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Removal of Dye from Synthetic Wastewater by Liquid Membrane

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ABSTRACT

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. This work focuses on extracting Methylene Blue (MB), a cationic dye using a simple BLM separation technique from its aqueous phase. It combines extraction and stripping in a single unit operation. The feed phase was an aqueous solution of MB, the solvent chosen was soybean oil for the liquid/organic membrane phase, and tri-octyl amine acted as a carrier. The strip phase was a hydrochloric acid solution for this study. A two-phase equilibrium study was done to choose the correct solvent, carrier, and receiving phase (soybean oil, tri-octyl amine, and HCl) were chosen, which was then followed by a three-phase study. Effect of various parameters like equilibrium time, feed and stripping phase pH, stirring speed, carrier concentration, initial feed concentration, and strip phase concentration were all studied to find out the most optimum working condition for maximum extraction and recovery of MB. The removal efficiency of MB by using soybean oil was found as 92%, at the optimum process conditions for the transport of MB were found as follows: pH in the feed phase (11), pH in the stripping phase (5), initial concentration of MB (20 ppm), carrier concentration (7%) (v/v) TOA and stirring speed (250 rpm), respectively.

Keywords: Bulk liquid membrane, dye (methylene blue), trioctylamine.

ازالة الاصباغ من المحاليل المائية باستعمال الاغشية السائلة

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الخلاصة

تركز هذا العمل على استخلاص صبغة المثيل الازرق (صبغة كاتيونية) من المحلول المائي باستخدام تقنية الفصل بالغشاء السائل، كتقنية مطورة حديثة مقارنة بتقنيات الفصل الاخرى ذات اختيارية واسترجاع وتدفق عالية وبكلفة تنفيذية وتشغيلية قليلة. عملية

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الفصل بالغشاء السائل تتكون من طور التغذية (محلول مائي يحتوي على صبغة المثيل الازرق)، الغشاء السائل وهو المذيب استخدم في هذه الدراسة زيت فول الصويا الذي يحتوي على مادة ثلاثي لوكتيل امين كمادة حامل، وطور الفصل (النزع) والذي هو عبارة عن محلو حامض الهيدروكلوريك. تم دراسة نوعين من المذيبات كغشاء سائل ، ودراسة تاثير عدد من المتغيرات التشغيلية مثل التركير الابتدائي لصبغة للمثيل الازرق والدالة الحامضية وتركير المادة الحاملة وسرعة الخلط وتركيز الحامض في طور الفصل. تم تحديد افضل ظروف تشغيلية لازالة صبغة المثيل الازرق من المحلول المائي بكفاءة 92% باستخدام فول الصويا كغشاء سائل عند دالة حامضية لطور التغذية وطور الفصل 11، 5 على التوالي وبتركيز ابتدائي لصبغة المثيل الازرق 20 جزء بالمليون وبسرعة خلط 250 دورة بالدقيقة وتركيز الحامل 7% نسبة حجمية.

الكلمات الرئيسية: الغشاء السائل، صبغة المثيليلن الزرقاء، النواقل.

1. INTRODUCTION

Colorants like methylene blue are widely used in the textile, paper, plastics, food, and cosmetics industries. Even in very low concentrations, the level of pollutants is obvious and will affect both aquatic life and the food web. Several dyes are hard to degrade. They are usually immune to light, oxidizing agents, and aerobic digestion **(Jodeh, S., et al., 2015)**. Due to their persistence in nature and non-biodegradable characteristics, pollution due to dyes thus poses not only a serious public health concern and many environmental severe problems **(Tahir H., et al., 2008)**. Approximately 15 percent of the total world production of dyes is lost and released in textile effluents during the dyeing process. The release in the ocean of these colored wastewaters is a drastic cause of non-aesthetic contamination, eutrophication, and aquatic life destruction **(Houas A., et al., 2001)**. Although MB is used in some 14 medical treatments and textile dying, it can cause eye injury to humans and animals alike. Inhalation can result in short periods of fast or difficult breathing. At the same time, ingestion through the mouth produces a burning sensation and can lead to nausea, vomiting, abundant sweating, diarrhea, gastritis, mental confusion, and methemoglobinemia. The removal of MB from industrial effluents has thus become one of the most significant environmental concerns **(Abd El-Latif M., Ibrahim A., et al., 2010)**.

