Recovery and Reuse of Malachite Green Using O-Chlorobenzoic Acid Through Bulk Liquid Membrane Technique

P.Jahfar Ali[a*], G. Muthuraman[b]

a-Department of Chemistry, The New College, University of Madras, Chennai, India
b-Department of Chemistry, Presidency College, University of Madras, Chennai, India

ABSTRACT

The textile industry consumes large amounts of water and produces wastewater heavily contaminated with dyes. Malachite Green (MG) is widely used for dyeing silk, wool, jute, leather and ceramics, but this dye has raised great concerns for its use due to its toxicity. This study gives an idea about the efficient recovery and reuse of malachite greens using o-chlorobenzoic acid by bulk liquid membrane method. Experimental conditions such as the concentration of dye, concentration of carrier, equilibrium time, the effect of pH, various stripping agents, and various diluents were investigated. Studies have shown that a dye concentration of 50 ppm, a carrier concentration of 0.15M, and the 11.5 pH of the stock solution, etc. are the optimal conditions for the extraction. Xylene was chosen as the solvent because of its lower toxicity. This study showed a maximum dye extraction of 90.72% for the above experimental conditions. The extracted dye was recovered using a 7.5 M acetic acid solution at 97% efficiency.

Key Words: Malachite Green, bulk liquid membrane technique, o-chloro benzoic acid, Acetic acid, Extraction, Carrier, Stripping.

INTRODUCTION:

From the prehistoric period, dyes are the main component that quenched the aesthetic sense of the man. The textile and leather industries produce large amounts of wastewater and these coloured wastewater streams can have a serious negative impact on both the environment and human health. Textile industries are one of the large level wastewaters producers [1] that contains organic and inorganic compounds and of them, dyes are the most important ones[2]. During the dyeing process in the textile industry, some of the dyes which are not fixed in the textiles will reach the wastewater stream. Textile wastewater streams may contain these left out dyes in high concentrations [3]. So they must be cleaned or discoloured before water is discharged or recycled.

MG is widely used in the textile industry as dyeing, in the food industry as a food coloring and food additive, medical disinfectant, and anthelmintic. It is also used as an antifungal, antibacterial, antiparasitic therapeutic agent in aquaculture and animal husbandry. Though it found enormous uses, it has been reported to cause carcinogenesis, mutagenesis, chromosomal breaks, teratogenicity, and respiratory toxicity [4]. MG, a triphenylmethane dye, is very difficult to degrade due to its synthetic origins and non-biodegradable aromatic structure. Therefore, discoloration of wastewater containing these dyes before discharging is mandatory in most countries according to environmental regulations [5].

In recent years, several techniques were reported for the removal of dyes from textile wastewater. Methods like adsorption[6,7,8], physio-chemical decolorization, membrane separation, electrochemical oxidation[9], ozonation, flocculation–coagulation [10], nanofiltration, colloidal gas aphrons[11], ultrasonic decomposition, reverse osmosis, chemical oxidation and photocatalytic processes[12], and liquid-liquid extraction [13] are some of the methods reported. Processes like integrated chemical biological degradation, solar photo-Fenton[14], and biological processes, Fenton biological treatments scheme, bulk liquid membrane technology, liquid membrane technology, sonochemical degradation, solvent extraction method, etc. are also reported[15,12].

Physical methods such as precipitation, flocculation, or adsorption using charcoal and activated carbon do not decompose pollutants, but transfer them from the liquid phase to the solid phase, causing secondary pollution or requiring regeneration, which is a costly and time-consuming process [16,17]. Chemical methods, including oxidative degradation by chlorine, hydrogen peroxide, and ozone, reductive

degradation by sodium hydrogen sulfide, photocatalysis, and electrochemical treatment require high doses of chemicals and produce large amounts of sludge and thus have proven to be expensive [18].

Among membrane technologies, liquid membranes have gained an important role in their use for separation, purification, or other analytical applications [19]. The use of liquid membranes in disposal processes has increased significantly in recent years [5]. Of great importance in membrane separation technology is that it is potentially energy-efficient and the membranes have high permeability, high selectivity [20] and have received a lot of attention recently due to their lower cost and greater flexibility [10].

