APPLICATION OF LIQUID MEMBRANE IN REMOVAL OF DYES

Thesis Submitted

by

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Rourkela

<u>CERTIFICATE</u>

*This is to certify that this thesis entitled as, "**APPLICATION OF LIQUID MEMBRANE IN REMOVAL OF DYES**" submitted by Ms. B LITUSHA PATRO (112CH0083) in partial fulfilment for the requirements for an award of Bachelor in Technology Degree in Chemical Engineering at National Institute of Technology, Rourkela (Deemed University) is an authentic work completed by her under my guidance and supervision and this work hasn't been submitted anywhere else for any degree.*

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ABSTRACT

Textile industries are one of the major sources of residual dyes and organic pollutants that are released into natural water resources. Treatment of this wastewater and its recycling is essential because of higher grades of impurities in finishing and dyeing processes (i.e. dyes and their by products for example pigments, dye intermediates, auxiliary chemicals and heavy metals, etc.). Dyeing process causes a loss of 10-25 % of the textile dyes, out of which two to twenty percent are removed as aqueous effluents causing harm to various environmental parts. Removal of effluents constituting dyes inside water bodies are unwanted due to their colour, & because many of them breakdown into products which are poisonous. To re-use the materials obtained from the waste products, new technologies have risen into popularity causing the Liquid membrane techniques to evolve over other separation techniques due to its high selectivity and recovery, increased fluxes, and reduced investment and operating cost. It combines extraction and stripping in a single unit operation. Removal of dyes by liquid membranes using organic solvents was found to be toxic and costlier. So vegetables oils are used instead of organic solvents in liquid membranes for extraction of different types of dyes and different parameters are optimized based on the extraction percentage.

This thesis focuses on the extraction of Methylene Blue (MB), a cationic dye using simple BLM separation technique from its aqueous phase. The feed phase was aqueous solution of Methylene Blue (MB) and the strip phase was Sulphuric Acid solution. Solvent chosen was Sunflower Oil for the liquid/organic membrane phase and phenol acted as carrier for this study. A detailed two phase equilibrium study was done which was then followed by three phase study. Effect of various parameters like equilibrium time, stirring speed, carrier concentration, feed phase pH, strip phase concentration, were all studied to find out the most optimum working condition for maximum extraction and recovery. In the above mentioned set up, 95% MB extraction was achieved from feed phase to organic phase whereas only 90% of MB was recovered from membrane/organic phase to the receiving phase. Optimum vlue for strip phase concentration parameter was 1.25 N and similarly for carrier concentration 1M of carrier is most favourable for the transport process when optimum 12 pH of feed phase if maintained increases the efficiency. Even stirring speed conditions affects the extraction and recovery to great extent and when all the three phase are stirred at 300 rpm it gives the best results.

Keywords: Methylene Blue, Bulk liquid membrane, Coupled transport, Vegetable Oils

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NOMENCLATURES

MB	Methylene Blue
BLM	Bulk Liquid Membrane
ELM	Emulsion Liquid Membrane
SLM	Supported Liquid Membrane
ILM	Immobilized Liquid Membrane
LLE	Liquid-Liquid Extraction
Cd	Cadmium
Pb	Lead
Na_2SO_4	Sodium Sulphate
D2EHPA	di-(2-ethylhexyl) phosphoric acid
Cu	Copper
Hg	Mercury
RB	Rhodamine B
CV	Crystal Violet
MV	Methyl Violet
CH_3COOH	Acetic Acid
H_2SO_4	Sulphuric Acid
UV	Ultra Violet
Min	Minute
%E	Percentage Extraction
%R	Percentage Recovery
HCl	Hydro Chloric Acid
ppm	Parts Per Million
Abs.	Absorption
Conc.	Concentration

1. <u>INTRODUCTION</u>

1.1 Liquid Membrane

A membrane acts as a semi permeable barrier between two phases that ensures separation to take place and prevents contact between the phases. They simply block the movement of molecules across the membrane in a particular manner. Membrane Separation associated is rate process which is performed by driving force and not by equilibrium of the two phases.

A liquid membrane (LM) is an immiscible liquid mainly which acts as a membrane or a semi permeable barrier between the two aqueous phases (gas or liquid) and can be in supported or unsupported form. It causes solute diffusion or transport of components from one side to other where driving force is concentration gradient or chemical potential gradient between the phases. Various solutes have different ranges of solubility and different diffusion coefficient in a liquid. These two factors multiplied measures permeability of liquid membrane. Diffusion coefficients of liquids are much greater in values compared to polymers giving large flux facilitating separation [1]. In 1968 when the first patent on liquid membrane was published the concept of liquid membrane grew more rapidly [2].
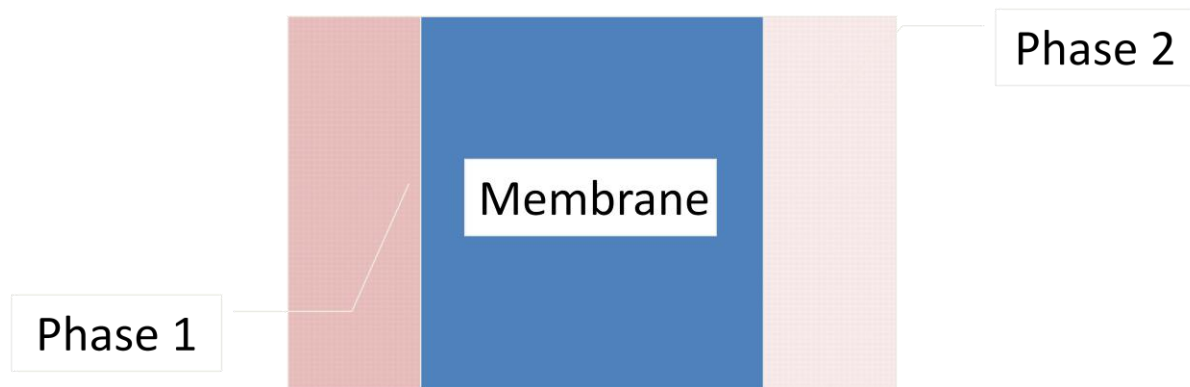
Figure 1.1: Schematic diagram of liquid membrane

LM selection depends on various factors:

1. Its solubility in water should be as low as possible
2. Selective solvent to be separated
3. Fugacity (when toxic) : low
4. Viscosity : low to obtain high diffusion coefficient

Advantages [3]:

1. LM combines stripping and extraction operations in single unit operation referred as Pertraction
2. Follows mass transfer at non-equilibrium state
3. Has higher recovery and selectivity, greater fluxes
4. Reduces the operating and investment costs (low energy consumption)

Disadvantage:

1. Lacks long term stability (evaporates or dissolves).

The most important properties of liquid membrane are:

1. Selectivity nature of the liquid membrane
2. Large flux for solutes
3. Mass transfer can take place on carriers
4. Great mechanical and chemical strength under working condition.
5. Low fouling liability under working environment.
6. Very Cost effective and no expensive pre treatment is required.
7. Can be processed in a continuous manner.

Application:

1. Facilitated transport of gases: Oxygen, Carbon Dioxide, Carbon Monoxide, Hydrogen Sulphide, Olefins, Nitric Oxide, etc
2. Metal ion separations
3. Control of heavy metals pollutants
4. Fermentation products separation
5. Citric and acetic acid transport
6. Amino acid extraction

1.2 Mechanism

1. Diffusion of solute across the boundary layer in the source/feed solution
2. Sorption at feed phase/ organic or liquid membrane interface
3. Diffusion across the boundary layer on the source or the feed side
4. Transport through the liquid membrane
5. Diffusion across boundary layer on the strip or receiving phase
6. Desorption at liquid or organic membrane/ receiving or strip solution interface
7. Diffusion across boundary layer on the strip or the receiving side

The effectiveness and selectivity of separation of solute species through the organic phase can be increased by using carriers in the LM phase. These mobile substances enhance the separation through the membrane phase by making a complex with required solute species. This whole complex formation process is referred as Carrier facilitated transport. These carriers are characterized by:

1. Quick bonding and release of particular substances
2. Ability to selective and reversible binding of a component in the solution
3. Non-binding with a solvent
4. Lack of ability to coalesce and are intoxicate

1.3 Types of Liquid Membrane

1. Bulk Liquid Membrane [BLM]
2. Emulsion liquid membrane [ELM]
3. Supported liquid membrane [SLM] or immobilized liquid membrane [ILM]

1.3.1 Bulk Liquid Membrane [BLM]

BLM is simple and made of source and receiving phases separated by a organic phase. This organic phase is composed of a carrier dissolved in a solvent. A magnetic stirrer is used which rotates at low speed in 100 to 300rpm to enhance performance rate. These are of two types: U-tube cells and Tube within a shell.
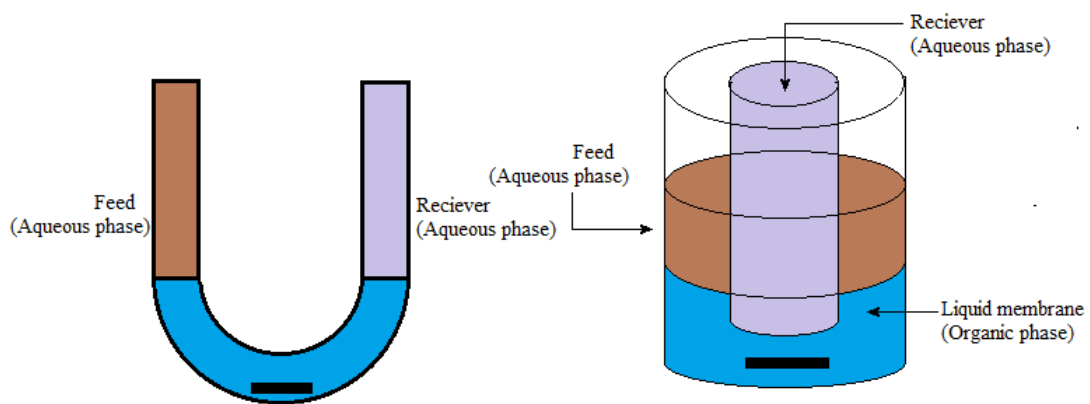
Figure 1.2: Two types of Bulk Liquid Membrane [4]

It is used to go through transport mechanism and influence of carrier structure upon transport efficiency. Its stability is maintained as long as the stirrer doesn't spin quickly.