Liquid membranes (LMs) are liquids that separate two aqueous phases of the source (feed) and the receiving (product) phases and are immiscible in these phases. These separation systems are being explored widely in many fields such as organic and inorganic chemistry, wastewater treatment, chemical engineering, biomedical engineering, and biotechnology **(Dargo H., et al., 2014)**. Research and development activities within these fields involve various applications of LM technology, such as removal of organic compounds, recovery of precious metals, removal of toxic metals, gas separations, and recovery of pharmaceutical compounds and fermentation products **(Jusoh, N., 2017)**

In the bulk liquid membrane (BLM), the membrane step is interposed between feed and stripping solutions, isolated by a strong barrier (e.g., a glass wall) and thus in contact with both solutions **(Jusoh, N., 2017)**. Due to the large LM phase thickness, the fluxes obtained are too low to make this process competitive with traditional separation processes. BLMs are often used to study novel carrier transport properties and to select suitable stripping solutions. It is, nevertheless, the simplest of all LM configurations and offers an understanding of an LM's separation feasibility for any method of concern **(Bradford A., 2015)**.

2. MATERIALS AND METHODS:

2.1 Preparation of methylene blue solutions:

One gram of methylene blue was taken in a 1000 mL volumetric flask and diluted to the mark with distilled water. Different concentrations; 5, 10, 15, 20, 25, 30, 40 and 50 mg/L were prepared by dilution.

2.2 Calibration Curve:

The concentration of MB was measured using the UV-visible spectrophotometer. A typical MB solution of 1000 mg/L was prepared, and absorbance was measured at different wavelengths to obtain a representative portion of absorbance per wavelength **Fig.1** the wavelength associated with the average absorbance defined by this plot was 664 nm

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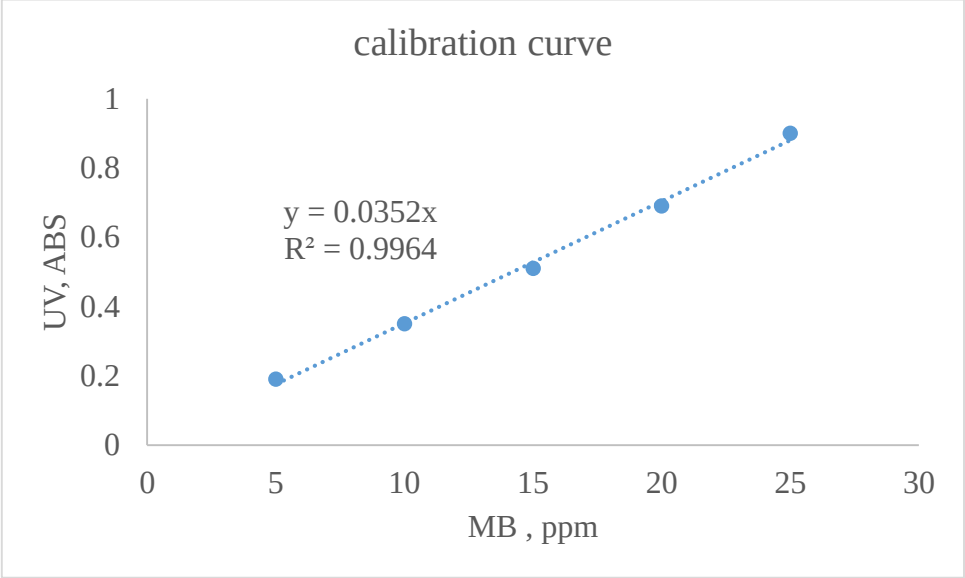

Figure 1. A typical plot of absorbance vs. wavelength for the regular MB solution.