Though Bulk Liquid Membrane (BLM) is one of the simplest, lowest, and most efficient types of liquid membranes among membrane technologies [21], little is known about MG removal by this method. This study explores the possibility of removing MG using BLM technology. In liquid membranes, many anionic carriers have been reported as carriers for various dyes. Compounds like D2EHPA (Di-(2-Ethylhexyl) Phosphoric Acid), TNBP (Tri-n-butyl phosphate) [22], salicylic acid [23], 2-nitrobenzoic acid [24] Tri-n-octyl amine [25], phenol [26] have been reported as anionic carriers by various researchers. Although most of these carriers are effective in removing dyes, their toxicity makes them harmful to the environment. D2EHPA are susceptible to formation of highly toxic and flammable phosphine gas in the presence of strong reducing agents such as hydrides and partial oxidation by oxidizing agents may result in the release of toxic phosphorus oxides[27] whereas phenol is a protoplasmic poison with myriad effects[28]. The European Chemicals Agency (ECHA) has classified TNBP as a category 2 cancer hazard and a suspected carcinogen [29]. Trioctyl amine (TOA) which is extensively used in metal and dyes removals is highly toxic towards Lactobacillus delbrueckii cells even at 0.1% concentration[30].This work focuses on the removal of cationic dye malachite green (MG) from wastewater using a relatively less toxic anionic carrier o-chlorobenzoic Acid [31,32] through bulk liquid membrane techniques.

2-**EXPERIMENTAL**

2.1 **Reagents**

Malachite Green, o-chloro benzoic acid (99%), Sulphuric Acid (95-98%), Acetic Acid (99%), Hydrochloric Acid (35%), Nitric Acid (99%), Sodium Hydroxide (97%), Sodium Sulphate(99%), Sodium Chloride 99.5(99.5%), Xylene(99),Benzene(99.5%), Chloroform (99%), Toluene (99.5%) etc. were obtained from Merck and of AR grade. Feed solution of Malachite Green is prepared by dissolving in distilled water and made up to 100ml. o-chloro benzoic acid was used as extractant and dissolved in xylene. Acetic acid was used as a stripping agent and sodium hydroxide and sulphuric acid were used to adjust the pH of the feed solution. The effect of salts was checked using Sodium Chloride and Sodium Sulphate.

2.2 **Apparatus**

pH meter(Elico India) was used to measure the pH of the aqueous solution. For UV measurements for the dye concentration in the raffinate and striped solution and agitation of the solution, a mechanical stirrer (REMI 1MLH, India) was utilized. FTIR spectral analysis was carried out using ThermoScientific NICOLET, (model iS5) using iD1 transmission with KBr pellets.

2.3 **PROCEDURE**

2.3.1 **Preparation of cationic dye solutions**

The cationic dye used in the present study is malachite green, in commercial purity, was purchased from Merck Chemicals, Mumbai, India, and used without further purification. The stock solution of 100mg/L was prepared by dissolving an appropriate amount of MG in 1L of deionized water. The working solutions were prepared by diluting the stock solution with distilled water in accurate proportions to give the required different initial concentrations namely 10, 30, 50, 80, and 100 ppm.

2.3.2 BLM Procedure

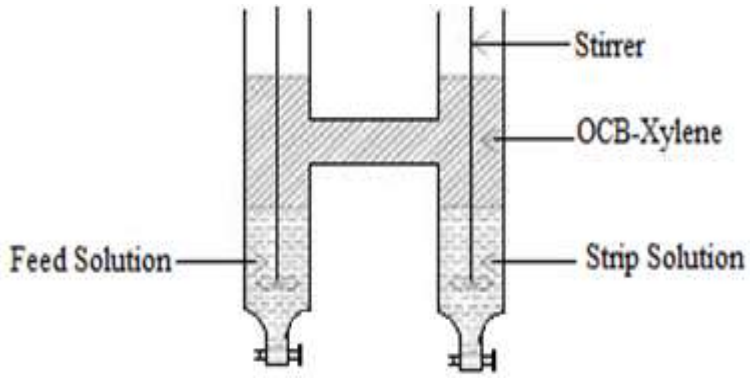

Figure 2.1 Experimental setup for H-type BLM for recovery of dyes from aqueous solution

The BLM apparatus used for the study is shown in Figure 2.1. This H-type BLM apparatus comprises three phases, two of which are aqueous, ie the feed (source) and strip (acceptor) phases, and the third phase is the membrane phase. The aqueous phase contains a dye solution (V = 280 ml) and the receiving phase contains a stripping agent (V = 280 ml). Equal volumes (280 ml) of aqueous solutions for the feed and stripping phases were placed in two compartments. The two phases were separated with an organic solvent which served as the LM phase. These three phases were mixed using a mechanical stirrer. Both aqueous solution samples were collected to measure the dye concentration. The dye concentration in the membrane phase was calculated according to the mass.

