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# Extraction and desextraction of a cationic dye using an emulsified liquid membrane in an aqueous solution

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## Abstract

The removal of methylene blue ($C_{16}H_{18}ClN_3S$) as a cationic dye which might be rejected in textile industry wastewaters during its production or its use was the main objective in this work. The extraction was performed by an emulsified liquid membrane (ELM) consisting of sorbitan mono-oleate (SPAN80) and di(2-ethylhexyl)phosphoric acid (D2EHPA) as a surfactant and an extractant respectively. The internal phase used was sulphuric acid.

Effects of important factors (concentration of $H_2SO_4$, stirring velocity, quantities of organic, aqueous, phases, external and emulsified phases, concentrations of extractant and surfactant were studied according to the stability of the ELM. Then using favourable conditions for a good stability of the membrane, the extraction and of methylene blue (MB) from an aqueous solution was investigated. Optimal conditions were then determined and the extraction efficiency reached 98.15%. The desextraction of this dye was performed at 81.91% and the membrane was regenerated.

*Keywords:* emulsified liquid membrane; emulsion W/O; extraction; methylene blue; desextraction

## 1. Introduction

Being soluble in aqueous and organic solutions, reactive dyes are used in homogeneous catalysis. They form complexes that possess remarkable electro-catalytic properties. Among 8000 dyes used in the textile industry, around 120,000 tons of reactive dyes are produced per year accounting over 60% of all dyes for cellulosic fibers [1]. A loss of 1 to 2% in production and 1 to 10% in use are a fair estimate. For reactive dyes in the textile industry, their loss can be about 4% [2]. Important quantities of synthetic dyes are discharged in the environment from industrial effluents [3].

A number of these chemicals which are more and more applicable in various fields, are left in the industrial waste and inevitably become a hazard to the environmental [4]. Reactive dyes contain chromophoric groups such as azo, anthraquinone, triarylmethane and some reactive groups (vinyl sulphone, chlorotriazine, trichloropyrimidine) and are not completely biodegradable [5]. Many dyes and pigments are toxic in nature with suspected carcinogenic and mutagenic effects that affect aquatic biota and humans [6].

Due to increasingly stringent restrictions on pollutant contents of industrial effluents, it is necessary to remove dyes from wastewater before they are discharged into the environment. The removal of colour from textile wastewater is

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one of the major environmental problems because of the difficulty to treat water by conventional methods. To remove dyes from reaction products, separation treatments and recycling or adapted reclamations are thus required. Many works have studied several methods for dyes removal such as biological treatment [7], coagulation/flocculation [8], chemical oxidation and photocatalytic processes [9,10], membrane processes [11,12], and adsorption [13].

The extraction process by emulsified liquid membrane ELM has been achieved for the first time by N. N. Li [14] and reaches now the practice stage which attaches great importance to its application in various fields: since, several works had emerged as the extraction of heavy metals [15], or precious metals [16], the extraction of heteropolyanion complexes [17], the separation of hydrocarbons [18,19], penicillin separation [20] etc. In medicine for example, the hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ which is the main constituent of human bones and teeth is widely used as implants or coatings to prostheses [21,22] and to study the effect of Ca/P ratio on the texture and morphology of this product, an extraction by ELM which was consisted of a biodegradable emulsifier and a fatty acid as extractant was used [23]. In hydrometallurgy, and using an ELM that was consisted of Span80 (sorbitan mono-oleate) as the surfactant, copper extraction was performed and effects of different parameters of the extraction process was studied using LIX-84 and sulphuric acid as the extractant and the internal phase respectively [24]. With the same emulsifier, the extraction of uranium from an aqueous solution was conducted by the extractant TOPO (trioctylphosphine oxide) in the presence of a thinner to 60% paraffin alkanes $C_{12}$ [25]. On the other hand, the selective extraction of gallium from acidic solution containing other components (Fe, Co, Ni, Zn, Cd, Pb, Cu and Al), was conducted by ELM that was composed of ECA4360J as the surfactant, in kerosene as the thinner, TOPO (trioctylphosphine oxide) as the extractant and HCl as the internal phase [26]. In biotechnology, extraction of penicillin G has been optimized by using an emulsifier mixture consisting of ELM Span80/ECA4360J in kerosene and Amberlite LA-2 as an extractant [27]. And in chemistry generally, the extraction of organic acids and many other products can be extracted using emulsified liquid membranes [28].

