Simultaneous Extraction and Stripping of Methylene Blue: A Liquid-Liquid Extraction and Bulk Liquid Membrane Approach

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ABSTRACT: *In this study, the Liquid-Liquid Extraction (LLE) method was used to demonstrate the extraction of Methylene Blue (MB) from aqueous solutions using 4.48 $\times 10^{(-1)}$ mol/L Phenyl Propiolic acid benzene. The operating parameters like the changes brought by varying pH (liquefied solution pH), diluents, the concentration of extractant, and stripping reagents were evaluated with fixed reaction conditions. A maximum recovery of MB was obtained at pH 7±0.1. Similarly, the maximum stripping efficiency of MB was achieved by the use of 1 N H_2SO_4. The optimized parameter obtained for the recovery of MB from the LLE process was implemented in the Bbulk Liquid Membrane (BLM) technique. The separation and procurement of MB were performed in a single step called the protraction process. The role of pH in the aqueous donor phase, the effect of phenyl propiolic acid concentration in the membrane phase, and the effect of stripping reagents concentration were evaluated in detail to understand the transport mechanism of MB from the aqueous phase to interface and interface to stripping solution.*

KEYWORDS: *Methylene blue; Phenyl propiolic acid; Stripping agents; Bulk liquid membrane; Receiving phase.*

INTRODUCTION

Dyes are extensively used in various industries for coloring fabrics, and it is of great importance in creating visual aesthetics. During the past few years, there has been an increasing concern regarding the residual dye in textiles, as it will be released into the environment. Residual dye is produced when an incomplete or excess of dyes onto textile fiber is incoming out during an aqueous dyeing and washing process [1]. The removal of residual dye present in the wastewater is a tedious process. Conventional treatment techniques such as adsorption, filtration, and sedimentation cannot treat such low-concentration dyes [2-8]. Most of the dyes used in the textile industries are stable and resistant to chlorination and aerobic bio-oxidation [1]. Generally, the dyes are direct, reactive, anionic acid, cationic basic, and non-ionic dispersed dyes [9]. A recent study showed that >100,000 different dyes are manufactured,

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and almost 7×10^5 tons of dyes are annually produced for commercial application [10]

Among various dyes, Methylene Blue (MB) is one of the most extensively used dyes for a range of applications. So, MB was chosen as the target pollutant to demonstrate its removal and recovery efficiency in the Liquid-Liquid Extraction (LLE) and Bulk Liquid Membrane (BLM) process. MB comes under the cationic dye category. It is extensively used for manufacturing coloring paper and as a dye for fabrics, wool, and hair. It's used as a photosensitizer and redox indicator in analytical chemistry. B is a heterocyclic aromatic compound, which is of vital importance in dyeing. Prolonged exposure to MB in humans causes high blood pressure, precordial pain, fever, bewilderment, staining of the skin, urine color change, cyanosis, and anemia [11]. The existing conventional treatment techniques to treat organic dyes present in water are either expensive or inefficient. Hence, there is an urgent need to develop an efficient and economically viable treatment technique to remove dyes from wastewater [12]

Recently, the Liquid Membrane (LM) process has emerged as an economically viable and efficient technique for removing cationic and anionic dyes from industrial wastewater [13]. LLM systems are being studied by various researchers in varying fields [14]. LLM has shown huge potential for the removal of a varity of pollutants. It is found to be highly useful even when the concentration of pollutants is low, where other techniques were proved inefficient [15]. LM is highly selective in nature, and a small amount of carrier is enough to transport the metal ions and dyes continuously. These qualities have served as the unique advantages of LMs over other techniques. The Liquid membranes are classified as Supported liquid membranes (SLM), Emulsion Liquid Membranes (ELM), Bulk Liquid Membranes (BLM), Polymer Inclusion Membranes (PIMs), And Activated Composite Membranes (ACM) [16]. Out of all, BLM is the most suitable method for screening different carrier-mediated transport systems on a laboratory-scale application [17].

Muthuraman et al. reported a study on the separation of MB from synthetic wastewater by the LLE process using benzoic acid [18]. A 99% of dye recovery was achieved from the aqueous solutions at fixed optimized conditions. In this study, the extracted dye present in the membrane phase was recovered using H_2SO_4. The extraction of MB was carried out using the carriers phenol and xylene in the initial phase, and diluent was used in the later phase. It was observed that the rate of extraction is directly proportional to the pH of the feed solution and carrier concentration. Therefore, on increasing the acid concentration using acetic acid, the stripping efficiency was found to increase. More than 99 % of dye extraction was achieved using (0.9 mol or 0.9 mol/L) of phenol. Similarly, 8 N acetic acid was used to strip or recover 99% of the extracted dye from the membrane phase [19].

The studies were carried out to recover azo dyes such as MO and CR from an aqueous solution using TOA as an extractant. It has been observed that the amount of Methyl Orange (MO) and Congo Red (CR) extracted is directly proportional to the amount of Trictylmine (TOA) added. Similarly, anionic dyes can be recovered using an aqueous solution at pH 2.0. The dye present in the organic phase was brought forth into aqueous solutions by adding NaOH, Na_2CO_3, and $NaHCO_3$[20].