2.3.3 Reaction Kinetics and Transport of Dye in BLM

In this study, the reaction kinetic transport scheme of dye, extraction of dye, and back-extraction (stripping) of dye through a BLM were given by the following equations [33].The transport of dye can be expressed by the following equations.

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_r$$

Where C_d, C_m, and C_r represent the dye concentration in the donor, membrane, and receiving phases respectively, k_1 and k_2 are the pseudo-first apparent rate constants for the membrane entrance and exit, respectively.

Variation of dye concentration with time was directly measured in both feed (source phase, R_d) and stripping solutions (receiving phase, R_r). The dye concentration in the membrane phase was established from the mass balance. For practical reasons, reduced dimensionless mole fractions are used [34].

$$R_s = \frac{C_s}{C_{so}}, R_m = \frac{C_m}{C_{so}}, \quad R_a = \frac{C_r}{C_{so}} \qquad \text{……..2.1}$$

Where C_{so} is the initial concentration of dye in the source phase; Thus,

$$R_s + R_m + R_r = 1 \qquad \text{……..2.2}$$

The kinetic scheme for consecutive reaction systems can be described by considering the reduced concentrations as follows;

$$\frac{dR_s}{dt} = -k_1 R_s = J_s \qquad \text{……..2.3}$$

$$\frac{dR_m}{dt} = k_1 R_s - k_1 R_m \qquad \text{……..2.4}$$

$$\frac{dR_r}{dt} = k_1 R_m = J_r \qquad \text{……..2.5}$$

Where 'J' represents the flux. When $k_1 \neq k_2$, integrating Eqns. (2.3. to 2.5), gives the following equations (2.6 to 2.8) [33].

$$R_s = \exp(-k_1 t) \qquad \text{……..2.6}$$

$$R_m = \frac{k_1}{k_2 - k_1}[\exp(-k_1 t) - \exp(-k_2 t)] \qquad \text{……. 2.7}$$

$$R_r = 1 - \frac{1}{k_2 - k_1}[k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \qquad \text{……..…….. 2.8}$$

Where k_1 and k_2 values denote the apparent extraction and stripping rate constants respectively.

$$R_m^{max} = \frac{k_1}{k_2}^{-k_2/k_1 - k_2} \qquad \text{……..2.9}$$

$$t_{max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} \quad \text{……..2.10}$$

By considering the first-order time differentiation of Equations: (2.3) to (2.5) at $t = t_{max}$, the following equations are obtained

$$\frac{dR_s}{dt}|max = -k_1 \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} = J_s^{max} \quad \text{…….. 2.11}$$

$$\frac{dR_m}{dt}|max = 0 \quad \text{…….. 2.12}$$

$$\frac{dR_r}{dt}|max = -k_2 \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} = J_r^{max} \quad \text{…….. 2.13}$$

At, $t = t_{max}$ the system is in the steady-state since the concentration of dye in the membrane (R_m) does not vary with time (equation 2.9) because the penetration (J_s) and exit (J_a) fluxes are equal though of opposite signs.

$$-J_s^{max} = J_r^{max} \quad \text{……..2.14}$$

3 RESULTS AND DISCUSSION

3.1 Influence of OCB concentration

Table 3.1 Influence of OCB concentration

OCB Con. (mol/L)	k_1 (10^{-2}min^{-1})	k_2 (10^{-2}min^{-1})	R_m^{max}	t_{max}	J_s^{max} (10^{-3}min^{-1})	Jr max (10^{-3}min^{-1})
0.05	0.32	1.48	0.189	132.02	-2.09	2.09
0.075	0.48	1.36	0.199	118.34	-2.72	2.72
0.1	0.79	1.32	0.278	96.86	-3.67	3.67
0.125	1.16	1.3	0.396	81.39	-4.51	4.51
0.15	1.85	1.27	0.439	64.86	-5.57	5.57
0.175	1.24	1.29	0.361	79.06	-4.65	4.65

(Experimental conditions: Source phase =140 mL of 80 mg/L MG, receiver phase = 140 mL of 7.5 mol/L acetic acid, diluent = xylene, stirring speed = 200 rpm, pH 11.5±0.1 *and transport time = 190 min*).

