Application of Emulsion Liquid Membrane Process for Cationic Dye Extraction

Manal Adnan Mohammed\textsuperscript{a}, Wasan Omar Noori\textsuperscript{a} and Huda Adil Sabbar\textsuperscript{b}

\textsuperscript{a}Chemical Engineering Department-University of Baghdad
\textsuperscript{b}Al-khwarizmi Engineering College -University of Baghdad

Abstract

In the present work studies were carried out to extract a cationic dye (Methylene Blue MB) from an aqueous solution using emulsion liquid membrane process (ELM). The organic phase (membrane phase) consists of Span 80 as emulsifier, sulfuric acid solution as stripping agent and hexane as diluent. In this study, important factors influencing the extraction of methylene blue dye were studied. These factors include H\textsubscript{2}SO\textsubscript{4} concentration in the stripping phase, agitation speed in the dye permeation stage, Initial dye concentration and diluent type.

More than (98\%) of Methylene blue dye was extracted at the following conditions: H\textsubscript{2}SO\textsubscript{4} concentration (1.25) M, agitation speed (200) rpm, dye concentration (10) ppm and the diluent type was hexane.

Keywords: dye extraction, Methylene Blue (MB), cationic dye, emulsion liquid membrane.

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1- Introduction

Discharging dyes within effluents of textile industries and other waste water is one of the major environmental problems [1, 2]. Dyes are commonly utilized in many industries such as paper and ink industries, textiles, cosmetics, dyeing & printing, leather, and plastics, used for coloring their final products [1].

Dyes are very toxic, carcinogenetic, risk to aquatic living organisms irritating to the skin; therefore, dyes are dangerous to human beings as well as environment [3].

Water properties are seriously affected by presence of colors [2]. A present of a little amount of dyes (less than 1ppm for some dyes) in water can be undesirable and highly visible [3].

There are many types of dyes [4]:

- Anionic dyes (acidic) which are water soluble dyes, containing one or more sulfonic acid substituents or other acidic groups.
- Cationic dyes (basic) which give brilliant colors with special fastness for acrylic fibers.
- Direct dyes which are water soluble because of sulfonic acid groups and can be used on linen, cotton, wool, rayon, nylon and silk.
- Reactive dye which the colour has a very long life because of the chemical reaction; silk cotton and wool can be dyed with this type of dyeing of Fabrics.
- Dispersive dyes which are insoluble in water

A cationic dye (Methylene blue) is a heavily used by printing industry. It is used also as an indicator and stabilizer in chemical industry. Many ways have been implemented to remove dyes from wastewater including as physical treatment (sedimentation, crystallization, gravity separation) or conventional treatment methods (solvent extraction, reverse osmosis, ion exchange, electro dialysis, electrolysis and adsorption) [5-8]. Removal of dyes by conventional treatment techniques can be difficult because of its resistant to aerobic bio-oxidation and the stability of dyes against light and oxidize agent [5].

In last year’s several physico-chemical decolorization processes have been improved in term of aflined pollutions removal, such as electrochemical, membrane separation and flocculation [6], Membrane technology has emerged as an alternative cost-effective, simple and safe method for dyes recovery and color removal from textile effluent [7].

In liquid membranes (LM) process a solute (solid species dissolve in the liquid membrane) transfer from a feed phase to stripping phase through an immiscible organic phase [9, 10]. Liquid membranes process has gained a crucial role for separation in different applications, such as biomedicine, ion selective electrodes, effluent treatment and hydrometallurgy [11].

LM have many advantages compared to other membrane methods such as high selectivity, efficient, high fluxes, high potential for removal cationic and anionic dyes [12-14].
According to configuration definition, LM is an effective technique for treating waste water contaminated with cationic and anionic dyes [9]. LM can be classified as emulsion liquid membrane (ELM), and supported liquid membrane (SLM) and bulk liquid membrane (BLM) [15, 16].

In emulsion liquid membrane (ELM), the membrane phase consists of (surfactant and diluent); a surfactant which is used to stabilize the emulsion and an organic diluent has low viscosity [17].

There are many advantages arising from using (ELM) technique such as, simplicity, high selectivity, rapid extraction, low energy, further, its high efficiency also this method is providing high interfacial area and the ability to remove a very low concentration of the solute among the existing methods.

However, ELM shows some disadvantages which limited the commercial application of it such as instability of emulsions and the difficulty of demulsification after extraction [18-20].

Emulsion liquid membrane system has many variables; so that In this present work some variables were chosen to be constant depending on previous experiments and researches, these variables are: volume ratio of organic phase to stripping phase = 3:1, emulsification time = 40 sec (because more than this time the w/o emulsion would be difficult to permeate the feed phase and then cannot extract MB dye), surfactant (span 80) concentration 3% and agitation time = 3 min.