~~Several s~~tudies on different types of dyes (cationic and anionic) recovered using LLE have been conducted and reported so far. *Muthuraman et al*. studied the simultaneous extraction and stripping of Methyl Violet (MV), Rhodamine B (RB), and MB from a synthetic dye solution with di-2-Ethylhexyl phosphoric acid (D2EHPA) [21]. The loading capacity of D2EHPA was 6.2, 5.04, 4.86 mg for RB, MV, and MB, respectively. *Akama et al*. reported the partitioning mechanism of MO in a two-phase system [22]. Similarly, the removal of astacryl golden and astacryl blue BG is demonstrated using the LLE process [23]. Recovery of 93% of astacryl golden yellow and 98% of astacryl blue BG was achieved using 2.89×10^{-2} mol/L of salicylic acid in toluene at pH 10 ± 0.1. Similarly, Cibacron Red FN-R extraction using Tetra butyl ammonium bromide (TBAB) has been reported using the LLE process [24]. Recently, benzene was used as an extractant to recover dye from textile wastewater using a solvent extraction method [1, 25].

A cheap, cost-effective, and economically feasible technology to recover dyes from textile wastewater is the need of time. Liquid Membrane (LM) technology demonstrates the selective removal of dye with a simple and efficient way to recover dyes from textile wastewater. LM plays a vital role in biomedicine, hydrometallurgy, ion-selective electrodes, and effluent treatment applications [26]. It's unique features like easiness in the recovery

of materials from a single unit, pollutants removal, non-equilibrium mass transfer, high fluxes, high selectivity, low energy consumption, and reusability [27], have gained the attention of researchers in recent times. This has caused a significant rise in the usage of the LM process for the selective removal of dyes [29-35].

The BLM is the simplest, and most efficient type of liquid membrane [36-38]. BLM technique is cheap due to its relatively small inventory and capital cost. In a BLM, the donor and acceptor phase is separated using a slightly thick layer of immiscible fluid. Hence, the membrane phase is separated from the external phases. BLMs separation has three phases: one organic phase where the carrier transports the target compound from one phase to a mother and two aqueous phases donor and an acceptor. The dye transportation starts from an aqueous donor phase, proceeds through an organic membrane phase, and reaches an aqueous acceptor phase. Usually, a H-type or a U-type configuration according to the solvent's density is used to carry out the procedure [39].

A study was conducted to remove Malachite Green (MG) dye using D2EHPA carrier [40]. While treating textile wastewater, D2EHPA extractant was used to filter out the MG dye. D2EHPA present in n-hexane is a particularly selective carrier that transports MG dye through BLM. The steps that control the experiments' speed in diverse conditions for the extraction of MG in the BLM phase were analyzed. Finally, the liquid membrane proved to be the best MG dye extraction method from textile wastewater [40]. Similarly, the RB dye was extracted using organic solvents [41]. These solvents contained several other organic compounds too, which stayed immiscible in water. This experiment made use of several aliphatic and aromatic stripping reagents like acetic acid, benzoic acid, salicylic acid, and oxalic acid. But, Acetic acid has so far delivered the best results in stripping the content-loaded organic phase to the aqueous phase [41].

In the BLM, flux values were found to be directly proportional to the stirring speed. Also, diffusion was determined as the rate-limiting step in the transport of dye from the feed solution to the membrane phase. When the stirring speed is low (50–300 rpm), the flux increases linearly with speed, and at higher stirring speeds (400–500 rpm) it stays constant [31]. In acidic pH, H^+ ion competed with MB cation and reduced the diffusion of dye. In addition, a carboxyl-based extractant exists as a COOH form and hinders the interaction between the MB molecules. This causes a considerable reduction in the amount of MB extracted. But, at higher pH values (pH 3 to 7), more occur. The existence of the group readily forms a complex with MB and diffuses into the organic phase from the aqueous phase. Hence, the extraction capacity of the extractant for MB increases. Almost 99.6% of the dye was recovered at pH 7 [39, 42].

A Calix [6], an arene-based derivative and a selective carrier for MR through BLM was studied. The selectivity of arena-based derivatives towards MR was the highest among most dyes like methyl violet (MV), MG, MO, MB, and Eosin Gelblich (EG) in LLE experiments. It also increased the effect of salts (NaCl, Na_2SO_4, and Na_2CO_3) on MB concentration and optimized the acceptor phase's pH during the LLE [43].

In this study, simultaneous removal and stripping of MB from textile effluent were demonstrated using phenyl propiolic acid in benzene. In LLE, the affecting parameters were studied; the effect of changing pH, different extractant concentrations, distinct diluents, and divergent stripping reagents were studied in detail. In BLM, the effect of different stirring speeds, different concentrations in the initial feed phase, time, and transport mechanism has been investigated. The optimized condition obtained by treating synthetic MB dye was used to treat the real-time textile wastewater, and the results were discussed in detail.