Since extraction of a dye is dependable on the concentration of carriers, the effect of carrier dosage was examined by adding o- chlorobenzoic acid (OCB) with various concentrations (0.05 M - 0.2 M) to the malachite green solutions. The result shown in table 3.1 indicates that the transport rate k_1 of MG increased by increasing the concentration of OCB and peaked at 0.15 M. An additional increase to the concentration caused turbidity which intern caused a depletion in the extraction and therefore 0.15M was chosen as carrier concentration for the rest of the BLM experiment.

3.2 Influence of pH on Source phase

Table 3.2 Influence of pH on Source phase

pH	k_1 (10^{-2}min^{-1})	k_2 (10^{-2}min^{-1})	R_m^{max}	t_{max}	J_s^{max} (10^{-3}min^{-1})	Jr max (10^{-3}min^{-1})
8	0.590	1.26	0.240	113.25	-3.02	3.02
9	0.815	1.57	0.256	86.84	-4.02	4.02
10	1.520	1.78	0.339	60.73	-6.04	6.04
11	1.74	1.96	0.346	54.11	-6.79	6.79
11.5	1.85	1.27	0.439	64.86	-5.57	5.57

(Experimental conditions:Source phase =140 mL of 80 mg/L MG, carrier= 0.15OCB, receiver phase =140 mL of 7.5 mol/L acetic acid, diluent = xylene, stirring speed = 200 rpm and transport time = 190 min).

pH is an important factor to be studied, for being the textile effluents are mostly basic or acids [3]. The Influence of pH on the extraction of MG in BLM methods was studied and is shown in table 3.2. Since the acidic condition does not favor the extraction [10]; the pH of the source phase in the BLM process was maintained between 7 to 14 pH ranges to check the influence of pH. The pH was adjusted using 2N Sodium Hydroxide and 1N Sulphuric Acid. Extraction increased as pH increased from 7 and the maximum value

attained at a pH of 11.5. After this pH, the colour of MG changed and therefore pH 11.5±0.1 was taken as the optimal pH for the process. Lower extraction of MG at acidic pH is may be due to the presence of the excess H^+ ions which are competing with dye cations [35]. It is known that pH can affect the structural stability of MG and consequently its colour intensity, the decrease of extraction after 11.5±0.1 may be due to the structural changes of MG molecules at high pH [36].

3.3 Influence of initial MG concentration

The effect of initial dye concentration on the extraction efficiency of MG in BLM was tested. MG Dye with 50ppm, 80ppm, and 100 ppm was subjected to BLM and the results are tabled (Table 3.3). It is clear from the result that the transport rate of dye is inversely proportional to the dye concentration. As dye concentration increased the value of k_1 and R_m^{max} also decreased. This may due to at higher MG concentration, the carrier molecules may not be sufficient to interact with dye molecules at the source/membrane interface resulting in the decrease of transport of MG [26].

Table 3.3 Influence of initial MG concentration

MG Concent-ration (Mol/L)	k_1 ($10^{-2}min^{-1}$)	k_2 ($10^{-2}min^{-1}$)	R_m^{max}	t_{max}	J_s^{max} ($10^{-3}min^{-1}$)	J_r max ($10^{-3}min^{-1}$)
50	2.42	1.57	0.45	50.9	-7.0	7.0
80	1.63	1.15	0.426	74.12	-4.9	4.9
100	1.41	1.19	0.399	77.11	-4.75	4.75

(Experimental conditions: Carrier= 0.15 OCB, Receiver phase = 140 mL of 7.5 mol/L acetic acid, diluent = xylene, stirring speed = 200 rpm, pH 11.5±0.1 *and transport time = 190 min*).