The linear calibration curve between absorbance and concentration was obtained with MB concentrations in the range of 5-25 mg /l (R^2 = 0.9964) as shown in **Fig. 1.**

2.3 Two-phase equilibrium setup and procedure:

The major industries that emanate these pollutants (methylene blue) are the textile industry. The two-phase balance distribution studies were conducted by combining the same amount of methylene blue solution (aqueous) and organic solution in a conical flask (250 mL), as shown in **Fig.2.** The mixture was stirred continuously using a magnetic stirrer at a steady stirring rate of 120 rpm for a duration of 6 h. The mixture was then kept undisturbed for some time until the separation process took place. The aqueous phase has been carefully separated from the organic phase. Samples were obtained from an aqueous solution every 1 hour. The concentration of methylene blue in the aqueous phase after extraction was measured by UV Vis absorption spectroscopy.

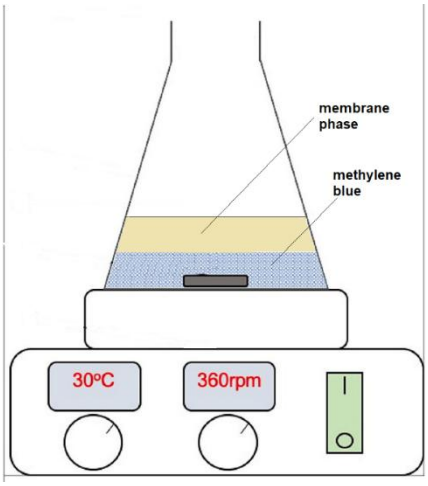

Figure.2. Two-phase setup.

Samples were obtained from the feed and strip side at regular intervals (1 hour) during the experiment.
Performance of the two-phase balance distribution and the three-phase transport results were obtained in terms of per cent removal, determined by equation Eq. (1)

$$\% \text{ Removal} = [(Cfin - Cf)/Cfin] \times 100 \quad (1)$$

Where $Cfin$ is an initial concentration in the feed phase (ppm), Cf is the final concentration in the feed phase following transportation (ppm).

2. Results and discussion:

Selection of Best suitable Organic Phase condition

The selection of compatible solvent for desired transport of the target element is a prime issue in liquid membrane techniques. The main factors that play central to the issue during solvent selection are low viscosity, ability to regenerate, chemically stability, non-toxicity, non-corrosive, and high distribution coefficient (higher extraction percentage) with no miscibility with aqueous phases. In contrast, the solvent in a liquid membrane is selected such that it should have a density fairly different enough from that of a feed stream.
Study of two-phase equilibrium was conducted; 20 ppm MB of 12 and an equal volume of the liquid membrane were added. The mixture was then placed on the stirrer at 120 rpm for 6 hrs. Various solvents such as soybean oil, rapeseed oil, and mustard oil followed this technique. The best extracting solvent to choose the best carrier among (TOA, DOA, and Aliquat 336) and strip phase among (HCl, salicylic acid, and acetic acid) has been selected.
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.
The experiment was performed to find suitable solvent among rapeseed oil, soybean oil, and mustard oil which distribution coefficient is shown in **Table 1.**

Table 1. Distribution Coefficient of MB in different solvents.

Solvents	Distribution Coefficient
Soybean Oil	9.69
Rapeseed Oil	4.74
Mustard Oil	0.69

The experiment was performed to find suitable carriers among tri-octyl amine, di-octyl amine, aliquot 336, whose distribution coefficient is shown in **Table 2.**

Table 2. Distribution Coefficient of MB in various carriers.

Carriers	Distribution Coefficient
Tri-Octyl Amine	9.14
Di-Octyl Amine	7.33
Aliquat 336	5.45

The experiment was performed to find suitable stripping agents: HCl, salicylic acid, and acetic acid, which distribution coefficient is shown in **Table 3.**

Table 3. Distribution Coefficient of MB in Strip Phase.

Strip Phase	Distribution Coefficient
HCl	10.26
Salicylic Acid	7.94
Acetic Acid	7.34

Therefore, the correct solvent, carrier, and receiving phase (soybean oil, tri-octyl amine, and HCl) were chosen from two-phase experiments, respectively, as this combination gave the highest distribution coefficient in all of the above cases.