EXPERIMENTAL SECTION

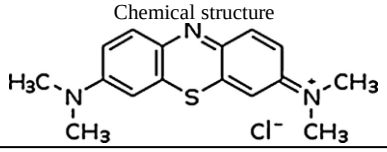
Chemicals

Phenylpropiolic acid, Benzene, MB, H_2SO_4, Xylene, Toluene, and Hexane were procured from Merck and of AR grade. A UV-Visible spectrometer (Spekol 1200, Analytical Jena, Germany) was employed to determine the concentration (λ max) of MB present in that reaction solution. A shaker was used to agitate the solution. (IKA-KS 501). The solvent to extract benzene from the reaction solution was Phenyl Propiolic acid. Distilled water is used to prepare the dye solution, and H_2SO_4 is used as a stripping agent.

Preparation of MB solution

MB is a cationic dye [34]. MB purchased from Sigma Aldrich (CAS No: 122965-43-9) was used as the target compound without any further purification. A kinetic reaction effect of concentration and time was optimized with the different concentrations of MB prepared from

Table 1: Properties of Methylene Blue.

Properties	
Suggested Name	***Methylene blue***
IUPAC name3,7-Bis(dimethylamino)-phenothiazin-5-ium chloride	
CI Name Basic blue 9	
CI number 52015	
Molecular formula $C_{16}H_{18}N_3SCl$	
Molecular weight (g/mol)	319.85
λ_{max}(nm)	662 (Measured value)
Chemical structure	

the stock solution (1000 mg/L). The detailed chemical and physical properties of MB are presented in Table 1.

Analytical procedure for liquid-liquid extraction of dye

The extraction efficiency of the reagents B present in the aqueous solution was evaluated using an organic phase containing Phenyl Propiolic acid and Benzene (mL). The above aqueous (dye solution) and organic solutions were carefully transferred into the 100 mL glass-stoppered bottle. The solution in the bottle was shaken for a reaction time of 30 min at the rate of 100 rpm. Then, the aqueous and organic solution present in the glass-stoppered bottle was transferred to a separating funnel and allowed to settle for 30 min. The aqueous solution was separated and stored in a clean-stoppered bottle for further analysis. The MB concentration present in the initial (mL) and final (mL) solution was measured at the wavelength of 662 nm. The experimental setup of the extraction of MB dye is given in Fig. 1. Further, the distribution ratio (*D*) and percentage of extraction (*E*) were calculated using the following equation [44].

$$D = [dye]_{org} [dye]_{aq} \quad (1)$$

$$E = 100 \times [dye]_{aq0} - [dye]_{aq} \quad (2)$$

Where,

$[dye]_{org}$ is the amount of MB (mg/L) present in the organic phase,

$[dye]_{aq0}$ is the initial concentration of MB (mg/L) present in the aqueous phase,

and $[dye]_{aq}$ is the amount of MB (mg/L) present after the extraction.

Similarly, the stripping reaction was performed with the dilute acid solution using the extracted organic phase from the above steps using a 100 mL stoppered glass bottle. A similar procedure was adopted for both the extraction and stripping reaction (shaken at 100 rpm; reaction time 30 min). At the end of the reaction, the MB concentration present in the aqueous stripping acid solution was measured at 622 nm.

Bulk liquid membrane

The H-type BLM made up of borosilicate glass was used for the continuous or discontinuous (volume is fixed 260 mL) extraction of MB from the aqueous solution (Fig. 2). The inner diameter and depth of the BLM were 70 and 195 mm, respectively. The connection between the feed and strip tube (the bridge between two tubes) was connected with a connection tube of 45 mm in height (from the bottom). The diameter and length of the connection tube or bridge were 30 and 120 mm, respectively. All the experiments were performed at ambient conditions. A fixed concentration of MB (50 mg/L) was maintained in the aqueous feed phase (total volume of aqueous phase 260 mL), and 1 M H_2SO_4 (strip solution volume 260 mL) was used as the strip solution. Both the feed and strip solution were stirred using mechanical stirrers at the rate of 200 rpm. The identical headspace for organic (containing Phenyl Propiolic acid and Benzene) and aqueous (containing MB) phases was maintained throughout the experiments [45]. The MB concentrations were monitored in both phases with regular time intervals.

RESULT AND DISCUSSION

Liquid-liquid extraction experiments

Effect of pH in the source phase

The effect of pH on determining the efficiency of LLE process in the extraction of MB is given in Fig. 3. The aqueous solutions had its pH varying from 4 to 10 with the fixed concentration of MB dye. The pH of the solution was monitored and the pH value of the solution was altered by using 0.01 N H_2SO_4 and 0.01 N NaOH. pH plays a critical role in the effective extraction of MB from an aqueous dye solution. MB is a cationic dye; when the pH of the aqueous solution is less than 3, the H^+ concentration in the aqueous solution considerably increases. The increase in H^+ ion concertation significantly reduces the extraction