3.4 Influence of Diluents

Table 3.4 Influence of Diluents

Diluents	k_1 ($10^{-2}min^{-1}$)	k_2 ($10^{-2}min^{-1}$)	R_m^{max}	t_{max}	J_s^{max} ($10^{-3}min^{-1}$)	J_r max ($10^{-3}min^{-1}$)
Xylene	1.85	1.27	0.439	64.86	-5.57	5.57
Benzene	1.79	1.21	0.442	67.52	-5.35	5.35
Toluene	1.89	1.29	0.44	63.66	-5.67	5.67
Cholroform	------	------	------	------	------	------
Hexane	------	------	------	------	------	------

(Experimental conditions: Source phase =140 mL of 50 mg/L MG, carrier= 0.15OCB, receiver phase =140 mL of 7.5 mol/L acetic acid, stirring speed = 200 rpm, pH 11.5±0.1 *and transport time = 190 min*).

The extraction is carried out using different diluents for OCB. Solvents like xylene, toluene, benzene, hexane, etc. (Table.3.4) were tested. Except for hexane and chloroform, all other diluents showed more than 90% extraction capacity for o-chlorobenzoic acid at pH 11.5. Toluene and hexane cannot remove the dye because of their less polar structure [37], and all other diluents used have a dipole moment and therefore tend to extract well. Xylene is the diluent of choice because it is less harmful than other diluents for OCB [38]

3.5 Influence of time on extraction and stripping

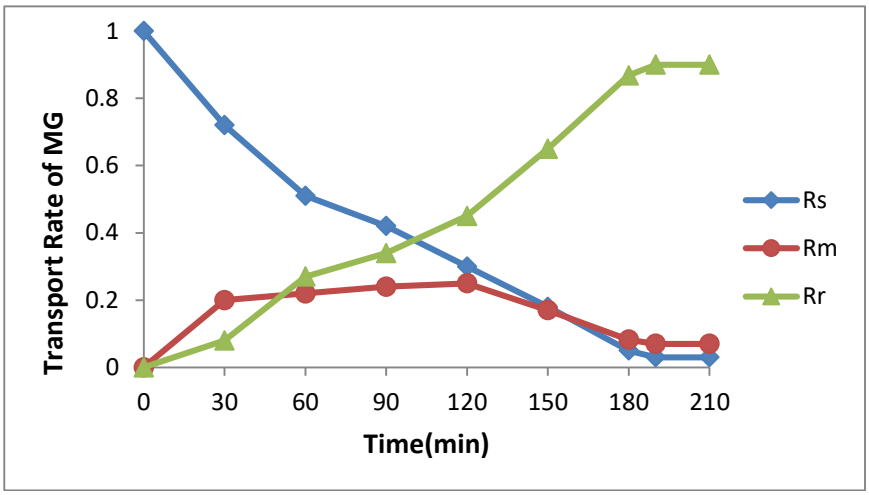

Figure 3.1 Influence of time on Extraction and stripping

(Experimental conditions: Source phase =140 mL of 50 mg/L MG, carrier= 0.15OCB, receiver phase =140 mL of 7.5 mol/L acetic acid, diluent = xylene, stirring speed = 200 rpm, pH 11.5±0.1)

The effect of contact time on extraction and stripping was experimented using 0.15 mol / L OCB in the membrane phase, 50 mg / L MG in the source phase, 7 M / L acetic acid in the receiver phase, and an agitating speed of 200 rpm at different time intervals. The investigated results put in Figure 3.1 show that the concentration of dye in the source phase (Rs) continuously decreased as time increased, it indicates that the dye has been successfully taken from the source phase to the membrane phase. The concentration of dye at membrane phase (Rm) increased gradually at first then decreased. The maximum transport speed (Rr) for stripping was observed at 190 minutes. Therefore, 190 minutes was recommended for further study.