The stability of the emulsified liquid membranes is very important and it must be optimized before their use. A good stability according to the composition of the membrane has being reported in different studies [17, 29-31].

Methylene blue ($C_{16}H_{18}ClN_3S$) is among the most often cationic dyes used. The objective of this work was to recover this dye under optimal conditions using an extraction process by an emulsified liquid membrane. The method consisted to contact the aqueous phase to be treated with a water-oil emulsion (W/O) which was formed of an organic phase (membrane) and an internal aqueous solution. Before extraction, a preliminary study of the emulsified liquid membrane was essential to deduce the favourable conditions for the emulsion stability. The recovery of the membrane in order to another use was also important to study carrying out a back-extraction (desextration) of the dye.

## 2. Stability of the emulsion

To ensure the stability of W/O emulsion, the method of tracer which was in this case $H^+$ ion of the internal phase, was chosen because this tracer is detectable by a pH-meter easily. The external phase was distilled water, pH and the known variation of acidity leaded to the rupture of the emulsion. The rupture rate (*Tr*) was defined by equation 1 as the percentage of the volume (*Vr*) of the internal phase expelled by breaking into the external phase compared to the initial volume (*Vi*) of the internal phase.

$$T_r = \frac{V_r}{V_{in}} \times 100 \qquad (1)$$

### 2.1 Composition of the membrane

The membrane for extracting the complex ($C_{16}H_{18}ClN_3S$) was consisted of bis (2-ethyl hexyl) phosphoric acid (D2EHPA) as the extractant, hexane "Riedel de Haen" as the thinner and sorbitan monooleate (SPAN80) "Federa" as the surfactant. This emulsifier nonionic ester was used to slightly acidic or alkaline and promoted an emulsion (W/O) with marked lipophilicity (HLB = 4.3).

### 2.2 Procedure

Emulsions were made using a homogenizer ULTRA-Turrax T 18-10; a volume of 15 ml of $H_2SO_4$ (concentration optimized) and 15 ml of organic phase (membrane) consisting of 4% (SPAN 80), 10% (D2EHPA) and 86% hexane,

was introduced into a beaker tall form. The disperser positioned at the interface was maintained for 5 minutes at constant temperature (25°C) and at a speed of 2000rpm. Then, the emulsion prepared was dispersed in a beaker containing 150ml of distilled water at known pH. The mixture was agitated by a stirrer propeller type RW20 Kjank & Kunkel, at a speed of 200 rpm. The pH variation of the external phase was monitored using a pH-meter type HANA Hi 8519N.

### 2.3- Determination of bursting volume (Vr)

From the material balance according to equation (2), the expression of the volume expelled by the rupture of the internal phase to the external phase was deduced from this equation.

$$V_r[H^+]_i = (V_r + V_{ex})[H^+]_t - V_{ex}[H^+]_o \qquad (2)$$

$[H^+]_i$: concentration of $H^+$ in the internal phase before contact
$[H^+]_o$: concentration of $H^+$ in the aqueous phase before contact
$[H^+]_t$: concentration of $H^+$ in the external aqueous phase at time t
$V_{ex}$: Volume of external phase before contact

### 2.4 Effects of operating parameters on the stability of the emulsion

In order to determine favourable conditions giving a stable emulsion, the following factors were monitored: stirring speed, emulsification time, tracer concentration, extractant and surfactant concentration, internal phase concentration, ratio of the membrane volume on the volume of internal aqueous phase (O/A). The effects of these parameters were studied by determining the rupture rate from equation (1) by measurements of the external phase pH.