Disadvantage: Thickness of the LM limits the quantity of solute species extracted and has no practical application. [4]

1.3.2 Emulsion Liquid Membrane [ELM]

ELM constitutes a dispersed inner receiving phase in a thin shell of immiscible LM, the middle phase forming an emulsion (water-oil-water or oil-water-oil types). This stable emulsion when dispersed in another 3rd continuous phase, a double emulsion is formed by the dispersed feed solution. Extraction and recovery of solute occurs by transport from continuous outer feed phase across the LM to the inside strip phase. During the solute transport emulsions formed should withstand the sheer created during mixing. To recycle and reformulate emulsion, it should be broken easily to recover the concentrated internal phase or the solute.

Disadvantage: Emulsion swelling and membrane rupture is associated with osmotic pressure. So difficulty is encountered when high metal ions are in internal phase causing the water to transport from dilute feed phase to concentrated internal solution resulting in separation loss. [5]
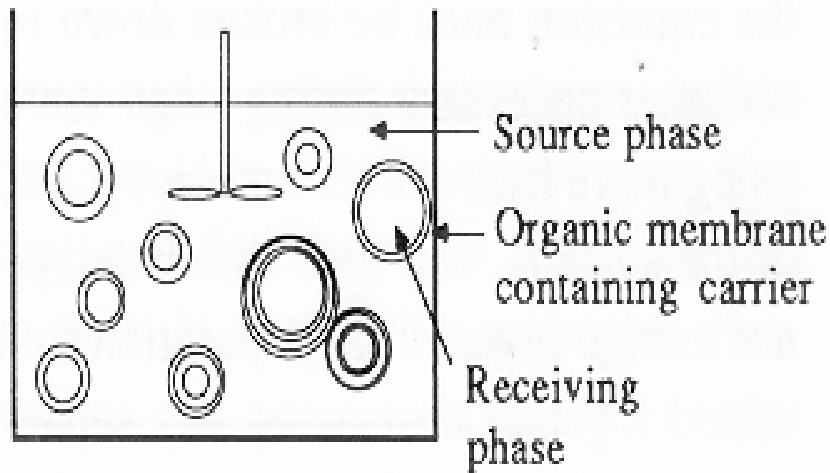
Figure 1.3: Emulsion Liquid Membrane [5]

1.3.3 Supported Liquid Membrane [SLM] or Immobilized Liquid Membrane [ILM]

An ILM made by a stiff polymer membrane with many microscopic pores impregnated on it. Organic phase (LM) fills these pores. The solvent and the carriers filled in these pores of the membrane are just equipped within the source/ feed phase and the strip/receiving phase. ILM seizes entities from one end (feed/source phase) to the other receiving/strip phase with the use of carriers. This LM follows the Equilibrium transport mechanism and requires emulsion formation and phase separation. [6]
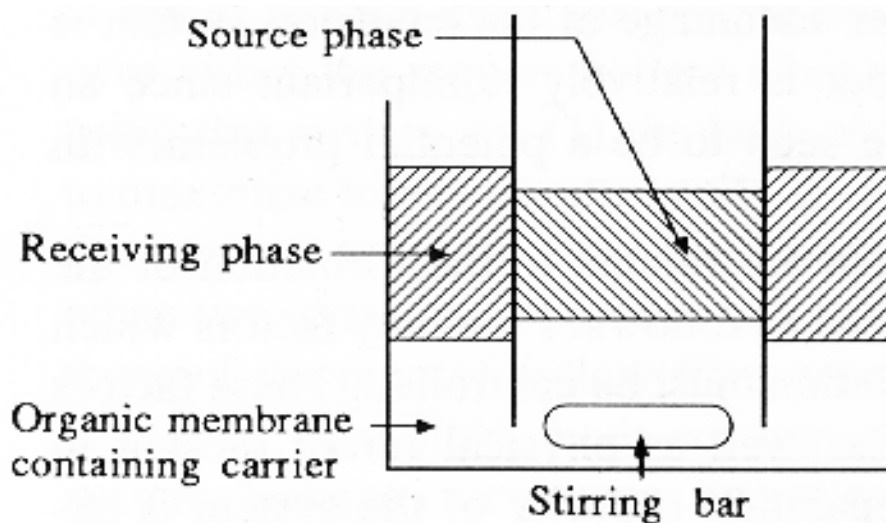
Figure 1.4: Supported Liquid Membrane [6]

1.4 Dyes

Dyes add colour to anything and are natural, synthetic substances. They are considered as coloured substances that have affinity to substrate being applied for. Dyes are commonly applied in aqueous solution and require a mordant (for example Cr is used to give colour for the fabric). Annually dyes production is estimated to be over one lakh and seven lakhs of the dye products [7].

Sources of Dyes are:

1. Dyeing and printing
2. Paper and ink industries
3. Textile industries
4. Cosmetics
5. Pharmaceuticals
6. Food
7. Leather and Plastic industries

Types of Dyes:

1. Anionic dyes (acidic)
2. Direct and reactive
3. Cationic dyes (basic)
4. Non-ionic dispersive dyes

Dyes Impact on Environment

1. The presence of residual colour, high levels of electrolytes, toxic effluents (S, vat dyes, enzymes, CH_3COOH, soaps, nitrates, and Cr compounds), heavy metals (Cu, Ar, Pb, Cd, Hg, Ni, and Co), mordants, dyeing auxiliaries affects aquatic life.
2. Carcinogenic by products are formed by reaction of disinfectants with dye fixing agents with formaldehyde functional group, chlorinated stain removers, hydro carbon based softeners, and non bio degradable dyeing chemicals.
3. These have allergic reactions.
4. Bad appearance and smell occur and sunrays required for photosynthesis are prevented to penetrate due to increased turbidity of water due to the presence of dyes [8].
5. Water sources self purification process and the aquatic lives in them are affected by the interference of oxygen transfer at water air interface.
6. Dyes decrease the soil productivity by clogging the pores in the soil.
7. There flow into rivers and other water bodies turns the hand pumps drinking water unfit or bad for the used by the humans.

Thus before the industrial effluents are disposed off dyes content must be removed which may have adverse consequences on environment and living beings which is of great concern in order to maintain a proper, balanced health of the ecosystem.

1.5 Methylene Blue
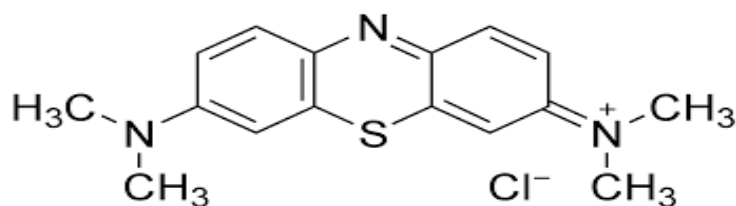
Figure 1.5: Methylene Blue

1. Cationic, phenothiazine dye
2. Cotton wool and silk is dyed using MB.
3. This dye is not harmful. However a little exposure can cause effects in humans like heart rate, vomiting shock, cyanosis, jaundice, and quadriplegia and tissue necrosis..
4. Traditional techniques like flocculation, chemical oxidation, ultrasonic decomposition, electrochemical oxidation, electro coagulation, coagulation and precipitation, and adsorption and ozonation, photo oxidation, pre-dispersed solvent extraction and aerobic and anaerobic biological processes for extraction of these dyes are inadequate and not cost effective processes where liquid membrane is considered to be a reliable and potential technique.

1.6 Green Liquid Membrane

Organic membrane phases in LM separation techniques mostly use solvents that are petroleum based for example kerosene and chloroform. These are mostly poisonous and non-biodegradable. Such solvents are flammable, volatile, and when used causes risk to surrounding and environment. So, LM can be changed to "green liquid membrane" by substituting eco-friendly solvents such as vegetable oils. Chemically vegetable oils are glycerides of fatty acids and even are bio-fuels and bio-diesels that are non toxic and non hazardous, available easily, occurring naturally. These are even cost effective and are renewable sources [3].

1.7 Objective

The Overall objective is to study transport efficiency of MB from its solution in a BLM set up.

Outlined below are the more detailed steps to acquire the objective:

1. To find a suitable membrane i.e. solvent and carrier by carrying out two phase experiments.
2. To study the effects of many parameters like equilibrium time, feed phase pH, carrier conc., strip/receiving phase conc., stirring speed conditions on the transport of MB and optimizing there values by carrying out three phase experiments.