3.6 Influence of receiving phase concentration

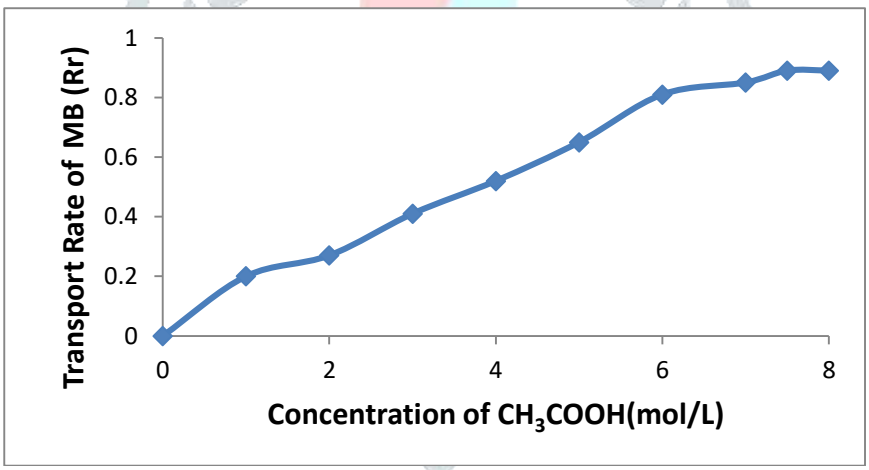

Figure 3.2 Influence of acetic acid concentration

(Experimental conditions: Source phase = 140 mL of 50 mg/L MG, diluent = xylene, stirring speed = 200 rpm, pH 11.5±0.1 and transport time = 190 min).

Since it was found that only acetic acid showed to have an extraction tendency for OCB-MG [11], acetic acid having a concentration ranging from 1M to 8M was used to control the maximum stripping percentage. As the acetic acid concentration increased, the transport speed for extraction and stripping also increased. When the stripping rate increases, OCB may be free to transport the dye molecules from the source phase and which intern may increase the extraction rate. Acetic acid showed a maximum stripping value of 97 % at a concentration of 7.5 M. The values are given in figure 3.2.

3.7 Influence of stirring speed

The effect of the mixing speed of both the source phase and the receiving phase was investigated to minimize the thickness of the aqueous boundary layer in the source and receiving phases. The stirring rate Vs time is shown in figure 3.3. At a higher mixing speed, it can be seen that the transport increases rapidly.

At a stirring speed of 250 rpm, the transport of the dye from the source to the receiving phase was completed in 190 minutes. This is mainly due to the increased contact between the aqueous and membrane phases.

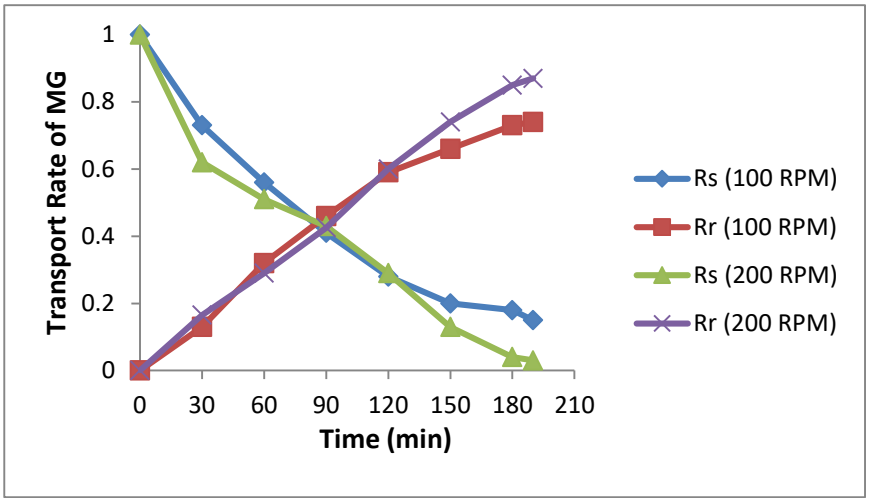

Figure 3.3 Influence of stirring speed

(Experimental conditions: Source phase =140 mL of 50 mg/L MG, receiver phase = 140 mL of 7.0 mol/L acetic acid, diluent = xylene, pH 11.5±0.1 *and transport time = 190 min*).

It is necessary to mix the feed and the strip to minimize concentration polarization on the feed side and to ensure better penetration of the dye into the strip. Accordingly, MG transport decreased at low mixing speeds. Both the extraction rate and the stripping rate decrease at a mixing rate of more than 250, because the solutions of the starting and receiving phases are mixed with a higher mixing speed [39]. Therefore, 250 rpm was chosen as the optimum mixing speed for the BLM-MG technique.

3.8 Reusability of the organic phase (OCB/Xylene)

Since BLM uses large amounts of reagents, the ability to reuse the organic phase is extremely important. To test the feasibility of reusing the membrane phase, BLM experiments were repeated using the used organic phase under optimal conditions. Figure 3.4 shows that the organic phase can be used for more than 5 times since there is no significant reduction in the extraction efficiency of these organic phases when used in 5 consecutive procedures. Although the result is satisfactory, the result is much smaller than the solvent extraction method. This low efficiency may be due to the leakage of OCB molecules into the receiving phase by continuous mixing of the receiver / organic phase [23].