• *Time of emulsification*

The figure 1 shows that the time of emulsification has an influence on the stability of the membrane. The rupture rate was studied according to different times of emulsification from 2 min to 7 min, in the following operating conditions: stirring speed: 200rpm, O/A: 1, Vex/Vem.: 10, D2EHPA: 6% Span80: 6%, thinner: hexane, contact time: 10min.

For a low emulsification time, the rupture rate is high relatively within 10 min of contact time. This can be explained by the shear of the internal phase resulting large droplets that can coalesce rapidly entraining the film rupture of the membrane. Emulsification for 5 min gives a low rupture rate.

• *Stirring speed*

The stirring speed from 100 to 300 rpm was studied at fixed emulsification time (5min) and the other operating parameters were kept identical to those of the previous experiment. From the figure 2, an average speed of 150 rpm can be chosen for two reasons; a high speed must be avoided because it would cause significant shearing of the interfacial film, and a low speed is not recommended for an appreciable extraction kinetically.
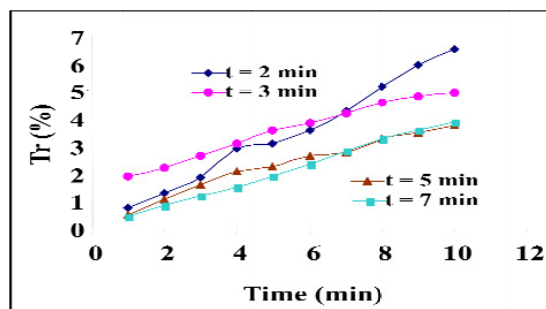


Fig.1. Effect of the emulsification time on the rupture rate.
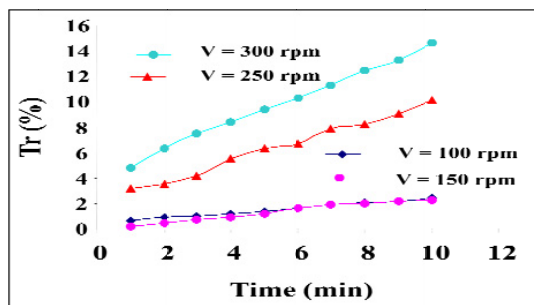(stirring speed: 250 rpm, O/A: 1, Vex / Vem.: 10, D2EHPA: 6% Span80: 6%,thinner: hexane)

Fig.2. Effect of the stirring speed on the rupture rate.
(emulsification time : 5min, O/A: 1, Vex / Vem.: 10, D2EHPA: 6%, Span80: 6%, thinner: hexane)

• *Concentration of the extractant*

The increasing of the extractant mass which has a high viscosity, improves the stability of the emulsion. Indeed, below 6% of extractant, the rupture rate reached a very low value.

• *Concentration of the surfactant*

The mass of the surfactant that is more viscous than the extractant, stabilizes the membrane. Above 8% of surfactant, the rupture rate 4 is below 1%.

• *Concentration of $H_2SO_4$ in the internal phase*

The acid concentration from 0.5 M to 1.5 M of the internal phase was studied in the following operating conditions: agitation speed: 150 rpm, O/A: 1, Vex./Vem.: 10, D2EHPA: 6% Span80: 6% thinner: heptane, contact time: 10min.

The experimental results obtained showed a constant rupture rate (approximately 1%) correspondent to an acid concentration equal to 0.5M. Beyond this concentration, the rupture rate increased slightly of about 1.58% for an acid concentration equal to 1.5 M. The increase of this rupture rate could be explained by the partial hydrolysis of Span80 which is catalyzed by protons. The reaction products may degrade the properties of surfactant Span80 and destabilize the emulsion resulting a high rupture rate. The 1M acid concentration of the internal phase can be regarded as a concentration limit not to exceed and 0.5M will be chosen as one of the operating conditions.