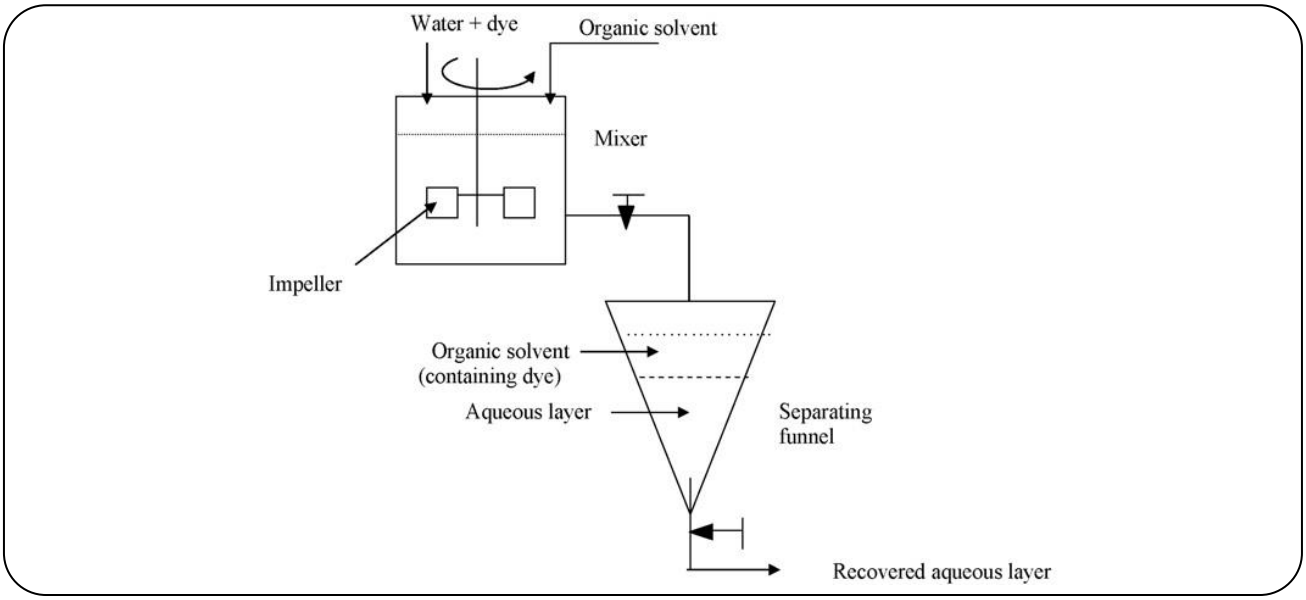


Fig. 1: Schematic experimental setup for liquid–liquid extraction for removal of dye from aqueous solution.

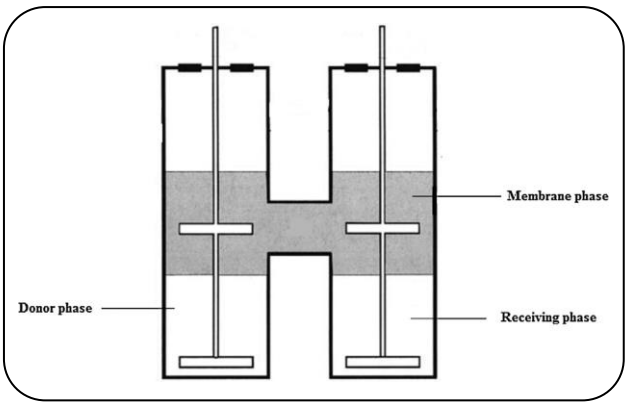


Fig. 2: Schematic experimental setup for bulk liquid membrane for transport of dye from aqueous solution.

efficiency of MB. Hence, the pH optimization studies were performed between the pH of 4 to 10. When the pH increases beyond 3, the H^+ ion concentration in the aqueous dye solution decreases, and the extraction efficiency of MB increases [39]. The extraction efficiency with different pH 4 to 10 is given in Fig. 3. The extraction efficiency was increased with increasing pH and reached the maximum value at 7. When the pH increased further, the extraction efficiency gradually decreased. This might be due to the increase in $^-OH^-$on concentration in the aqueous solution. Further, in basic conditions, the structure of the dye is altered and that gives erroneous results [46]. Hence, the pH of the dye solution was maintained at 7±0.1 for the rest of the studies.

Effect of Phenyl propiolic acid concentration

The concentration of phenyl propiolic acid (extractant) in the organic phase varied from 0.56×10^{-1} to 8.96×10^{-1} mol/L. The distribution ratio (D) was monitored at each concentration and the results are given in Fig. 4. Extraction of MB study was performed in the absence of phenyl propiolic acid in the organic phase. At the end of the reaction, it was observed that no transport of MB to the organic phase and that helped us confirm the importance of phenyl propiolic acid in the optimum extraction of MB from the solution. The distribution ratio of dye increased with increasing phenyl propiolic acid concentration in the organic phase. At a lower concentration of phenyl propiolic acid, the extraction efficiency was much lower due to the non-availability of extractant concentration in the solution. When the concentration of phenyl propiolic acid was increased, the extraction efficiency of MB significantly increased (up to 98.1% with 50 mg/L of MB) and reached a maximum of 4.48×10^{-1} mol/L. There was no further increase in extraction of MB beyond 4.48×10^{-1} mol/L of phenyl propiolic acid concentration. Hence, further extraction studies were conducted at the fixed concentration of (4.48×10^{-1} mol/L) phenyl propiolic acid for the rest of the experiment.