2- Materials and Equipment

2.1. Materials

Normal hexane (supplied by Chem.-Lab NV, purity 95%, Belgium) was used as diluent; also heptane (supplied by B.D.H Laboratory Reagent, purity 98%, England) and kerosene (supplied by midland Iraqi refineries company) were used for some experiments. Sorbitan monooleate which is commercially known as (span 80) (supplied by Wuhan Kemi-Works Chemical Co., Ltd) was used as a surfactant for emulsion stabiliser. Sulfuric acid (H₂SO₄) was used in the stripping phase as a stripping agent. Methylene blue (MB) (supplied by HiMedia, purity 80%, India) was used as a cationic dye.

To prepare all aqueous solutions deionised water was used. All the chemicals were used as received without further purification. The chemical structure of the methylene blue (C₁₆H₁₈N₃SCL) is given in Fig. 1. By dissolving accurately weighted of MB dye in distilled water the dye solution was prepared.

2.2. Equipment

Equipment was needed to experiments ELM such as high speed homogenizer mixer for emulsion preparation (ULTRA-TURRAX JANKE & KUNKEL KG) and (Heidolph) RZR 2020 over head stirrer was used for extraction experiments. The absorbance of dye sample was determined using UV visible spectrophotometer (Thermo Genesys 10 UV Electron Corporation Madison W1 53711, USA) was used for absorbance measure.

3- Methodology

3.1. Calibration Curve

Methylene blue was detected in the solutions using UV-visible spectrophotometer at 664 nm wavelength. To measure any unknown concentration of samples, calibration curve was made by prepared various MB concentrations 5, 6, 7, 8, 9, 10, 11 and 12 ppm. We get the plot showed in Fig. 2 from the UV results with absorbance (in Y-axis) versus concentration of MB (in x-axis).

![Absorbance vs Concentration of MB](image)

Fig. 2. Calibration curve of MB absorption

3.2. Experimental Work

The experimental work consists of three stages. First stage: the emulsion was prepared by adding sulfuric acid (with a various concentrations) to organic phase in a beaker of 200 ml volume by using high speed mixer (homogenizer) at a constant rotational speed 10000 rpm for 40 second. Second stage: (dye permeation stage) by adding the emulsion which prepared in the first stage into a beaker of 1000 ml volume containing 250 ml of MB dye solution (with a different values of concentrations) using overhead stirrer (with various rotational speed) for 3 minutes. Third stage: in this stage MB dye was extracted by settling after 15 minutes and the samples were measured by uv spectrophotometer. Fig. 3 shows a schematic diagram for emulsion liquid membrane for extracted MB dye from aqueous solution.

![Schematic Diagram](image)

Fig. 3. Schematic diagram for emulsion liquid membrane for extracted MB dye from aqueous solution.
At different values of operating conditions, several parameters were examined as shown in Table 1.

Table 1. Operation conditions and extraction parameters

| No. | Operating conditions | Values        |
|-----|----------------------|---------------|
| 1   | H₂SO₄ conc.          | 0.25-1.5 M    |
| 2   | Agitation speed      | 50-250 rpm    |
| 3   | Dye conc.            | 6 -16 ppm     |
| 4   | Diluent type         | hexane, heptane, kerosene |

By using UV the concentration of dye ion was determined by absorbent of light through the dye solutions. The percentage of extraction efficiency was calculated by using the following equation:

\[
\text{Extraction Efficiency} \% = \frac{C_0 - C}{C_0} \times 100
\]  

Where: \(C_0\): Initial dye concentration in the feed phase at \(t = 0\) (ppm). \(C\): final dye concentration in the feed phase at the end of the extraction process (ppm).

4. Results and Discussion

4.1. Effect of H₂SO₄ Concentration in the Stripping Phase

Effect of sulfuric acid concentration (H₂SO₄) of the stripping phase on extraction of the MB was studied from 0.25 M to 1.5 M.

Fig. 4 shows that the increase in sulfuric acid concentration increases the percent of MB extraction. At 1.25 M of H₂SO₄ conc maximum extraction of 98.7% was occurred. Further increase (higher than 1.25M) would decreases the extraction efficiency because reduces less active H⁺ to decompose the complex the higher strength of the acid solution which results in a lower activity coefficient of hydrogen ions.

The properties of Span80 may be degraded and destabilized the emulsion which resulting a high rate of rupture by the reaction products [22].