• *Ratio (O/A)*

In the operating conditions chosen just above, the effect of volume ratio of the membrane on the volume of internal aqueous phase (O/A: 1 to 3) was followed. The results showed that the increase of O/A implies a decrease of the rupture rate; this can be explained by the fact that the increasing of the membrane volume causes an increase of the emulsion viscosity (high viscosity is generally favourable for the stability of the emulsion). However, a high ratio O/A creates a very thick film on the membrane, slowing the transfer of the solute. The O/A ratio equal to 1 would be a good choice if the stability of the membrane and the kinetics of extraction were considered.

## 3. Extraction of methylene blue

### 3.1 Experimental Procedure

The membrane prepared as mentioned above, was composed of Span80 (6%), D2EHPA (6%) and hexane (88%) as surfactant, extractant and thinner respectively. The internal phase was a solution of $H_2SO_4$ (0.5M). These operating conditions were determined previously and which provided a stable emulsion.

Using a mechanical stirrer (150rpm), this emulsified membrane was dispersed in a beaker containing 150mL of the solution to be treated (external phase). The volume ratio of the external phase on the emulsified volume Vex/Vem was equal to 10. The initial concentration of the complex in the external phase was equal to 10mg/L.

The concentration of the residual complex methylene blue at different reaction times ranging from 3 to 15 minutes was determined by measuring the absorption intensity using a visible spectrophotometer (Boeco S-24). The wavelength 665nm was determined experimentally and was used in these conditions. The kinetics of extraction was followed with up taking samples of 2mL which were analyzed to determine the concentration of the residual complex methylene blue from a calibration curve carried out at pH 6 at concentrations ranging from 0 to 10mg/L. The extraction efficiency was calculated by equation 3.

$$Y_{ext} = \left[1 - [(C_{fext} \times V_{fext})/(C_{0ext} \times V_{0ext})]\right] \times 100 \qquad (3)$$

$V_{0ext}$: initial volume of the external phase
$V_{fext}$: final volume of the external phase.
$C_{0ext}$: initial concentration of MB in the external phase.

$C_{fext}$: final concentration of MB in the external phase.
$Y_{ext}$: Extraction yield.

### 3.2- Optimal extraction

The extraction of MB by the emulsified liquid membrane was studied according to the following factors: volume ratio of the external phase on the emulsion volume (*Vex/Vem*), stirring speed, concentration of extractant D2EHPA, initial concentration of (BM) in the external phase, contact time and pH of the external phase.

#### • Ratio Vex/Vem

To study the influence of the *Vex/Vem* ratio on the kinetics of extraction, different values of this ratio from 3 to 10 were used. The results showed that for high Vex/Vem ratio (beyond 10), the extraction efficiency was low (57% for a ratio of 10). This can be explained by the phenomenon of swelling (water passage from the external aqueous phase to the internal phase). The increase of the volume emulsion would cause the decrease of the membrane film thickness. The emulsion was very unstable. The optimal value of *Vex/Vem* was around 5 and the performance was about 70%.

#### • Stirring speed

The speeds used are 150, 200, 250 and 280 rpm. The results of the influence of stirring speed on the kinetics of extraction showed that the increasing of the stirring speed beyond 250rpm caused high shear, implying the rupture of the emulsion and the expulsion of the solute already extracted from the internal phase to external phase. This causes a decrease in the extraction yield. For low stirring speeds, the kinetics was slow. The optimum stirring speed was in order of 200rpm for a higher extraction yield until 90.3%.

#### • Mass of the extractant

The weight percentages of the extractant in the membrane tested were 7%, 8% and 9%. The increase of the quantity of the extractant provided better efficiency of the extraction. The optimum percentage was 9% corresponding to a stable membrane and which gave the best efficiency 99.9%.

#### • Concentration of BM in the external phase

To study the influence of the dye concentration in the external phase on the extraction kinetics, different values ranging from 30 to 100 mg/L were studied. The extraction yields indicated that a higher initial concentration of methylene blue in the external phase decreases the extraction yield, in agreement with what the technique of extraction by emulsion liquid membrane which is effective for solutes at low concentrations. For concentrations above 10 mg/l, the extraction yield decreased slightly this is due to the saturation of the internal phase droplets by methylene blue. The best extraction yield was obtained for a dye concentration about 10 mg/L with an extraction yield equal to 99.9%.