Effect of diluents

The use of a suitable solvent for the LLE process is an important factor in achieving maximum extraction

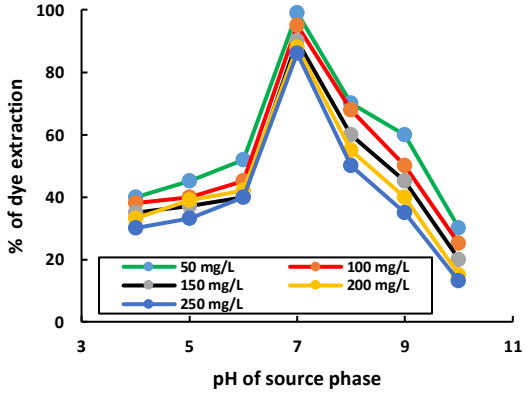


Fig. 3: Effect of pH in source phase(volume of feed 25 mL, carrier concentration 4.48 × 10^{-1} mol/L, volume of organic phase 25 ml and equilibration time 3 min).

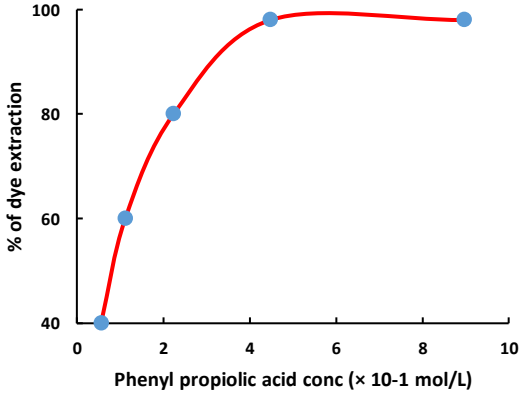


Fig. 4: Effect of carrier concentration (feed 25 mL of 50 mg/L of dye at pH 7 ± 0.1, the volume of organic phase 25 mL, equilibration time 3 min).

efficiency in the extraction of MB from the targeted wastewater. Phenyl propiolic acid is sparingly soluble in water; however, its solubility significantly increased in organic solvents due to the lengthy hydrophobic side chain. A preliminary study was conducted using both aliphatic (hexane) and aromatic solvents (benzene, toluene, and xylene) with Phenyl propiolic acid as the organic phase. Hexane with Phenyl propiolic acid (4.48×10^{-1} mol/L) displayed lesser extraction efficiency at pH = 7 ± 0.1. However, aromatic solvents (benzene, toluene, and xylene) containing 4.48×10^{-1}ol/L of phenyl propiolic acid showed higher efficiency at pH = 7 ± 0.1. The extraction efficiency of MB dye with aliphatic and aromatic solvents is given in Table 2. Table 2 shows, benzene displayed the maximum extraction efficiency of 99.0% at the fixed concentration of (50 mg/L) MB dye and phenyl propiolic acid (4.48×10^{-1} mol/L). At the same time, toluene and xylene showed 95.3 and 89.5%, respectively, at the fixed concentration of (50 mg/L) MB dye and phenyl propiolic acid (4.48×10^{-1} mol/L). Benzene has a high polarity (11.1) compared to toluene (9.9) and xylene (7.4). Similarly, phenyl propiolic acid, a partially polar compound, effectively binds with benzene and displayed maximum MB dye extraction efficiency (99%). However, toluene and xylene are less polar than benzene and showed lesser extraction efficiency than benzene. The above observation clearly shows that solvent plays a significant role in the extraction of MB in the LLE process [39, 40].

Effect stripping agent

The striping of MB from the organic phase completely depends on the nature of the acid and its concentration. The different concentrations of inorganic acid (HCl, HNO_3, and H_2SO_4) were tried for the extraction of MB from the organic phase. A preliminary study was conducted using all three acids and found that H_2SO_4 displayed maximum MB stripping efficiency compared to HCl and HNO_3 [48]. Different concentrations of (0.1, 0.5, and 1 N) H_2SO_4 were used as the striping reagent, and found that 1N H_2SO_4 showed a maximum stripping efficiency (99%) reaction time of 5 min. Increasing the acid concentration any more did not improve stripping efficiency further. The effect of varying concentrations of stripping agent in the extraction of MB in the LLE process is given in Table 3.

Bulk Liquid Membrane Experiments

Effect of stirring speed

Stirring speed is one of the important factors for transporting pollutants from one phase to another. Five different speeds of rpm (100, 200, 300, 400, and 500 rpm) were observed and analyzed to find the optimum speed at which maximum extraction and stripping of MB is achieved in the BLM process. The rate of stripping and extraction of MB with the different stirring rates (100, 200, 300, 400, and 500 rpm) is given in Fig. 5. When the stirring rate increases, the permeability of MB in aqueous to organic and organic to stripping also increases. The permeability of MB is directly proportional to the increase in stirring speed. The increase in permeability was observed up to 400 rpm, and beyond that caused more turbulence, and no significant improvements were observed [31]. A similar observation was reported by other researchers, too [18, 34]. Hence, 400 rpm is observed to be as optimum

Table 2: Effect of diluents on the extraction of dye efficiency.