4.2. Effect of Agitation Speed

Agitation speed during extraction is an important factor. 50, 100, 150, 200 and 250 rpm are the speeds used Fig. 5. The results of the influence of agitation speed on the extraction showed that the increasing of the agitation speed from 50 to 200 rpm increased the shear force which acts on the globules of emulsion (the emulsion globules would be smaller) because the area of mass transfer increased.

Beyond 200 rpm not only the extraction percent decreases slightly, also makes the emulsion unstable which affected and caused implying the rupture of the emulsion, the solute expulsion already extracted from the stripping phase to feed phase [23].

The optimum agitation speed was 200 rpm for a higher extraction percent 96.8%.

Fig. 5. Effect agitation speed on extraction of MB (diluent = hexane, H₂SO₄ concentration 1.25 M, dye conc. 10 ppm)
4.3. Dye Concentration

The effect of initial dye concentration in the feed phase on the extraction process was investigated at different concentrations ranging from 6 to 16 (ppm) (these concentrations were chosen because that the products of textile factories do not exceed this range) Fig. 6. The extraction percentage showed that a high concentration of methylene blue dye in the feed phase decreases the extraction efficiency, in agreement with the extraction technique by ELM that is effective at low concentration of solute.

The extraction percent decreased for concentrations above 10 ppm, this is due to the membrane saturation of the feed phase droplets by MB, and this behavior has also been shown in some studies [22, 24]. The optimum extraction percent (98.7%) was achieved for 10 ppm of a dye concentration.

Fig. 6. Effect dye concentration on extraction of MB (diluent = hexane, H2SO4 concentration 1.25 M, agitation speed 200 rpm)

4.4. Effect of Diluent Type

Experiments were done under optimum conditions as mentioned previously by also using heptane and kerosene as diluents. It was noticed that the diluents influence the efficiency of ELM process. Fig. 7 presents the behavior of methylene blue dye extraction using hexane, kerosene and heptane as diluents; it shows that hexane provided a better extraction percent. Also, the hexane shows higher efficiency of extraction than that result using kerosene and heptane.

Dielectric constant (the permittivity of a substance to the permittivity of the free space) of solvent was the reason caused this behavior; hexane has a dielectric constant (1.89) that is lower than the dielectric constant of kerosene (2.1) and heptane (1.92) that made the rate of transfer higher. And the water oil emulsion produced using hexane is much more stable than that prepared using heptane and kerosene [23].

Fig. 7. Effect of diluents type on extraction efficiency: H2SO4 concentration 1.25 M, agitation speed 200 rpm, dye conc.10 ppm

5- Conclusion

The extraction of the methylene blue (MB) was the main objective of this study. The study of an emulsion liquid membrane process using several important factors indicated that:

1- For high H2SO4 concentrations, SPAN 80 loses its surfactant properties, and then the optimum concentration of acid was 1.25 M.
2- Increasing the agitation speed causes rupture of emulsion.
3- Increasing the initial concentration of MB dye above 200 rpm decreases the extraction efficiency because the saturation of the stripping phase droplets by the dye.
4- The optimal diluent was hexane because of that the lower dielectric constant.

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تطبيق عملية الغشاء السائل المستحلب لاستخراج الصبغة الكاتيونية ميثيلين الزرقاء

Methylene Blue

مثال عدنان محمد، وسن عمر نوري، و هدى عادل صبار

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الخلاصة

يصف العمل الحالي تطبيق عملية الغشاء السائل المستحلب على استخراج صبغة كاتيونية (ميثيلين الزرقاء) من محلول مائي. طور الغشاء يتكون من 80% من محلول مائي. طور الغشاء يتكون من 80 span80 كمستلحب ، محلول حامض الكبريت كعامل لانتزاع الصبغة و الهكسان كمخفف.

في العمل الحالي، تم دراسة العوامل ذات التأثير الواضح على استخراج صبغة الميثيلين الزرقاء. وتشمل هذه العوامل تركيز $\text{H}_2\text{SO}_4$ في طور الانتزاع، وسرعة التحريك عند مرحلة تخلل الصبغة، وتركيز الصبغة الابتدائية ونوع المادة المخففة.

أكثر من 98% من صبغة الميثيلين الزرقاء تم استخلاصها عند الظروف الآتية: تركيز الحامض $\text{H}_2\text{SO}_4$ (1.25) مولاري، سرعة التحريك (200) دورة في الدقيقة، تركيز الصبغة (10) جزء في المليون. وفضل نوع مخفف كان الهكسان.

الكلمات الدالة: إزالة صبغة، الميثيلين الأزرق (MB) ، الصبغة الكاتيونية ، الغشاء السائل المستحلب.