH و غلظت رنگ، غلظت استخراج کننده در فاز غشا، ماهیت حلال آلی، ترکیب فاز دریافت کننده، سرعت اختلاط و پارامترهای سینتیک رشد بررسی شد. K1و k2 برای واکنش برگشت ناپذیر مرتبه اول برای انتقال رنگ MG از فاز آبی، فاز BLM و (BLM) به فاز پذیرنده استفاده شد. تجمع MG در فاز BLM و گام نرخ کنترل در شرایط مختلف نیز مورد بررسی قرار گرفت. در نهایت غشا به صورت موثری برای انتقال رنگ MG از پساب نساجی استفاده شد.