2. <u>LITERATURE REVIEW</u>

2.1 Literature Review on LM and Extraction of Metals using LM

In 1902, Nernst and Riesenfeld were the first scientists who described liquid membranes (LM). Oil layer separating electrolyte solutions were initially investigated by them. When ELM was produced using lithium developed techniques, interest for manmade LMs increased. LM has been useful in extraction of many metals from waste water. [9]

Kamal kumar Bhatluri and Mriganka Sekhar Mana published a journal on separation of cadmium, lead both together from waste water by taking SLM. 79% Cd and 84% Pb was extracted using Aliquat 336 as carrier in coconut oil as solvent and EDTA as strip phase [10].

Siu Hua Changa, Tjoon Tow Tengb have published data on optimized parameters values for extraction and recovery of copper by the use of soybean oil in a BLM set up. They found an extraction of more than 90%. 500mg/l of Cu(II) and 250mM Na2SO4 in 0.1M acetate buffer solution as feed using 87.88mM D2EPHA as carrier in soyabean oil gives highest extraction and good recovery in sulfuric acid solution [11].

Phenol extraction of 90% was done using BLM in rapseed oil as solvent and recovered using potassium buffer solution by Moamer Ehtash, Marie-Christine Fournier-Salaün[12].

2.2 Literature Review on Dye extraction by LM

In 2008, Chandan Dasa and Meha Rungtab studied the extraction of MB and CV using ELM. They made an ELM by using n-heptane as solvent, NaOH at the internal phase and dye solution as the feed or the external phase. Emulsion was stabilized using surfactant span 80. They experimented for both single and binary system giving results of maximum extraction of 99% MB and 95% CV for single system and 97% MB, 90% CV for binary system. [13]

In 2009, G. Muthuraman and Tjoon Tow Teng published journal on transport efficiency of MB from industrial wastewater taking benzoic acid extractant and Xylene as solvent. They studied at 27°C using BLM in a range of 0.36-5.8 x 10^{-2} M of Benzoic acid. Considering all the optimised parameters other than dye conc. value, 90-99% of dye was extracted after 15 min of phase separation. Finally considering all effects and optimising them a maximum extraction of 96% was found out. [14]

In the very same year they even published journal on transport efficiency of cationic dyes RB, MV, MB using D2EHPA extractant. Hexane in LM was used as the carrier. A maximum recovery of 98% was shown while using 8.5mol l^{-1} CH_3COOH as the strip phase. Optimizing all the parameters gave 95 to 98% of extraction of the three dyes from its mixture contaminent. [15]

In 2015, Lynda Bahloul and Farida Bendebane demonstrated possibilities for extraction and recovery of anionic dye Yellow 99 using ELM consisting of Aliquat336 extractant, Span80 surfactant and cyclohexane solvent. An extraction yield of 99.98% showed by optimizing eight parameters.[16]

2.3 Literature Review on Green LM

In 2006, G. Muthuraman and K. Palanivelu were suuccessful in using vegetable oils like alm oil, sunflower oil and coconut oils for extarcation of textile dyes using SLM. Polypropylene supported Teflon membrane was used. Maximum extraction of 97 % was shown when processed for about 5 hours.[17]

In 2009, N.Hajarabeevia and I. Mohammed Bilal demonstrated cationic dyes facilitated transport through a SLM where D2EHPA acts as the carrier. They used coconut oil as the solvent to extract MB and RB. Using feed phase at a pH of 4, 50% D2EPHA carrier concentration and 100ml acetic acid as strip phase the SLM set up gives an extraction of 94.2% for MV and 90% for RB when run for 7 hours and at 600rpm.[18]

G. Muthuraman, Tjoon Tow Teng in the same year found out that 100 % extraction of RB is possible using Palm oil as the solvent in supported liquid membrane. Feed phase of 11 pH at 300rpm with sulphuric acid as strip phase after 5 hours goves the above result.[19]

2.4 Literature review on MB

Lynda Bahloul and Fadhel Ismail in 2013 published a journal on cationic dye extraction by taking ELM. This cationic dye was MB taken in the feed phase with D2EHPA as carrier in hexane as solvent of the LM. At a pH of 5 and 200 rpm stirring spped maximum extraction of 98.15% and recovery of 81.91 % was shown after a contact time of 7 min. [20]

In 2013, Pezhman Kazemi and Mohammad Peydayesh performed experiments on pertraction of MB taking both D2EHPA/M2EHPA and sesame oil mixture as a organic phase. They used SLM separation technique with acetic acid as the strip phase. Optimizing the parameters to feed phase pH of 6, stirring speed of 350 rpm, and an equilibrium time of 7 hour 62% of dye was extracted. [21]

In 2015, G. Muthuraman and M. Soniya conducted a comparative experiment within LLE and BLM for the transport of MB from textile wastewater using salicylic acid in benzene and oxalic acid as strip phase. Liquid-liquid extraction at 100 rpm gave 93% MB extraction in just 5min while bulk liquid membrane at 200 rpm gave 99.6% MB extraction in 2 hour. [22]

3. MATERIALS AND METHOD

3.1 Liquid Membrane Setup

Two cells of BLM, made are fabricated as shown in Figure 3.1 is for liquid membrane having higher density then water and figure 3.2 is for lower density liquid membrane. Set up consists of a Square glass frame (160mm length and 100 mm in height), stirrers (2 in no of impeller length- 70 mm), and two regulated motor and has two compartments separated by thin glass plate of thickness 3.0mm. This plate is fixed using an adhesive for glass. To ensure no leakage blank test was performed. This set up is used for three phase study. At the bottom of the cell, clearance of 10mm allows solute to travel from source solution to receiving solution across membrane phase. Feed and strip phases were taken in the both the compartments separately and the LM/organic phase being lighter was placed at the top of the phases. Motor driven stirrers were used to stir the solutions and voltage regulators helped checks the speed (rpm) timely.
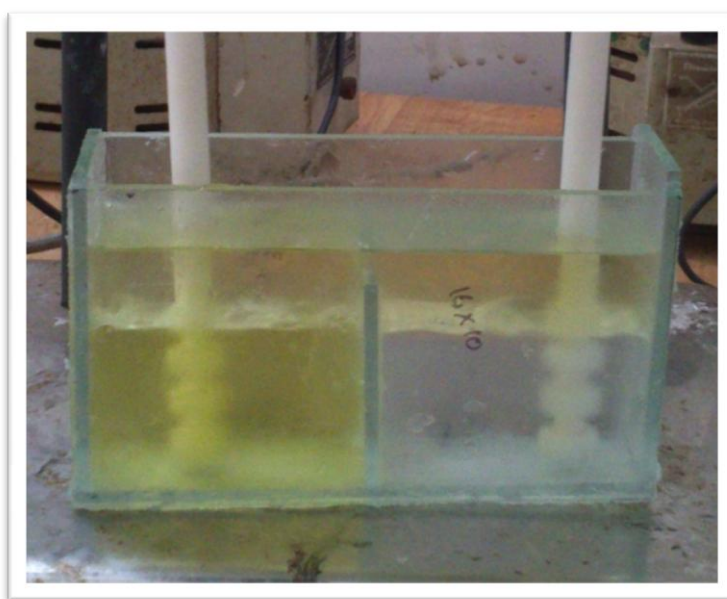
Figure 3.1: BLM set up for lighter LM
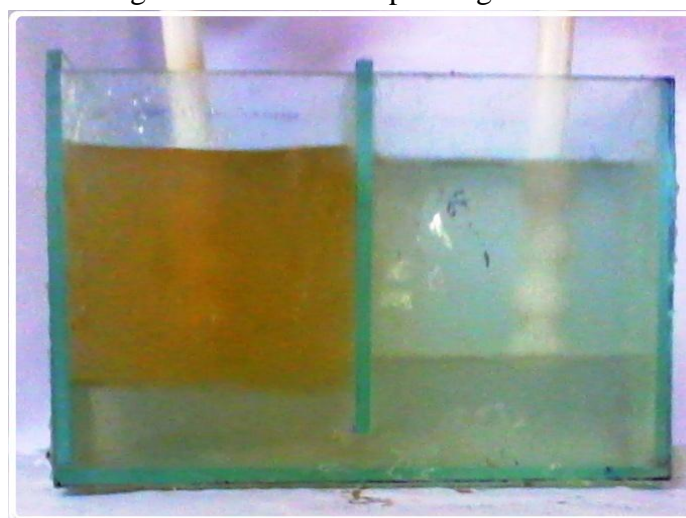
Figure 3.2: BLM set up for heavier LM

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Sufficient care prevents source and receiving phases from mixing. To maintain this, levels of feed and strip phases were maintained just below the top edge of the plate separating the comartments. On the top of that, the stirring speed was always regulated to prevent formation of emulsions at the feed membrane interface and to not disturb organic phase.

3.2 Chemicals and Analytical Instuments

Required chemicals list includes MB, Phenol, Sulphuric Acid of AR grade. Phenol dissolved in Sunflower oil was used as Liquid membrane and Sulphuric Acid as the strippant with varrying concentration. Miili-Q water was taken to make the dye solution and its pH adjustment was done using Sodium hydroxide solution. Absorbance of the dye was measured using UV–visible spectrophotometer and even to establish its maximum wavelength and its concentration.