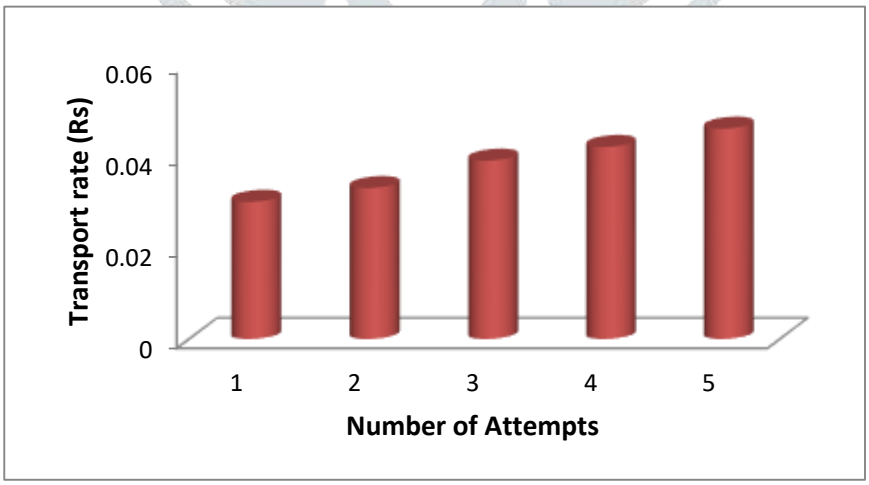

Figure-3.4 Reusability of the organic phase (OCB/Xylene)

(Experimental conditions: Source phase =140 mL of 50 mg/L MG, receiver phase = 140 mL of 7.0 mol/L acetic acid, pH 11.5±0.1 *and transport time = 190 min*).

FT-IR Spectral Studies

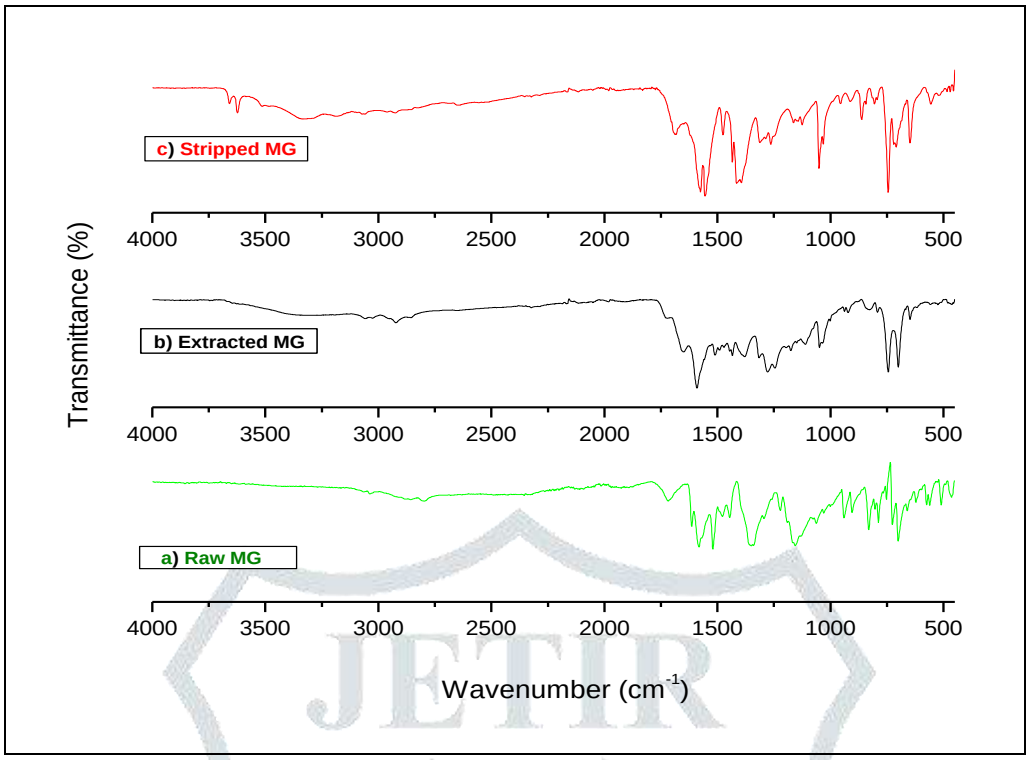

Figure 3.5 IR spectra of a) Raw MG Dye, b) Extracted MG dye, and c) Stripped MG Dye

Spectral data of a compound will tell you the exact bonds and functional groups present in the particular compound. Figure 3.5 represents the FT-IR spectrum of Raw, extracted, and stripped MG dye.