#### • Contact time

The emulsion remains stable during 7 min, beyond this contact time the concentration of the solute in the external phase increases because from the rupture of the membrane (leakage of the solute from the internal phase to the external phase). The best extraction efficiency of methylene blue was obtained at 7min which may be considered as an optimal contact time (Fig.3).

#### • pH of the external phase

In this experiment the kinetics of extraction of methylene blue was studied as a function of pH (Fig. 4). Indeed, the external phase pH affected the extraction yield, among the three values used, pH 5 seems to give the best result. The effect of pH from 4 to 6 is quadratic; pH 5 must be considered as an optimized factor.
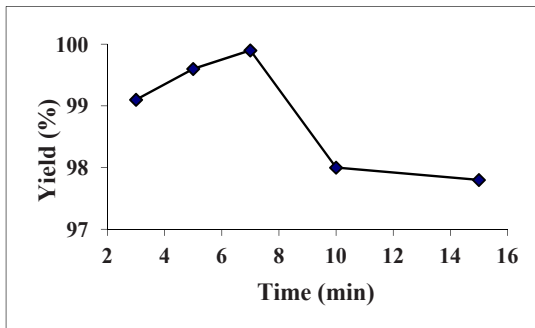
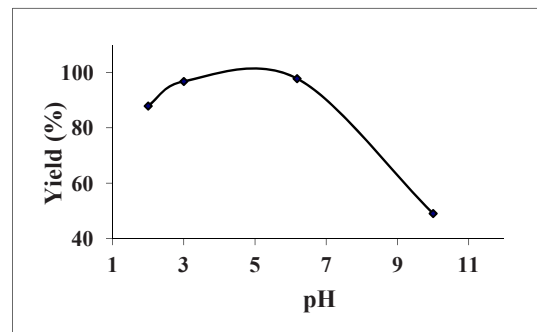Fig.3. Optimization of the contact time on the extraction of MB by ELM

Fig.4. Optimization of the initial pH the extraction of MB by ELM

## 4. Regeneration of the membrane

After studying the stability of the membrane and determining the optimal conditions to attempt the maximum of the extraction efficiency, the regeneration of the membrane is now another objective of this work. This procedure allows an inverse process which is called back-extraction and which depends essentially on the nature of the acid used in the internal phase and its concentration. In this perspective sulphuric acid and hydrochloric acid were tested using different concentrations 0.5M, 1M and 1.5 M. The regeneration process consisted to break down the emulsion and to separate the membrane (organic phase) and the internal phase. The breaking of the emulsion was obtained by chemical means, using octanol as a destabilizing [31,32].

### 4.1 Procedure

The extraction of methylene blue was carried out in the conditions obtained previously. A decantation within 30 minutes allowed to separate the treated water (external phase) from the emulsion. The concentration of the residual dye in the external phase was determined by the spectrophotometer and the final volume of the external phase was also measured. Then the membrane containing the dye extracted was broken with 10 ml of octanol stirred moderately to separate of the internal phase containing the dye from the organic phase (membrane). Figure 5 resumes the experimental procedure.
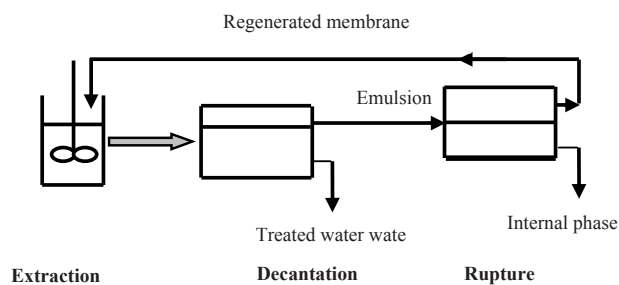