Figure 3.3: Photograph of UV-Visible spectrophotometer

3.3 Two Phase Study

To perform two phase equilibrium study, 20ppm MB of pH 12 and equal volume of liquid membrane were added. Then the mixture was put on the stirrer for 6hrs at 100rpm. This procedure was followed with various solvents such as sunflower oil, Rapeseed oil, soybean oil, mustard oil, and coconut oil. The most extracting solvent was chosen which was used to select best carrier (among phenol, Tri-octyl amine, Di-octyl Amine, Aliquat 336, Cyanax 21) and strip phase (among H_2SO_4, HCl, Salicylic Acid, Acetic Acid, Nitric Acid) .

Figure 3.4: Two phase study

3.4 Three phase study

As described in section 3.1 the same BLM set up was used to perform the three phase experiments. Carrier phenol in Sunflower Oil solvent together made the organic phase liquid membrane. MB is taken in the source phase and H_2SO_4 as the receiving phase while we optimize various factors such as strip concentration, pH of feed phase, carrier concentration to give highest recovery of MB. Before that equilibrium time and stirring speed to give maximum recovery is determined. MB is transferred through the interfaces between feed, strip and organic phase. 200 ml of feed phase and receiving phase separately were taken and the volume of organic phase was 100ml. 300 rpm stirring speed ensured the solution was properly mixed and maintained uniform bulk conc. throughout. One ml of both the phases is to be collected periodically for further analysis.

Methylene Blue Reaction Mechanism:

Extraction and Recovery of MB ($C_{16}H_{18}N_3SCl$) can be explained by the following mechanism:

$$(C_6H_5OH)_{org} + [Dye]_{aq}^+ = [(C_6H_5O)^-(Dye)^+]_{org} + HCl^- \tag{1}$$

$$[(C_6H_5O)^-(Dye)^+]_{org} + (H_2SO_4)_{aq} = (C_6H_5OH)_{org} + [Dye]_{aq}^+HSO_4^- \tag{2}$$
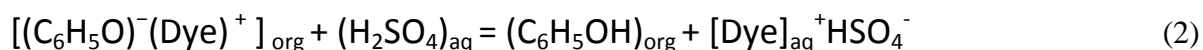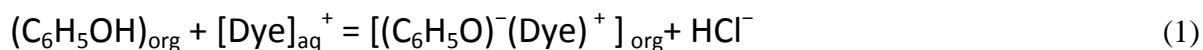
Following the results, the dye transport across the suggested BLM system may be described by the under mentioned points:

(1) MB, cationic dye extraction from source phase through the liquid membrane is associated with the presence of carbolic acid (phenol) that acts as the carrier and both forms ion pair complex: $[(C_6H_5O)^-(Dye)^+]_{org.}$

(2) This results in formation of complex with a paired neutral ion that is more favourably distributed in the LM.

(3) When reaches liquid membrane/strip phase interface, the complex formed by the anionic carrier or carbolic acid and dye decomposes back into neutral phenol, the carbolic acid and leaves the dye free.

(4) And now the neutral phenol or the carrier diffuses back through the LM to source phase and liquid membrane interface which makes the cyclic process to begin once more.

(5) The MB free at the LM/strip phase interface diffuses into the receiving phase causing recovery to take place.

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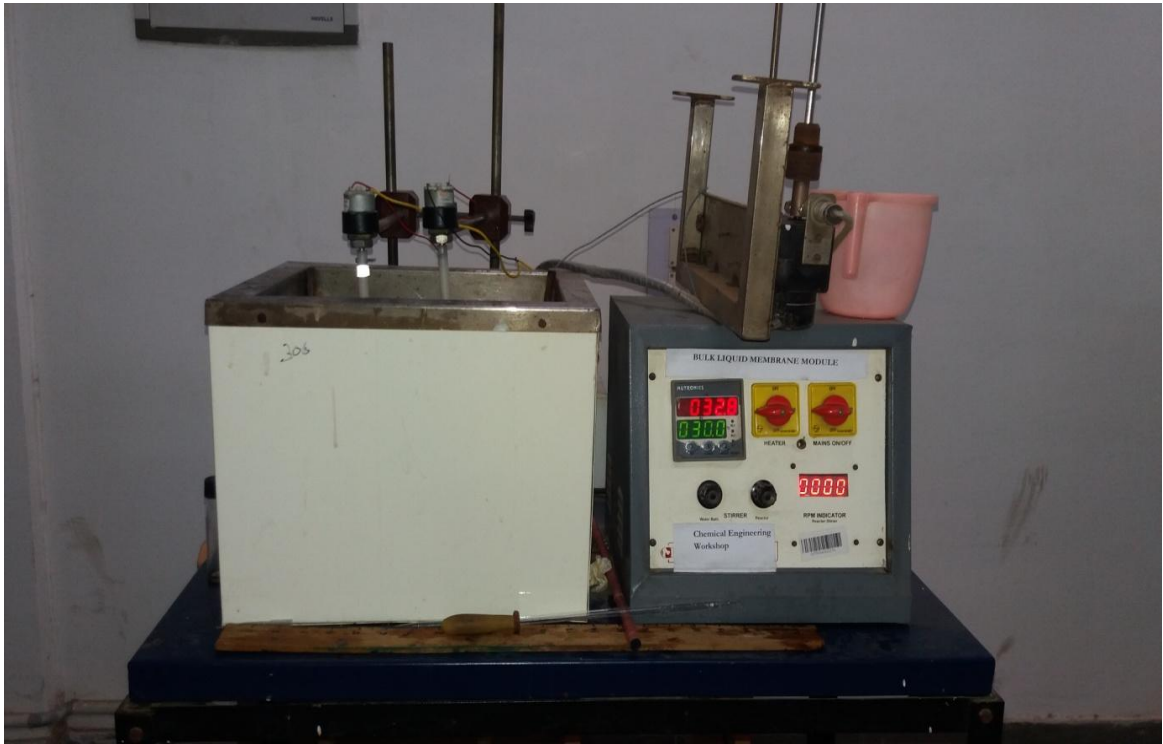
Figure 3.5: BLM set up for Three Phase Study

4. <u>RESULTS AND DISCUSSIONS</u>

4.1 Calibration Plot

At 664nm MB substances were detected in the solution of the different aqueous phases using the UV-visible spectrophotometer. By mass balance method concentration of organic phase was calculated. To measure any unknown sample's concentration calibration curve was made by taking samples of concentration 0, 5, 10, 15, 20, and 25 ppm at 664 nm wavelength. From the UV results we get the plot with concentration (in x-axis) versus absorbance (in Y-axis). As concentration and absorbance follow linear relationship, linear regression analysis was done to find the mathematical relation between them giving the equation "y = 0.0346x + 0.0009" (Coefficient of determination, R^2=0.9993). Distribution coefficient of MB (m) was measured by taking ratio of MB in organic phase to MB in the aqueous solution. To obtain more separation efficiency this (m) value shoulld be high.
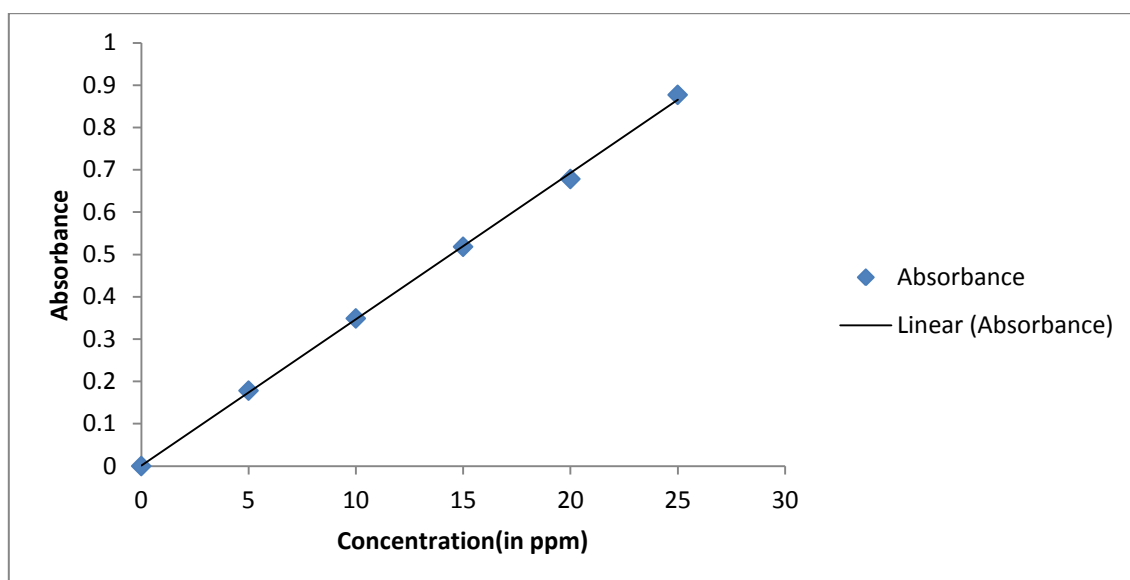
Figure 4.1: [Calibration Plot] Absorbance vs Concentration of MB

4.2 Two Phase Studies

LM separation techniques are primarily associated with the selection of approriatet solvent for transport of the required solute. In this work different solvents based on their solubility were chosen to find the best fit for the transport of MB. Important parameters to be considered while choosing solvent are low viscosity, stability, non- corrosive, ability to re-generate, non-toxicity, along with a high distribution coefficient or a higher %E with no miscibility with aqueous phases. Density of the solvent in the LM is measured to take care of the fact that it should have quite different densities than that of the feed solution. Under two phase study, many combinations of carriers and solvent and strip phase were made to find the best suitable for the transport of MB.