Transportation of solute through three-phase BLM

Three-phase transportation studies were performed through the BLM configuration with the two-phase equilibrium studies' operating conditions. In addition, the concentration of the stripping phase was optimized for efficient transportation of solute from LM to strip phase. Contrary to the two-phase study where the carrier is needed for complexation purposes, three-phase BLM involves a de-complexation phenomenon whereby the complex is dissociated at the membrane-strip interface and frees itself for back-diffusion the feed-membrane interface and thereby re-complexation of solute with a stripping agent.

3.1 Effect of feed phase pH on MB removal

One of the major factors that can make a different extraction from the source phase to the receiving phase is the source phase solution's pH. In order to study the effect of pH, the pH of the aqueous feed phase is increased/change from (8-12) because of the cationic nature, and it's adjusted by adding some drops of 0.1M NaOH and that lead to an increase in the extraction percentage of the source (feed phase), pH of the feed effects on the transport efficiency of the MB as represented in the **Fig. 3.** the aqueous solution of MB 20 ppm concentration but of different pH values ranging from 8 to 12 were used to study extraction and recovery efficiency. It is viewed that dye extracted percentage increased up to pH 11. A good charge distribution is shown when a pH of 11 is used for the feed solution, making it basic, and methylene blue has a negative charge. Therefore, MB forms a complex carrier at the feed/organic phases interface. Recovery of MB by strip phase is maximum at pH 11. Since the maximum extraction and even recovery was at pH 11 of the feed solution so for upcoming studies, it was maintained at pH 11.

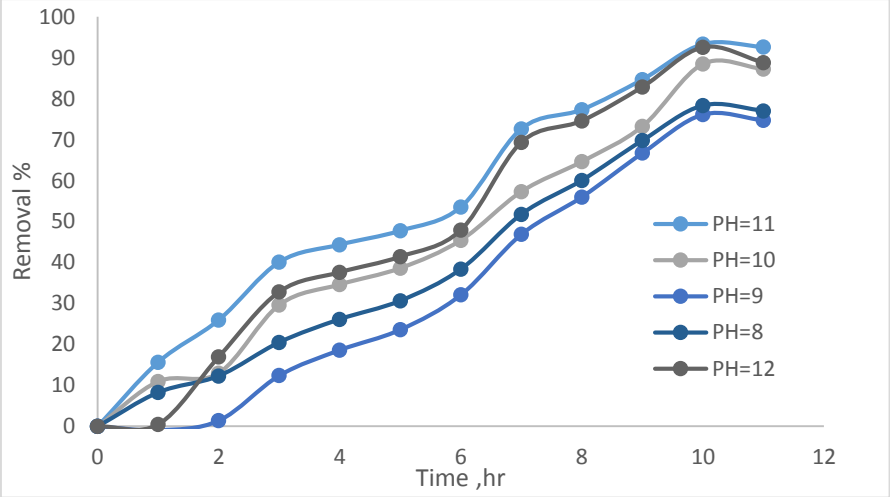

Figure 3. Effect of feed phase pH on MB removal, 300 rpm; 20 ppm of MB; 1M of HCl and 10% w/w TOA.

Table 4. show the distribution coefficient of MB at different feed pH. As can be seen from this table, these coefficients values are high at 11 pH and decrease as the feed's pH increases **(Fig. 3).**

Table 4. Distribution coefficient of MB at different feed pH.

pH	8	9	10	11	12
K_d	0.2737	0.5284	0.5905	0.8502	0.7111

3.2 Effect of stripping phase pH on MB removal

To study the effect of the strip phase pH, the pH of the stripping phase was varied in the range of (1- 6). The experiments were carried out at an ambient temperature of (20±2 °C) and mixing speed at 300 rpm. The experimental results are presented in **Fig. 4.** The removal efficiency of MB increased significantly when the pH of the stripping phase increased up to 5, in which the extraction efficiency reached 95%, as shown in **Fig. 4.** If the MB-complex is not completely

stripped, the membrane phase becomes saturated with complex, and the transport rate may therefore decrease. **(Muthuraman et al., 2009)** also investigated the same behavior. They concluded that this behavior could be due to the saturation of driving force for diffusion through the bulk liquid membrane due to an increase in MB-complex concentration at the membrane-strip interface. Therefore pH of the strip phase should be lower than that of the feed phase for efficient transport of MB. There is an insignificant increase in the removal efficiency observed at pH levels of five since the maximum extraction and even recovery was at pH 5 of the stripping, **Fig. 4.**