Fig.5. Regeneration of the membrane

### 4.2 Results and discussion

The dosage of the methylene blue in all aqueous phases was performed by spectrophotometric method as indicated above. The quantity of MB extracted in the membrane ($M_{MB}$) was determined from the material balance presented by equation 4, the yield of the extraction ($Y_{ext}$) and the back-extraction ($Y_{b-ext}$) were calculated from equations 5.

$$M_{MB} = [(C_{0ext} \times V_{0ext}) - (C_{fext} \times V_{fext})]/1000 \qquad (4)$$

$$Y_{b-ext} = \left[ (C_{f\,int} \times V_{f\,int}) / (C_{0ext} \times V_{0extt} - C_{fext} \times V_{fext}) \right] \times 100 \qquad (5)$$

$V_{0ext}$: initial volume of the external phase
$V_{fext}$: final volume of the external phase.
$V_{fint}$: initial volume of the internal phase.
$C_{oext}$: initial concentration of MB in the external phase.
$C_{fext}$: final concentration of MB in the external phase.
$M_{MB}$ : mass of MB
$Y_{b-ext}$: Extraction yield.

Table 1. Experimental results of the extraction and the back-extraction of MB.

| Acid | [acid] M | $V_{0ext}$ mL | $V_{f\,ext}$ mg/L | $V_{f\,int}$ mg/L | $C_{0\,ext}$ mg/L | $C_{f\,ext}$ mg/L | $C_{f\,int}$ mg/L | $Y_{ext}$ % | $Y_{b-ext}$ % |
|---|---|---|---|---|---|---|---|---|---|
| **H₂SO₄** | 0.5 | 100 | 75 | 32 | 10 | 0.31 | 23.93 | 97.68 | 78.4 |
|  | 1 | 100 | 71 | 40 | 10 | 0.26 | 20.10 | 98.15 | 81.91 |
|  | 1.5 | 100 | 65 | 44 | 10 | 0.77 | 12.78 | 95.00 | 59.19 |
| **HCl** | 1 | 100 | 71 | 39 | 0.93 | 0.93 | 16.39 | 93.40 | 68.44 |

Experimental results are summarized in table 1. Sulphuric acid   seems to give results better than those obtained by hydrochloric acid. The best performance was obtained with sulphuric acid 1M giving a stable emulsion relatively with a higher extraction yield (98.15%) and a higher desextraction yield (81.91%). The type and the concentration of the acid in the internal phase are then important to take into consideration.

## 5. Conclusion

The extraction of the cationic dye methylene blue (MB) ($C_{16}H_{18}ClN_3S$) was the subject of this work. The study of an emulsified liquid membrane consisting of Span80 and D2EHPA as a surfactant and an extractant respectively according to different important parameters showed that the stability of the emulsion W/O requires certain operating conditions. Indeed, for high concentrations of $H_2SO_4$, the SPAN80 loses its surfactant properties. Increasing the stirring speed causes a rupture of the emulsion. The increase of the O/A ratio leads to an increase in the viscosity of the emulsion making the transfer slow probably. Increasing the ratio Vext/Vemul causes the phenomenon of osmosis (swelling). Increasing the concentration of the extractant and the surfactant stabilizes the emulsion and makes the membrane more viscous slowing the diffusion of the solute. Taking into account the stability of the liquid membrane emulsion, the optimum operating conditions for the extraction yield (98.15) of the complex ($C_{16}H_{18}ClN_3S$) and the desextraction yield (81.91) which  depends of the nature and the concentration of the acid used in the internal phase, are: concentration of acid in the internal phase: 1M, speed of agitation: 200 rpm,     O/A: 1, Vex / Vem: 5, percentage of the extractant in the membrane: 9%, percentage of the surfactant in the membrane: 6%, pH of the external phase: 5 and the solvent is hexane. It would be interesting to apply the membrane in a real wastewater and in a continuous system, with a regeneration of the membrane and its reuse according to the process outlined above.

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