Figure 3.5 a) shows the important peaks present in the raw MG dye. Frequencies 2919 cm^{-1} and 700 cm^{-1},744 cm^{-1} represent C-H (aromatic) and C=C (aromatic) respectively [40].A frequency of 1441cm^{-1} represents C-N-CH_3 of dye.

Figure 3.5 b) gives the different peaks exhibited by the extracted dye. A frequency of 1590 cm^{-1}represents O=C of OCB. The absence of frequencies at around 3000 - 3500 cm^{-1} and 1584 cm^{-1} implies that the OH group of the OCB is missing which indicates that the bond between MG dye and OCB is formed through the carboxylate oxygen of OCB. Also, the missing of a frequency at 1584 cm^{-1} indicates that oxygen is bonded with the N of C=N.

Figure 3.5 (c) represents the FT-IR spectrum of stripped dye. When comparing the frequencies of (b) and (c), the presence of frequency at 1584 cm^{-1} indicates that the bond between N of MG dye and oxygen of OCB is broken and the C=N bond which was in the raw dye is appeared again clearly shows that extracted dye is stripped from the OCB. Moreover frequencies at 1689cm^{-1} and 3623cm^{-1}, 3333cm^{-1} which represents C=O of carboxylic acid and OH group respectively; prove that acetic acid is acted as a strippant.

3.10 Proposed mechanism for the transport of MG through BLM

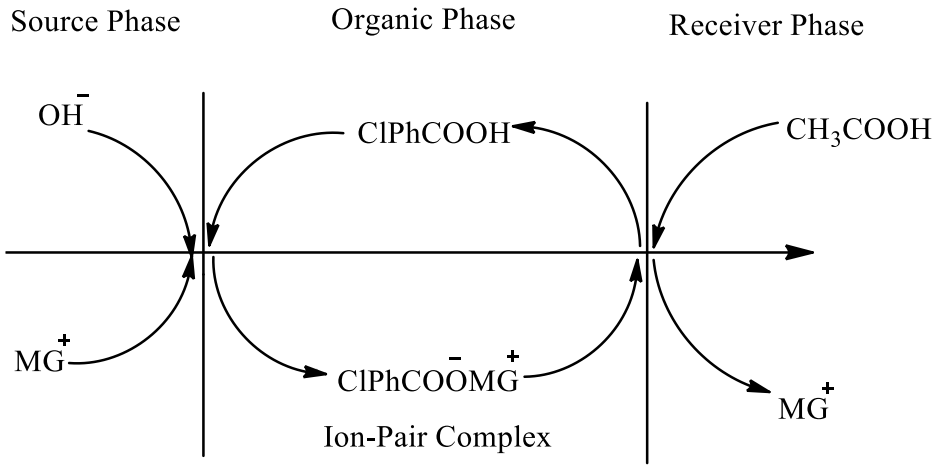

Figure 3.6 Proposed mechanisms for the transport of MG through BLM

The proposed mechanism of transport of MG through the OCB-BLM system based on the above experimental observations can be explained as follows. The schematic diagram is shown in Figure 3.6.

- ✓ At the source/liquid membrane interface, OCB may get deprotonated in the basic condition and form an ion pair with cationic MG [OCB^-MG^+].
- ✓ This ion pair may travel through the organic membrane and reaches the liquid membrane /receiver interface.
- ✓ At the liquid membrane /receiver interface the ion pair [OCB^-MG^+] gets dissociated into neutral OCB + MG^+ by the absorption of a proton from the acetic acid present in the receiver phase.
- ✓ The neutral carrier (OCB) diffuses back to the membrane/source-interface where the cycle repeats.
- ✓ Again at the liquid membrane /receiver interface, the dissociated MG^+ will form an ion pair with CH_3COO^-[$CH_3COO^-MG^+$] and diffuse into the receiver phase.

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