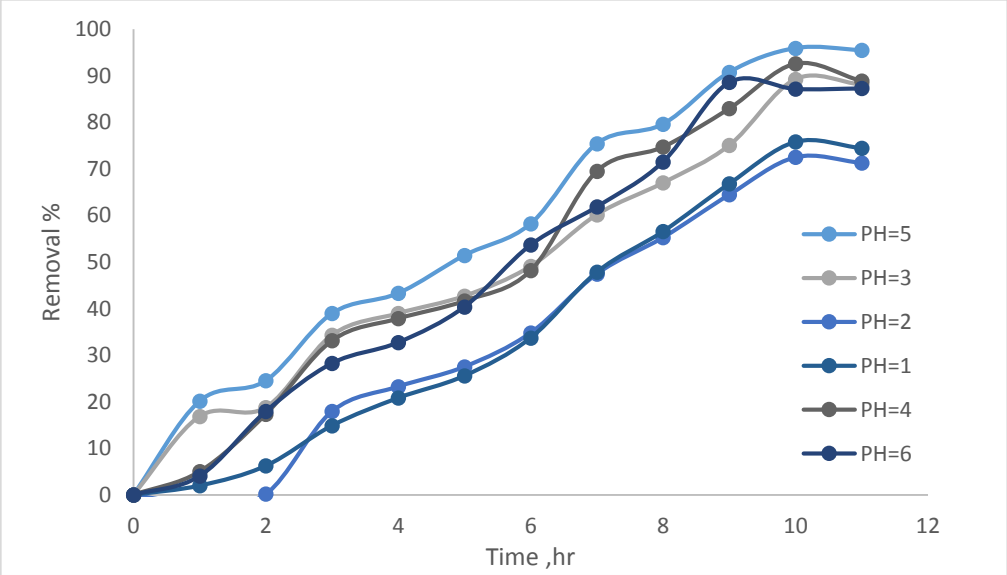

Figure 4. Effect of pH stripping on MB removal.

The values of distribution coefficients for MB as a function of pH of stripping phase are listed in **Table 5.** Increasing the pH in the stripping phase greater than 5 decreases the distribution of MB between the receiving and membrane phase, as shown in **Table 5.** The highest value of K_d was at pH=5**.**

Table 5. Distribution coefficient of MB at different stripping pH.

pH	1	2	3	4	5	6
K_d	0.372093	0.384444	0.607692	0.63	0.892308	0.803922

3.3 Effect of carrier on MB removal

The effect of tri-octyl amine concentrations in soybean oil constituting the membrane phase on MB transport efficiency across the membrane. In order to investigate the effect of carrier concentration in the organic phase on the transport efficiency of MB, the experiments were carried out by varying the amount of TOA as a carrier in the organic membrane phase in the range from 7% to 10% (w/w) in soybean oil at room temperature of (20±2 °C) and 300 rpm stirring speed. The other conditions, such as pH of the feed phase 11, stripping phase 5, MB concentration 20 ppm, and volume, were not changed.

It is a general trend that the effectiveness of membrane transport increases as carrier concentration increases and gets saturated at some point. After that, carrier concentration delays the diffusion rate as the viscosity of the membrane increases. The experimental results are shown in **Fig 5.** The extraction efficiency was about 92% at (7%) w/w carrier.