Diluent	% of dye extraction
Hexane	5.0
Toluene	95.3
Benzene	99.0
Xylene	89.5

Table 2: Effect of stripping agents on the percentage of dye stripping from the organic phase.

Stripping agent	Percentage of stripping
HCl (1N)	75
HNO_3 (1N)	78
H_2SO_4(1N)	99
H_2SO_4 (0.5N)	75

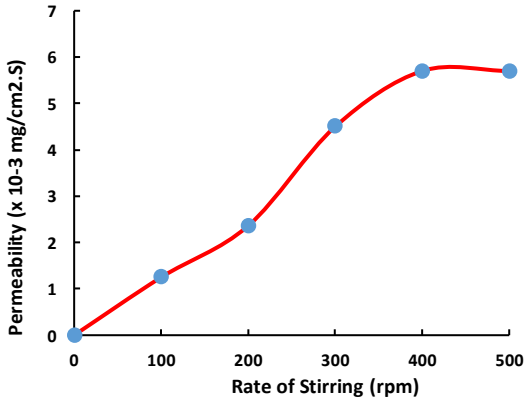


Fig. 5: Effect of stirring speed (volume of source phase 260 mL of 50mg/L of dye at pH 7 ± 0.1, carrier concentration 4.48 × 10^{-1} mol/L, volume of receiving phase 260 mL of 1N H_2SO_4, and effect of time 70 min).

stirring speed for the extraction and stripping of MB in the BLM process.

Effect of pH on the feed phase in BLM process

A BLM experiment was performed to find the optimum aqueous dye solution pH in the BLM process. The pH of the solution was altered from 4 to 10 and the effect of the changes was analysed. The fixed operating parameters like Phenyl propiolic acid concentration (4.48×10^{-1} mol/L in benzene), stirring rate (400 rpm), and MB concentration (50 mg/L) were used throughout the studies. As expected, the MB showed maximum extraction at the pH of 7 and a further increase in pH the extraction if MB was decreasing. This might be due to the increase in cationic (H^+) and anionic (OH^-) properties of the aqueous solution. When the pH is low (4 or 5), the H^+ ion hinders the transport of MB from the aqueous to the organic phase. Similarly, at higher pH OH^- destabilizes the MB and reduces the extraction efficiency. At pH 7, 99.6% of MB extraction was achieved; hence the optimum pH was maintained for the rest of the experiments. The extraction efficiency of MB with different pH is reported in Fig. 6.

Effect of dye concentration in the donor phase

The effect of MB concentration in the BLM process was evaluated by varying the initial or loaded concentration from 50 to 250 mg/L. The stirring rate, Phenyl propiolic acid concentration, and pH were maintained around 400 rpm, 4.48×10^{-1} mol/L in benzene, and 7, respectively. When the concentration of dye was increased from 50 to 250 mg/L, the extraction efficiency of MB decreased considerably. At low concentrations, the MB interacts well with phenyl propiolic acid at the donor membrane interface: hence, the transport of MB increases. Further, an increase in MB concentration decreases percentage transport due to the limited or fixed concentration of phenyl propiolic acid present at the interface. At low concentrations, the interaction between MB and phenyl propiolic acid follows pseudo-first-order kinetics. The reaction rate depends only on the MB concentration because of excess phenyl propiolic acid at the interface. When the MB concentration is increased, the rate of reaction shifts from pseudo-first-order to second-order. The rate of reaction depends on both the phenyl propiolic acid and MB concentration. In BLM process, 98.1, 95.1, 90.5, 88.2, and 86.1% extraction was achieved for 50, 100, 150, 200, and 250 mg/L of MB, respectively. The above observation indicates that the performance of the BLM process is very effective at the low concentration of MB. The percentage of extraction with different concentrations of MB in the BLM process is given in Fig. 7.

Effect of time

Reaction time is one of the important factors in the BLM process. When the reaction started, the MB concentration in the source phase gradually decreased and approached near zero at 80 min. Similarly, in the receiving or stripping phase, the MB concentration increased gradually

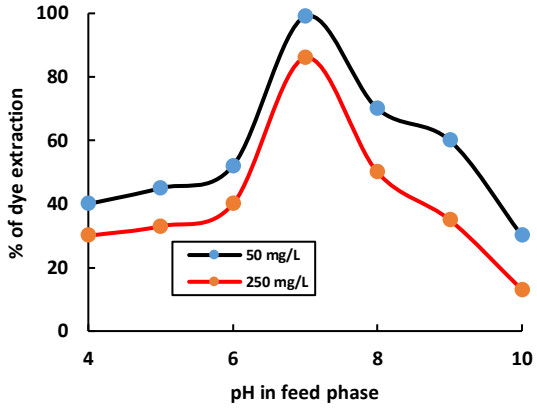


Fig. 5: Effect of pH of feed phase (volume of source phase 260 mL of 50 mg/L and 250 mg/L of dye at various, pH carrier concentration 4.48 ×10^{-1} mol/L, volume of receiving phase 260 mL of 1 N H_2SO_4, rate of stirring 400 rpm and effect of time 70 min. .