Experiment performed to find suitable solvent among: sunflower oil, rapeseed oil, soybean oil, coconut oil and mustard oil whose distribution coefficient is shown in table 4.1.

Table 4.1: Distribution Coefficient of MB in different solvents

Solvents	Distribution Coefficient
Sunflower oil	12.43
Soybean Oil	9.69
Rapeseed Oil	4.74
Mustard Oil	0.69
Coconut Oil	1.24

Experiment performed to find suitable carriers among: phenol, Tri-octyl amine, Di-octyl Amine, Aliquat 336, Cyanax 21 whose distribution coefficient is shown in table 4.2.

Table 4.2: Distribution Coefficient of MB in various carriers

Carriers	Distribution Coefficient
Phenol	12.43
Tri-Octyl Amine	9.14
Di-Octyl Amine	7.33
Aliquat 336	5.45
Cyanax 21	0.24

Experiment was performed to find suitable stripping agent: H_2SO_4, HCl, Salicylic Acid, Acetic Acid, Nitric Acid whose distribution coefficient is shown in table 4.3.

Table 4.3: Distribution Coefficient of MB in Strip Phase

Strip Phase	Distribution Coefficient
H2SO4	12.43
HCl	10.26
Salicylic Acid	7.94
Acetic Acid	7.34
Nitric Acid	1.39

Thus from the two phase experiments, suitable carrier chosen was phenol for the transport study of MB in sunflower oil as a solvent and H_2SO_4 was chosen as receiving phase as these combination gave the highest distribution coefficient of 12.43 in all the above cases.

4.3 Three Phase Studies

4.3.1 Equilibrium time distribution

Taking all the parameters like feed phase concentration (200ml of 25 ppm MB) with pH of 12, strip phase concentration (200ml of 0.5N-H_2SO_4), and 1M phenol carrier in 100ml of sunflower oil fixed value, first a twelve hours three phase experiment was performed. Samples of feed solution and strip solution were collected at certain intervals for analysis by UV spectrophotometer to study amount of dye extracted into organic and that recovered by the strip phase at different times. Figure 4.2 shows that at around 480min maximum extraction of dye occurs followed by a steady extraction with further time at around 7 hours whose values are given in Appendix A. Hence an equilibrium time of 480min is recommended.
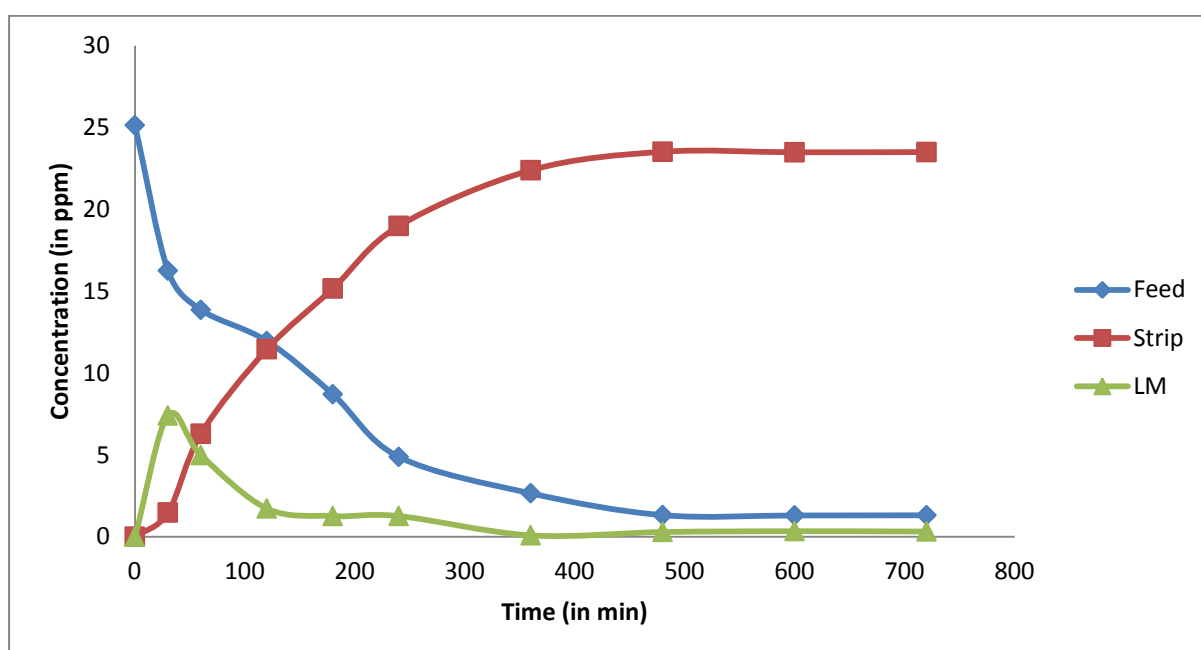
Figure 4.2: Graph of concentration of Feed, Strip and LM in y-axis with Time in x-axis

4.3.2 Effect of stirring speed

An important factor stirring speed during both extraction and recovery procedures is varied from 200rpm to higher values up to 400rpm. The effect on the transport efficiency is depicted in fig 4.3. The result as tabled in appendix B shows a maximum extraction of MB at 300rpm which decreases with higher rates due to mixing of the source and the receiving phases. Since stirring of both phased is required to minimize concentration of polarization in the feed side and provide effective transport of MB, low stirring rates are not effective
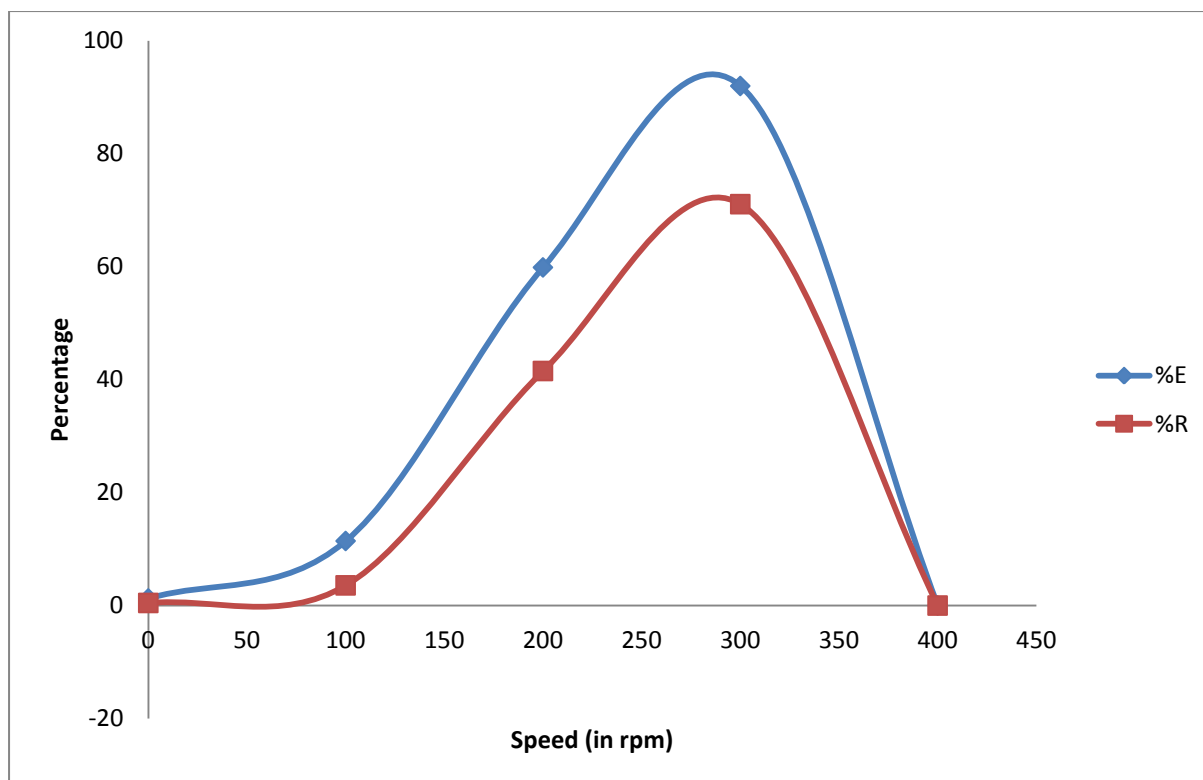
Figure 4.3: Graph of extraction and recovery percentage in y-axis at different Speeds in x-axis

4.3.3 Effect of receiving/strip phase concentration

Effect of sulphuric acid concentration in strip phase on distribution ratio (D) of the MB was studied in concentrations 0.25N, 0.5N, 0.75N, 1N, 1.25N, and 1.5N. The detailed values of the effect for different concentration values are mentioned in appendix C. Figure 4.4 and 4.5 shows that increase in H_2SO_4 concentration the efficiency of dye extraction also increases. Maximum extraction of 95% from the feed solution occurred at H2SO4 concentration of 1.25N which also gave maximum recovery of 93.5% MB by strip phase. Further increase (beyond 1.25N) in strip phase concentration extraction efficiency did not show considerable effect. This produces higher strength of the solution which results in a lower activity coefficient for hydrogen ions and reduces less active H+ to decompose the complex. Hence in the following tests H2SO4 conc. was considered 1.25N.