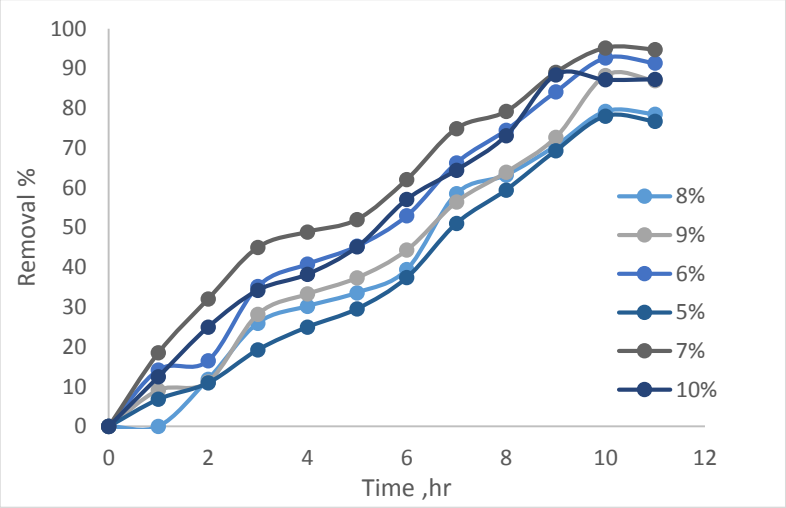

Figure5. Effect of TOA% on MB removal.

MB extraction increased with increasing carrier concentration up to 7% but then was decreased probably due to an increment of viscosity of LM. Since maximum extraction and recovery of MB through BLM was at a carrier concentration of 7%, further experiments were carried out with this value, as shown in **Table 6.**

Table 6. Distribution coefficient of MB at TOA %.

Carrier Conc.%	5	6	7	8	9	10
K_d	0.2	0.511	0.784	0.529	0.582	0.525

3.4 Effect of stirring speed on MB removal

Smooth agitation or stirring during feed and stripping phases may facilitate the transportation of MB dye through BLM. The effect of stirring speed in the 100-300 Rpm range on the efficiency of transporting the MB dye. MB transport efficiency leads to higher entry and exit flux values. As a result, the rate of transportation of MB from the feed phase to the LM phase and the LM phase to the stripping phase increased with a higher stirring speed of 250 rpm. Feed and strip stirring are necessary where the flux increases with increasing stirring rate due to a decrease in the thickness of the diffusion boundary layers at both membrane interfaces, minimizes the feed side's polarization, and provides better penetration of MB in the strip. Some mixing of feed and strip solutions was found at a low, stirring speed **(Yang and Fane, 1999),** and similar effects were observed at a slower stirring speed. MB conveyance decreased at low, stirring rates, **Fig. 6.**

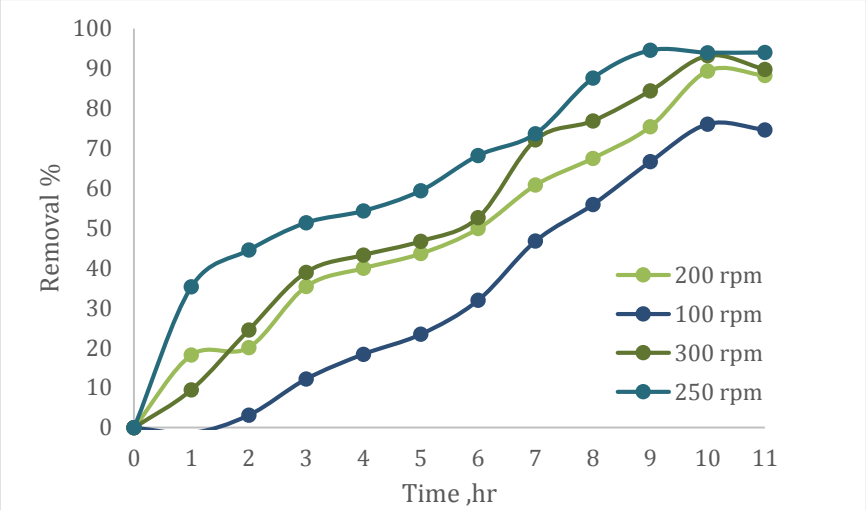

Figure 6. Effect of stirring speed.