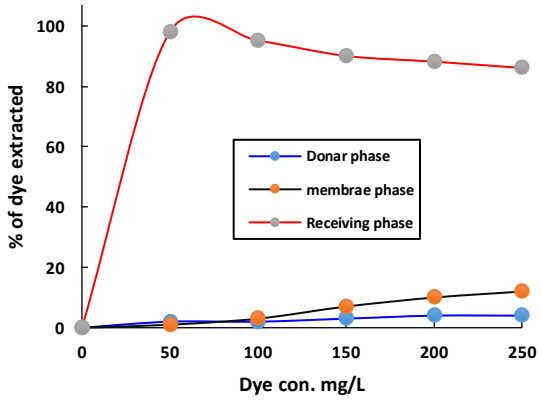


Fig. 7: Effect of dye concentration (volume of source phase 260 mL of different concentration of dye at pH 7± 0,1 carrier concentration 4.48 × 10^{-1} mol/L, volume of receiving phase 260 mL of 1N H_2SO_4, rate of stirring 400rpm and effect of time 70 min).

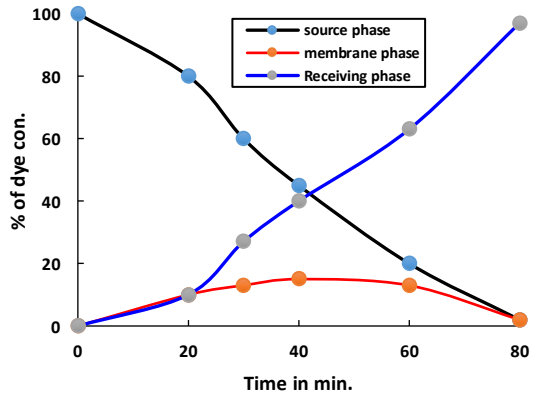


Fig. 8: Effect of time (volume of source phase 260 mL of 50 mg/L of dye at pH 7± 0,1 carrier concentration 4.48 × 10^{-1} mol/L, volume of receiving phase 260 mL of 1N H_2SO_4 and rate of stirring 400rpm).

and reached a maximum (97% recovery) at 80 min. The decrease in MB concentration in the aqueous phase and increase in MB concentration in the stripping phase with respect to time is given in Fig. 8. However, 3 and 2% of MB is left accumulated in the aqueous phase and organic phase, respectively. Further, an increase in time does not make any changes in the concentration of MB in either the aqueous phase or organic phase. The effect of time on the change in concentration of MB in the source phase, membrane phase, and organic phase is given in Fig. 8.

Mechanism for the extraction and stripping reaction

The reaction mechanism of the interaction of phenyl propiolic acid and MB in the aqueous, membrane, or organic and stripping interface is given in Fig. 9. The S and N present in the heterocyclic ring of the MB pull the electron from its adjacent dimethyl aniline groups and make MB more electro-positive. The electrophilic nature of MB at neutral pH (pH 7) readily reacts with phenyl propiolic acid present in the organic phase and forms an MB-Phenyl propiolic acid complex molecule. This MB-Phenyl propiolic acid complex diffuses through the organic or membrane phase and reaches the membrane-stripping solution interface. The presence of 1N H_2SO_4 in the stripping solution readily reacts with MB-Phenyl propiolic acid complex molecule and liberates free MB into the stripping phase. This transport reaction is highly favored in neutral pH 7.

Comparison of LLE and BLM for previous and current work

Transport of dye by BLM and LLE of feed and receiving phase of previous and current work have been compared. For LLE, it requires two steps extraction and stripping whereas in BLM, a single step that is extraction and striping occurs simultaneously. The important parameters of both the work compared and the results are presented in Table 4. It reveals that a maximum percentage of dye is extracted in LLE than BLM. Because BLM process is slow, more or less extraction and striping occur simultaneously.

BLM application for textile wastewater

The optimum parameter found in this study was tested with real-time wastewater. The textile industrial wastewater collected from the nearby area was tested for