Figure 4.4: Graph of % Extraction of MB with Time for different strip phase concentration
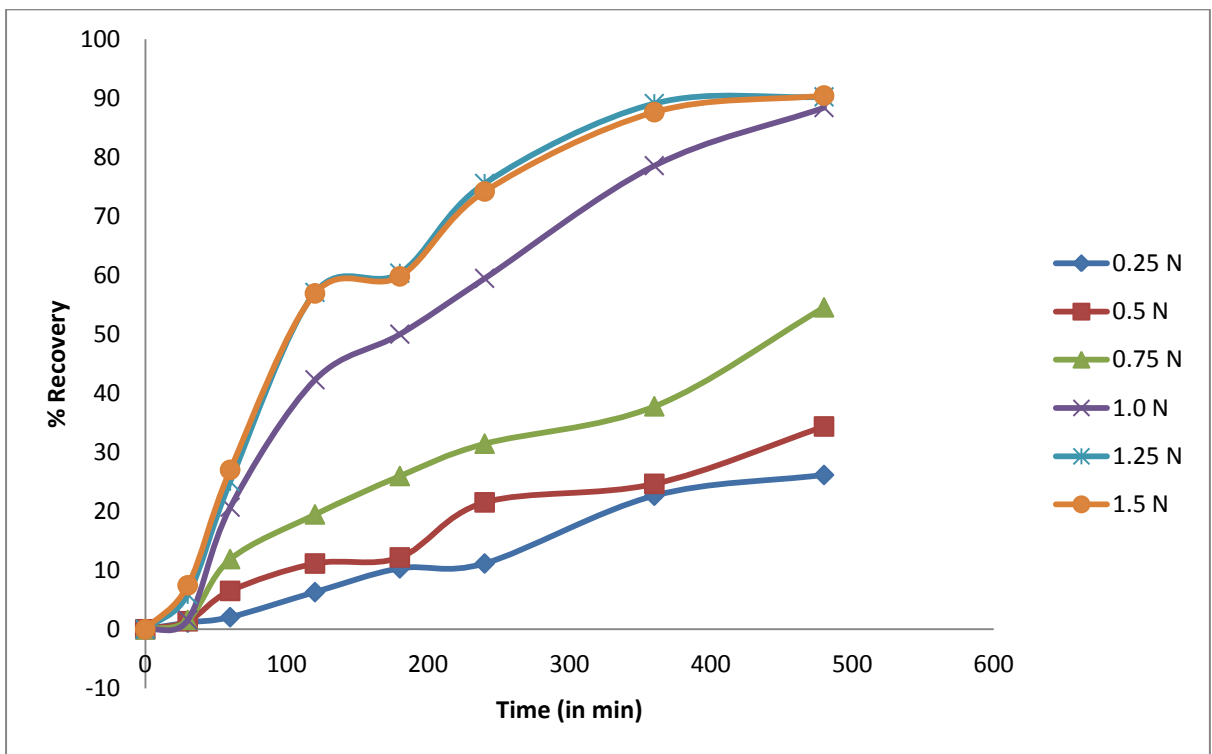
Figure 4.5: Graph of % Recovery of MB with Time for different strip phase concentration

4.3.4 Effect of feed phase pH

pH of the feed solution affect the transport efficiency and permeability of MB as represented in the figure 4.6 and 4.7 and values are displayed in appendix D. Aqueous solution of same MB concentration but of different pH values ranging from 10 to 13 were used to study extraction and recovery efficiency. It is viewed that dye extracted percentage increases up to pH 12 and then decreases. A good charge distribution is shown when pH of 12 is used for the feed solution making it basic and phenol having a negative charge on it. Therefore, MB forms a complex with the carrier at the feed/organic phases interface. Recovery of MB by strip phase doesn't have much effect with higher pH values but is maximum at pH 12. Since the maximum extraction and even recovery was at pH 12 of the feed solution so for upcoming studies it was maintained at pH 12.
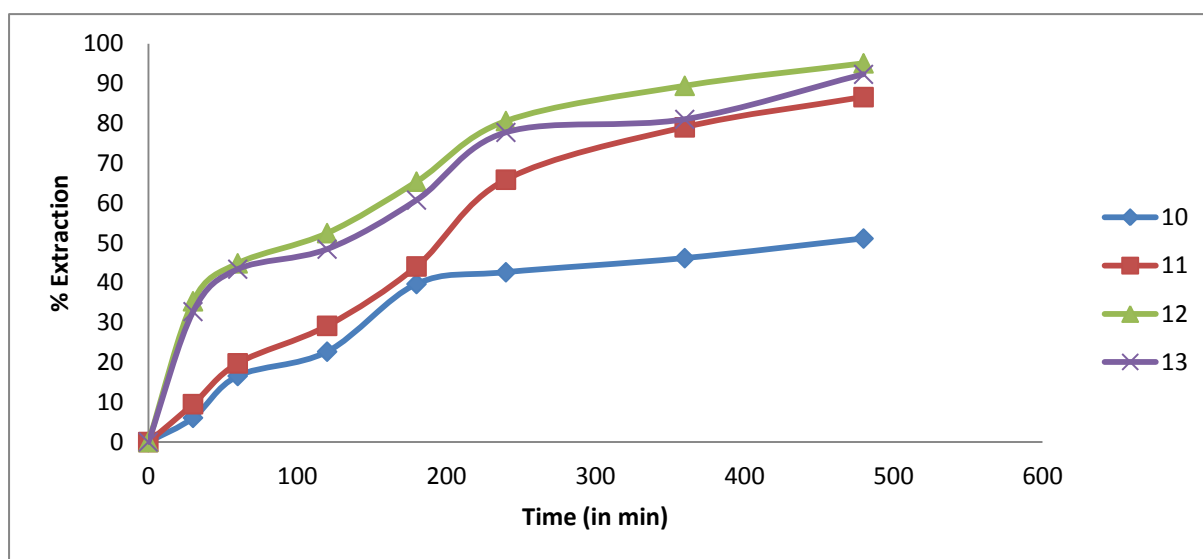
Figure 4.6: Graph of % Extraction of MB with Time for different pH of feed phase
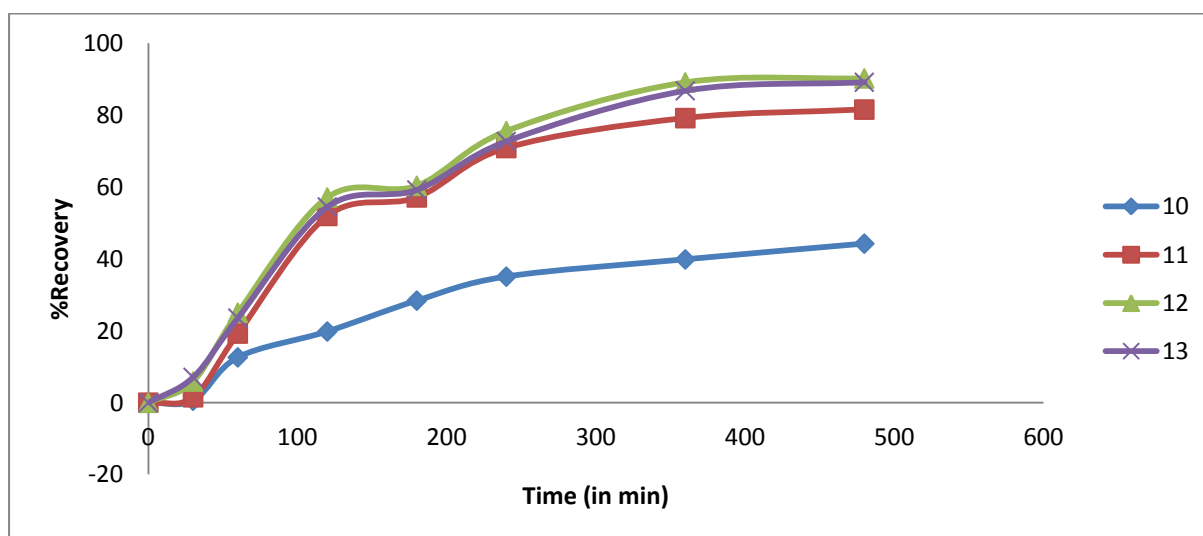
Figure 4.7: Graph of % Recovery of MB with Time for different pH of feed phase