The values of distribution coefficients for MB as a function of stirring speed are listed in **Table 7.** Increasing the stirring speed greater than 250 Rpm decreases the distribution of MB. The highest value of Kd was at stirring speed, as shown in the table below.

Table7. Distribution coefficient of MB at a different stirring speed.

Stirring speed	100	200	250	300
K_d	0.128	0.156	0.195	0.184

3.5 Effect of initial feed concentration

In industrial effluents, the concentration of methylene blue can be varied greatly. It is, therefore, necessary to study its influence on the initial concentration. The variation of initial feed concentration on the transport of MB was investigated by varying the dye concentration in the range of 20 to 100 ppm. **Fig. 7.** Shows the effect of initial feed concentration on extraction and stripping results. The maximum transport rate occurred at an initial concentration of 20 ppm, in which the extraction efficiency was 92%.

According to Fick's law, an increase in the initial feed concentration will raise the MB driving force in both the stagnant aqueous layer and organic phase, increasing the overall metals ions flux rate through the bulk liquid membrane. However, the percentage transport of metal ions decreases with increasing initial concentration in the aqueous feed phase. This decrease may be due to the metal ions' driving force between the aqueous and organic phases. Perhaps this could be attributed to the fact that the membrane phase quickly saturated with the metal ions affecting mass transfer in the feed/membrane interphase.

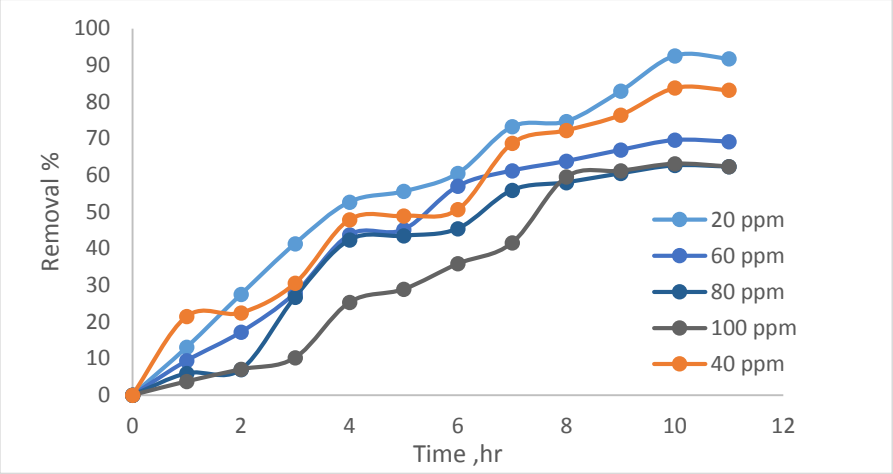

Figure 7. Effect of initial concentration on MB removal.

The distribution coefficient of MB under initial concentration in the range of 20 to 100 ppm was estimated as shown in **Table 8.** The distribution of MB between the feed and membrane phase decrease with the increase of initial concentration in the feed phase.

Table 8. Distribution coefficient of MB at different initial concentration.

Initial conc. ppm	20	40	60	80	100
K_d	0.5	0.4895	0.35	0.31	0.296

It is clear from the table, the kinetic constant and the rate of the feed and stripping transport have the highest value at 20 ppm.

3.6 Effect of concentration of HCl in the strip phase

Stripping phase selection plays an important part in the success of the LM technique. Generally, an acidic solution is used for the stripping phase, and in this study, HCl is used as a stripping agent for this experiment. Experiments were conducted with different stripping solutions ranging from 0.25 M to 1.5 M HCl with an initial feed concentration of 20 ppm, feed pH 11, and carrier concentration of 7% (w/w) in soybean oil. The experimental results are reported in **Fig. 8.** It was observed that with an increase in the concentration of the stripping phase up to 1 M, the extraction of the solute increased. The maximum extraction was 92%. However, after 1 M concentration, the extraction starts decreasing.