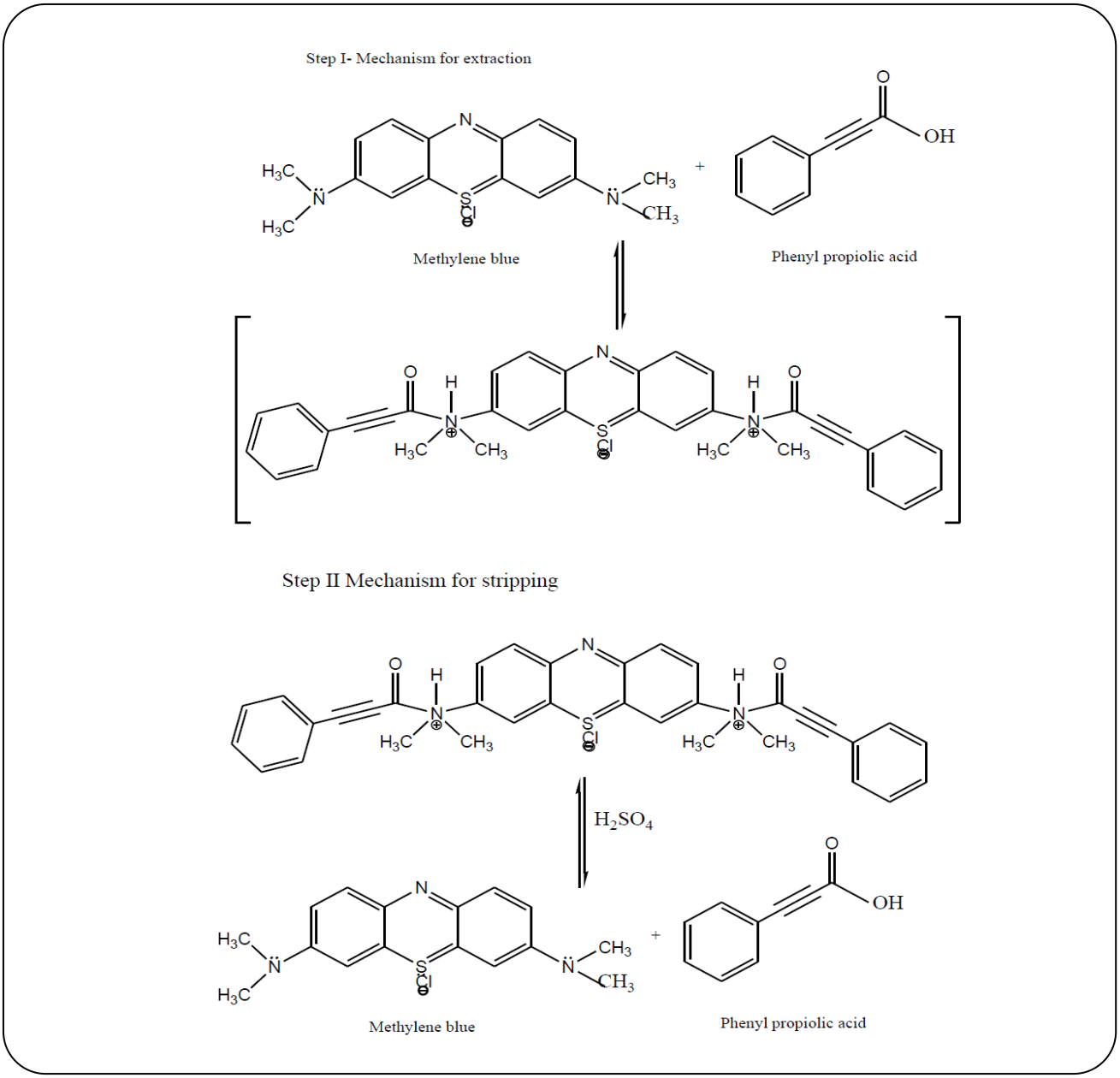


Fig. 9: Extraction and stripping mechanism for MB.

the recovery of MB in the BLM process. In this study, 260 mL of both textile wastewater (containing 50 mg/L of MB and trace of other dyes) and stripping solution (1.0 N H_2SO_4) were fed in the BLM reactor. Similarly, 4.48×10^{-1} mol/L of Phenyl propiolic acid in benzene was used in the organic phase, and the reaction was performed at a fixed time duration (70 min). The results showed that almost 98% of the dye was recovered using textile dye, and the presence of salt does not affect the extraction and stripping efficiency in the BLM process.

CONCLUSIONS

Utilizing phenyl propiolic acid - benzene as an extractant, this work successfully demonstrated the extraction and recovery of MB using the BLM technique. Critical parameters such as pH (pH 7), MB concentration, carrier concentration, stirring speed, and temperature all affect BLM efficiency. It was discovered that as the flux rate increases, the stirring speed increases as well. Within the reaction time of 70 minutes, 99.1% recovery was accomplished, and no substantial transport was detected

Table 4: Comparability study of previous and current work.

Parameters	Liquid-liquid extraction		Bulk liquid membrane	
	Previous work	Current work	Previous work	Current work
Name of dye	Rhodamine B	Methylene Blue	Rhodamine B	Methylene Blue
pH	12±0.1	7±0.1	12±0.1	7±0.1
Extractant	0.8M Phenol	Phenyl Propiolic	0.8M Phenol	Phenyl Propiolic
Concentration		Acid ($4.48\times10^{(-1)}$ M)		Acid ($4.48\times10^{(-1)}$ M)
Diluent	Xylene	Benzene	Xylene	Benzene
Strippingagent	10 M acetic acid	1N H_2SO_4	10 M acetic acid	1N H_2SO_4
Time	5 minutes for extraction and 8 minutes for stripping	3 minutes for extraction and 5 minutes for stripping	Transport time 150 minutes	Transport time 70 minutes
% of extraction	99.5%	99.0%	97.0%	97.0%

after that. In addition, the study used real-time textile wastewater and discovered that BLM had nearly equal extraction (95%) and stripping efficiency. The presence of various organic contaminants in the textile wastewater, as well as the high salt level, could explain the minor loss in efficiency. The proposed technology can be used to recover precious dyes in the textile sector. One of the benefits of this method is that it produces no sludge, and the solvent used in the membrane phase can be reused multiple times.

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