4.3.5 Effect of carrier concentration

Phenol concentration's effect in sunflower oil constituting the membrane phase on MB transport efficiency was followed starting with 0.25M to 1.25M of carrier in the said LM volume (100 ml) for existing setup. The values are shown in appendix E. The results are depicted in figure 4.8 and fig 4.9. As transport of dye or flux of MB is related to carrier concentration, MB extraction increases with increasing carrier concentration up to 1M but then was decreased probably due to an increment of viscosity of LM. Since maximum extraction and recovery of MB through BLM was at carrier concentration of 1M further experiments were carried out with this value.
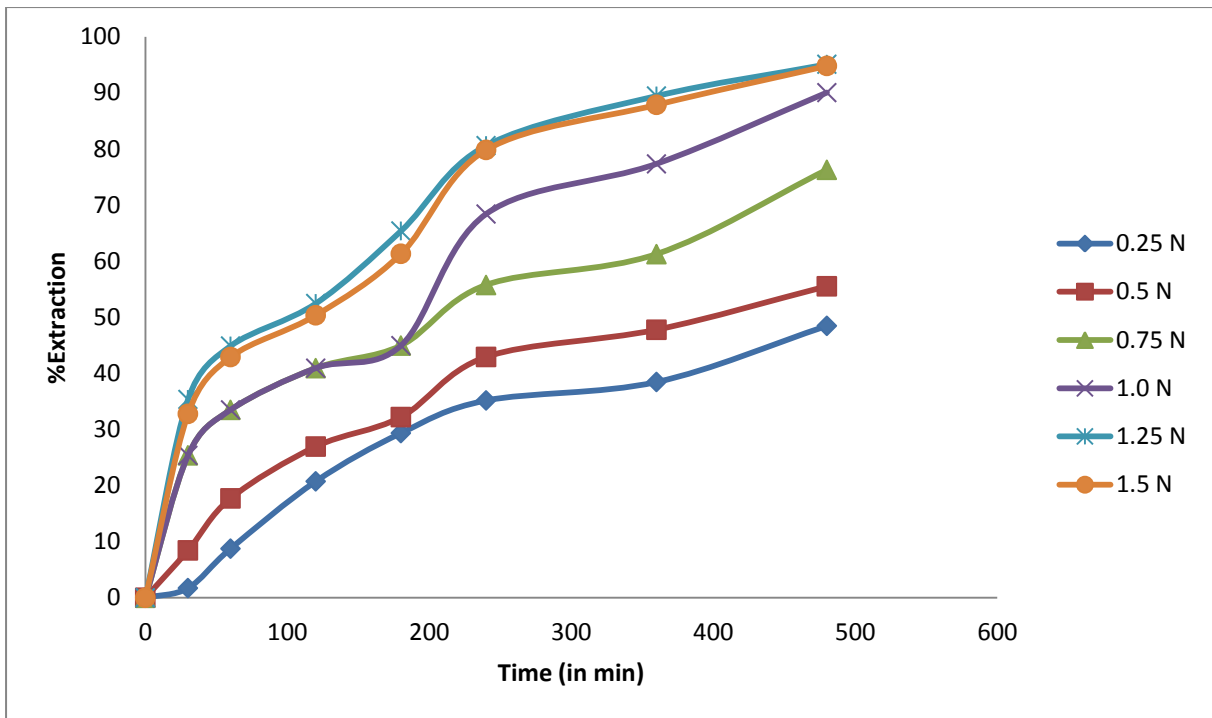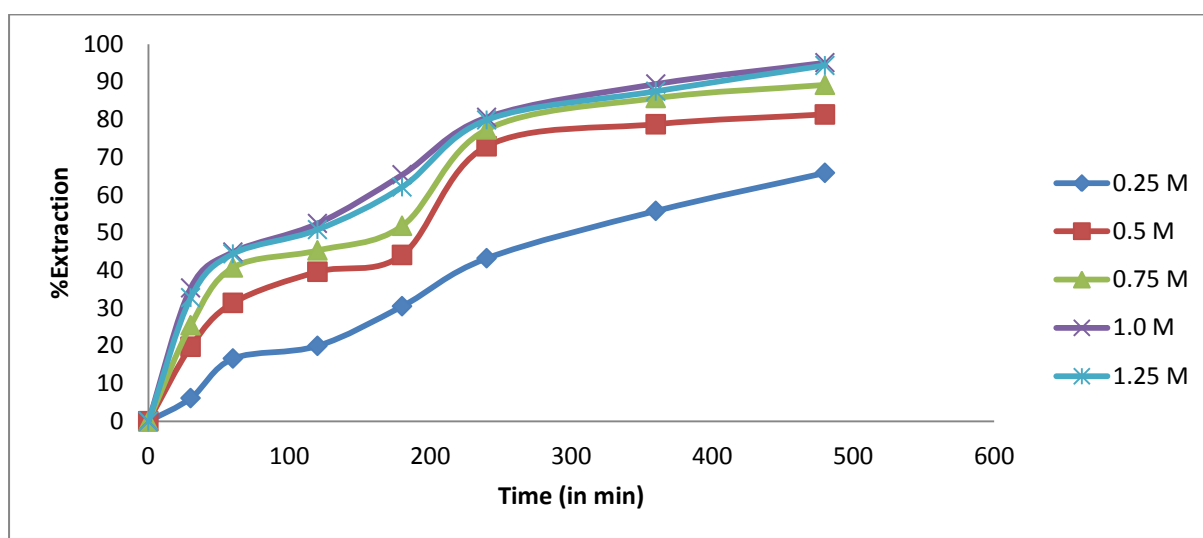

Figure 4.8: Graph of % Extraction of MB with Time for different carrier concentration
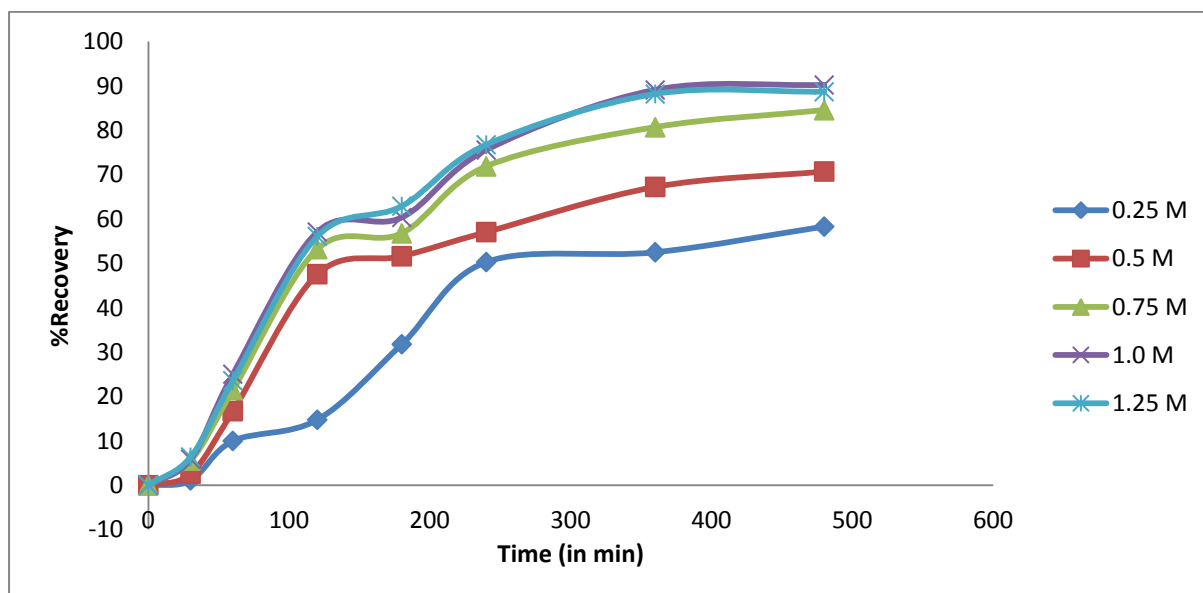
Figure 4.9: Graph of % Recovery of MB with Time for different carrier concentration

5. <u>CONCLUSION</u>

5.1 Conclusions

In this work we studied three phase experiments using bulk BLM separation technique to extract MB from its aqueous phase. The feed or the source phase was MB aqueous solution. Following green liquid membrane concept sunflower oil was taken as the solvent for organic membrane phase based on its distribution coefficient from two phase experimental study. Phenol was chosen as the carrier and strip phase was H_2SO_4 solution based on results of two phase study. Effects of various parameters like carrier concentration, feed phase pH, and strip or receiving phase concentration were studied to optimise the working conditions. From the above experimental set up MB was extracted up to 95% from feed phase to liquid/organic membrane phase whereas MB recovered from liquid/organic membrane phase to receiving phase was only 90%. Strip or receiving phase concentration was optimised to 1.25 N and similarly carrier concentration was optimised to 1M favouring the extraction and recovery processes where the feed phase pH was optimised to be 12. Even stirring speed conditions affects the extraction and recovery to great extent and when all the three phase are stirred at 300 rpm it gives the best results..

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7. <u>APPENDICES</u>

Equilibrium Time

Experiment:

    Feed phase- 25.1329ppm MB (Initial Concentration) (200ml)
    LM- 1M Phenol in Sunflower Oil (100ml)
    Strip Phase- Sulphuric Acid (1.25N) (200ml)

Observation Table: Concentration of Feed, Strip and LM with Time

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc (in ppm)	Strip Conc (in ppm)	LM Conc (in ppm)
0	0.869	0	25.132	0	0
30	0.562	0.051	16.248	1.479	7.404
60	0.479	0.107	13.855	3.109	8.167
120	0.413	0.296	11.950	8.563	4.618
180	0.301	0.424	8.702	12.271	4.158
240	0.168	0.549	4.878	15.884	4.369
360	0.091	0.744	2.656	21.511	0.965
480	0.045	0.813	1.323	23.511	0.297
600	0.045	0.812	1.306	23.479	0.346
720	0.045	0.812	1.315	23.491	0.326

APPENDIX B

Optimisation of Stirring Speed

Experiment:

    Feed phase- 25.1329ppm MB (Initial Concentration) (200ml)
    LM- 1M Phenol in Sunflower Oil (100ml)
    Strip Phase- Sulphuric Acid (1.25N) (200ml)

Observation Table: Percentage extraction and Recovery with different Stirring Speed

Stirring Speed (in rpm)	%E	%R
0	1.256	0.456
100	11.425	3.568
200	59.861	41.523
300	91.982	71.059
400	0	0

Optimisation of Strip Phase Concentration

Experiment:

   Feed phase- MB (12pH, 25 ppm, 200ml)
   LM- 1M Phenol in Sunflower Oil (100ml)
   Strip Phase- Sulphuric Acid (98% purity) (200ml)
   Phase Ratio- 1.8:1
   Temperature- 30°C
   Stirring Speed-300rpm

Keeping all other constraints as mentioned earlier.