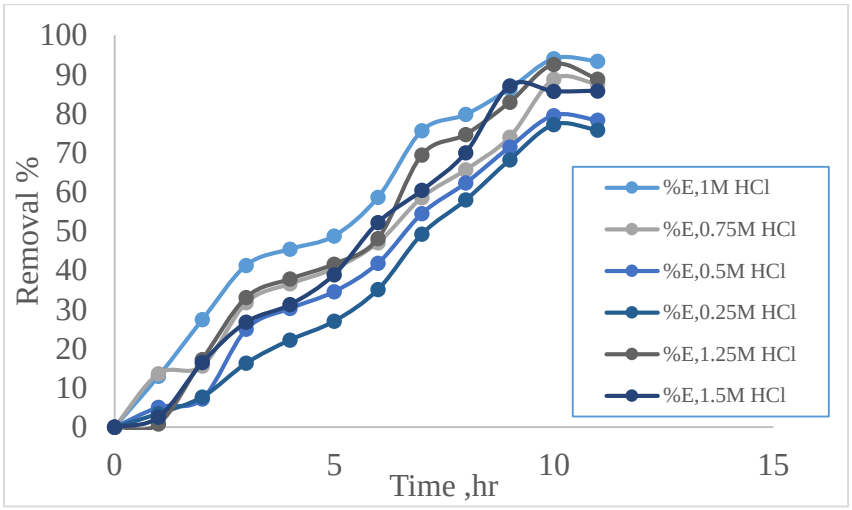

Figure 8. Effect of acid concentration in stripping phase, 250rpm; 20 PPM of MB and 7% w/w TOA.

As the concentration of the acid decreases, the methylene blue transferred between the aqueous solution and the membrane decrease. The curves obtained are not very dependent on the time of methylene blue, and after 9 hours of operation, 85% of the initial methylene blue is transferred for 20 ppm. This phenomenon occurred due to the limitation of the receiving phase's ability to strip more methylene blue after 8 hours, as shown in **Fig. 9.**

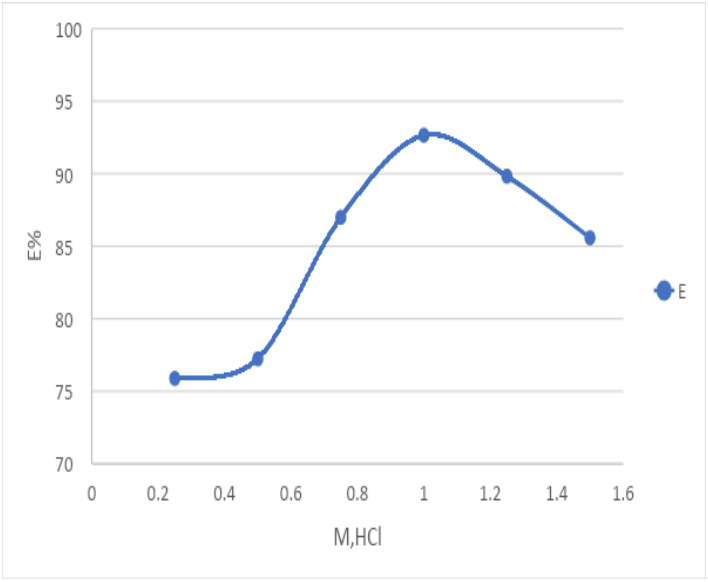

Figure 9. Effect of acid concentration on max removal.

The max removal of the methylene blue from the experimental results is shown in **Fig. 9.** With the acid concentration. It's very clear the effect of the acid concentration was in the presence of a carrier in the membrane phase. The carrier complex is formed at the feed-membrane interface,

which results in the increase of mass transfer rate through the interface, and hence higher separation is achieved, as shown in **Table 9.**

Table 9. Distribution coefficient of MB at different HCl molarity.

HCl ,M	0.25	0.5	0.75	1	1.25	1.5
K_d	0.35	0.42	0.49	0.52	0.43	0.45

The results demonstrated that the optimum extraction and stripping (removal %) of MB by using soybean oil could be obtained at the following operating conditions: pH of the feed phase 11, pH of stripping phase 5, initial MB concentration 20 ppm, the carrier concentration in the membrane phase 7 % (w/w) TOA, and stirring speed (250 rpm).

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