1.   Strip Phase- Sulphuric Acid (0.5N)

Observation table for 0.5N Sulphuric Acid:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.796	0.011	23.011	0.341	8.441	1.357
60	0.715	0.056	20.682	1.632	17.711	6.498
120	0.635	0.096	18.361	2.799	26.946	11.138
180	0.589	0.105	17.040	3.057	32.202	12.167
240	0.496	0.186	14.346	5.401	42.921	21.495
360	0.454	0.214	13.130	6.190	47.763	24.634
480	0.386	0.298	11.182	8.632	55.514	34.353

2.   Strip Phase- Sulphuric Acid (0.75N)

Observation table for 0.75N Sulphuric Acid:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.648	0.013	18.754	0.398	25.382	1.587
60	0.578	0.103	16.716	2.988	33.490	11.891
120	0.513	0.169	14.849	4.890	40.919	19.459
180	0.478	0.225	13.838	6.526	44.945	25.969
240	0.384	0.273	11.124	7.901	55.744	31.443
360	0.337	0.328	9.742	9.491	61.242	37.768
480	0.206	0.474	5.965	13.705	76.273	54.537

3. Strip Phase- Sulphuric Acid (0.25N)

Observation table for 0.25N Sulphuric Acid:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.854	0.009	24.699	0.283	1.724	1.127
60	0.793	0.017	22.933	0.514	8.751	2.047
120	0.689	0.054	19.919	1.580	20.741	6.290
180	0.614	0.089	17.757	2.592	29.350	10.316
240	0.563	0.096	16.294	2.800	35.169	11.144
360	0.535	0.196	15.468	5.684	38.458	22.622
480	0.448	0.227	12.953	6.569	48.464	26.141

4. Strip Phase- Sulphuric Acid (1N)

Observation table for 1N Sulphuric Acid:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.648	0.013	18.754	0.398	25.382	1.587
60	0.578	0.179	16.716	5.196	33.490	20.678
120	0.513	0.367	14.849	10.624	40.919	42.277
180	0.478	0.434	13.838	12.563	44.945	49.994
240	0.274	0.516	7.945	14.939	68.395	59.448
360	0.197	0.682	5.699	19.736	77.331	78.539
480	0.086	0.768	2.508	22.208	90.028	88.372

5. Strip Phase- Sulphuric Acid (1.25N)

Observation table for 1.25N Sulphuric Acid:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.562	0.051	16.248	1.479	35.353	5.888
60	0.479	0.217	13.855	6.289	44.876	25.025
120	0.413	0.496	11.950	14.343	52.455	57.078
180	0.301	0.524	8.702	15.161	65.382	60.333
240	0.168	0.656	4.878	18.982	80.598	75.537
360	0.091	0.774	2.656	22.384	89.442	89.074
480	0.045	0.813	1.323	23.511	94.744	93.559

APPENDIX D

Optimisation of pH of Feed Phase

Experiment:

 Feed phase- MB (25 ppm, 200ml)
LM- 1M Phenol in Sunflower Oil (100ml)
Strip Phase- Sulphuric Acid (98% purity, 1.25N) (200ml)
Phase Ratio- 1.8:1
Temperature- 30°C
Stirring Speed-300rpm

Keeping all other constraints as mentioned earlier.

1.   Feed Phase- 10pH MB

Observation table for 10 pH of Feed phase:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.816	0.004	23.604	0.138	6.083	0.551
60	0.725	0.109	20.965	3.167	16.582	12.603
120	0.672	0.172	19.430	4.973	22.688	19.790
180	0.524	0.246	15.161	7.132	39.673	28.380
240	0.498	0.304	14.419	8.809	42.628	35.050
360	0.468	0.346	13.531	10.014	46.159	39.845
480	0.425	0.384	12.291	11.115	51.092	44.227

2.   Feed Phase- 11pH MB

Observation table for 11 pH of Feed phase:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.786	0.013	22.742	0.381	9.509	1.517
60	0.697	0.167	20.167	4.835	19.756	19.238
120	0.615	0.451	17.800	13.054	29.174	51.943
180	0.486	0.496	14.054	14.349	44.077	57.095
240	0.296	0.615	8.580	17.800	65.857	70.825
360	0.182	0.688	5.274	19.890	79.013	79.139
480	0.116	0.708	3.369	20.488	86.591	81.520

3. Feed Phase- 12pH MB

Observation table for 12 pH of Feed phase:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.562	0.051	16.248	1.479	35.349	5.887
60	0.479	0.217	13.855	6.289	44.871	25.023
120	0.413	0.496	11.950	14.343	52.449	57.072
180	0.301	0.524	8.702	15.161	65.374	60.326
240	0.168	0.656	4.878	18.982	80.588	75.529
360	0.091	0.774	2.656	22.384	89.431	89.064
480	0.042	0.784	1.236	22.667	95.078	90.191

4. Feed Phase- 13pH MB

Observation table for 13 pH of Feed phase:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.584	0.061	16.904	1.776	32.739	7.068
60	0.492	0.204	14.228	5.919	43.387	23.551
120	0.448	0.473	12.965	13.687	48.412	54.461
180	0.341	0.514	9.869	14.872	60.729	59.176
240	0.193	0.631	5.598	18.265	77.725	72.674
360	0.165	0.754	4.771	21.800	81.014	86.741
480	0.066	0.774	1.933	22.395	92.306	89.110

APPENDIX E

Optimisation of Carrier Concentration

Experiment:

Feed phase- MB (12pH, 25 ppm, 200ml)
LM- Phenol in Sunflower Oil (100ml)
Strip Phase- Sulphuric Acid (98% purity, 1.25N) (200ml)
Phase Ratio- 1.8:1
Temperature- 30°C
Stirring Speed-300rpm

Keeping all other constraints as mentioned earlier.

1. Carrier Concentration- 0.25 M

Observation table for 0.25M carrier concentration:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.816	0.009	23.589	0.277	6.140	1.103
60	0.724	0.086	20.950	2.511	16.639	9.993
120	0.695	0.128	20.106	3.708	19.997	14.753
180	0.604	0.276	17.465	7.985	30.508	31.773
240	0.493	0.437	14.268	12.638	43.226	50.287
360	0.384	0.456	11.112	13.193	55.784	52.495
480	0.296	0.506	8.578	14.647	65.869	58.279

2. Carrier Concentration- 0.5 M

Observation table for 0.5M carrier concentration:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.697	0.022	20.167	0.648	19.756	2.581
60	0.596	0.145	17.245	4.196	31.382	16.697
120	0.524	0.413	15.170	11.953	39.638	47.562
180	0.486	0.448	14.052	12.968	44.089	51.598
240	0.235	0.496	6.809	14.338	72.907	57.049
360	0.184	0.584	5.343	16.895	78.737	67.226
480	0.162	0.614	4.690	17.768	81.336	70.699

3. Carrier Concentration- 0.75 M

Observation table for 0.75M carrier concentration:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.648	0.048	18.734	1.395	25.459	5.554
60	0.514	0.186	14.881	5.384	40.788	21.423
120	0.475	0.462	13.745	13.372	45.308	53.208
180	0.418	0.493	12.106	14.263	51.828	56.750
240	0.196	0.624	5.684	18.054	77.380	71.837
360	0.124	0.701	3.592	20.271	85.706	80.657
480	0.093	0.734	2.710	21.236	89.213	84.498

4.   Carrier Concentration- 1 M

Observation table for 1M carrier concentration:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.562	0.051	16.248	1.479	35.349	5.887
60	0.479	0.217	13.855	6.289	44.871	25.023
120	0.413	0.496	11.950	14.343	52.449	57.072
180	0.301	0.524	8.702	15.161	65.374	60.326
240	0.168	0.656	4.878	18.982	80.588	75.529
360	0.091	0.774	2.656	22.384	89.431	89.064
480	0.042	0.784	1.236	22.667	95.078	90.191

5.   Carrier Concentration- 1.25 M

Observation table for 1.25M carrier concentration:

Time (in min)	Abs.(feed)	Abs.(strip)	Feed Conc. (in ppm)	Strip Conc. (in ppm)	%E	%R
0	0.869	0	25.132	0	0	0
30	0.584	0.055	16.895	1.601	32.773	6.370
60	0.483	0.204	13.973	5.921	44.399	23.562
120	0.427	0.487	12.364	14.092	50.804	56.071
180	0.329	0.546	9.526	15.803	62.097	62.879
240	0.174	0.667	5.059	19.283	79.887	76.725
360	0.108	0.766	3.147	22.156	87.476	88.155
480	0.049	0.770	1.424	22.280	94.330	88.650