Remove of a mixture cationics dyes in aqueous solution by a green emulsion liquid membrane

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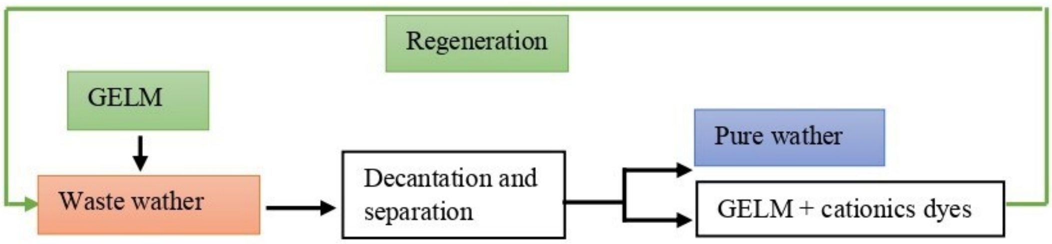
GRAPHICAL ABSTRACT



Application of a green emulsion liquid membrane to remove a mixture malachite green and rhodamine B.

ABSTRACT

The objective of this work is the treatment and purification of an aqueous solution loaded with a mixture of dyes, malachite green (MG) and rhodamine B (Rh-B) using a green emulsified membrane GELM. The proposed GELM process consists of a surfactant (Span 80), an internal phase (sulfuric acid) and a diluent (soybean oil). A Box-Behnken design was implemented to optimize the operating parameters. Three factors were varied: the mass percentage of Span 80, the concentration of the internal phase and a volume ratio V_{ext}/V_{em}, while keeping the other parameters constant.

The results of the optimization give an extraction yield of the dye mixture of 99.77% under the following optimum conditions:
10% by mass for Span 80, a concentration of 0.5 M for the internal phase and a V_{ext}/V_{em} volume ratio of 7.

Keywords: Box-Behnken design, green emulsion liquid membrane (GELM), mixture dyes, pollution control, soybean oil.

1. Introduction

GELMs, or emulsified liquid membranes without organic solvents, are an innovative approach that consists of completely replacing organic solvents with biological hydrophobic materials, thereby further limiting the environmental impact of the process (Venkateswaran, P., et al. 2019) (Kondo, K., et al. 2016).

Green emulsified liquid membranes (GELMs) are an advanced separation technique that uses emulsions as a barrier to selectively extract specific compounds from complex mixtures (Sarmah, P., et al. 2017).

This system combines the advantages of conventional liquid-liquid extraction processes with those of modern membrane technologies, providing a more efficient, energy-efficient method that is adaptable to a variety of applications (Kumar, A., et al. 2020), (Kumbasar, R. A. 2015).

The process is based on the selective transport of a solute across the liquid membrane.

This solute migrates from the external phase to the internal phase via the organic phase, where it is concentrated in the receiving phase. Unlike other membrane techniques, GELMs enable solutes to be concentrated in the internal phase while purifying the external phase. The organic solvent and extractants (low-cost, non-toxic extraction agents) can be recovered and reused, improving cost-effectiveness and environmental impact (Shin, H. S., et al., 2001), (Goyal, V. K., et al. 2018).

GELMs find applications in various fields, including wastewater treatment and environmental decontamination, precious metals and minerals recovery, biotechnology and pharmaceutical industry and chemical industry (Rajendran, A et al., 2018). Auparavant, plusieurs solvants verts à base d'huile végétale ont été utilisés dans différentes membranes liquides émulsifiée vertes GELM (P.A Thakur, 2022), (Othman et al., 2016), (Jusoh et al., 2017) , (Jusoh et al., 2020), (Sujatha et al., 2021), (Sujatha et al., 2022), (Daraei et al., 2019), (Zereshki et al., 2021), (Kumar et al., 2019a), (Kumar et al., 2018), (Kumar et al., 2019).

In this study, the application of soybean oil as a non-toxic diluent for the preparation of a green liquid membrane (GELM) to remove water pollution from a mixture of cationic dyes was investigated. The emulsified liquid membrane prepared was composed of Span80, H_2SO_4 and soya oil. Optimisation of the operating parameters with a significant influence on the extraction yield of the dye mixture (malachite green and rhodamine B) was carried out using response surface methodology. The Box-Behnken design was used to determine the optimum conditions for obtaining the greatest dye response.

2. Materials and methods

2.1. Reagents and materials

The two dyes used (4-[(4-dimethylaminophenyl)-phenyl-methyl]- N,N-dimethyl-aniline and [9-(2-carboxyphenyl)-6-diethylamino-3-xanthenylidene]-diethylammonium chloride) are known respectively as malachite green ($C_{23}H_{25}ClN_2$) and Rhodamine B ($C_{28}H_{31}ClN_2O_3$). They were purchased in powder form from Fluka, with a reported purity of ≥98% for malachite green and ≥99% for Rhodamine B, and conforming to analytical-grade standards (ISO 6353-1).

The green emulsified liquid membrane used to extract the mixture of Rhodamine B (**Fig.1**) and Malachite Green (**Fig.2**) dyes was composed of Span80 (sorbitan monooleate), a lipophilic ester-type non-ionic surfactant (HLB = 4.3) supplied by Sigma Aldrich and used in the preparation of the organic phase.

The soya oil produced by Alwafia , conforming to Codex Alimentarius standards for edible oils, was used as a thinner. It is a stable product with a primary function. Analytically pure sulphuric acid (≥98% purity), obtained from Fluka, was used, conforming to ISO 6353-2 standards for analytical reagents. The Ultra-Turrax T8 homogeniser is a Junk & Kunkel RW20 type mechanical agitator fitted with a marine propeller, was used to create a double emulsion of water, oil and water (W/O/W). The device conforms to DIN EN ISO 12100 safety standards for machinery.

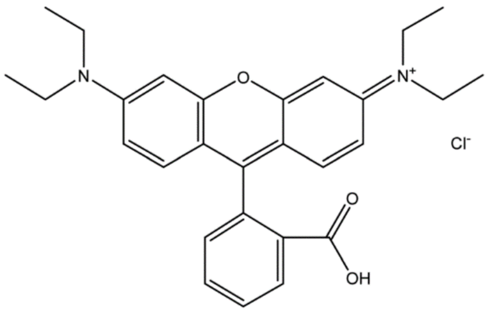


Figure 1. Chemical structure of rhodamine B. (Yusuf et al., 2022).

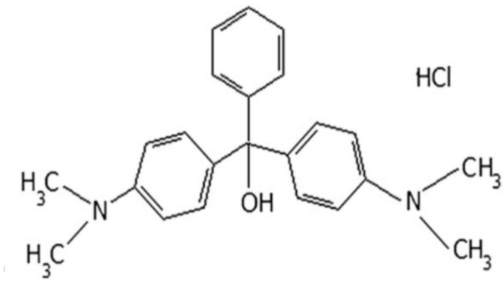


Figure 2. Chemical structure of MG dye. (Mahmood & Waisi, 2021).

2.2. Bio-diluent

The ELM synthesis uses bio-diluents, which are natural green sources, to maintain the viscosity and selectivity of the system (Wakle & Khuntia, 2023). By modifying viscosity, bio-diluents can change the interfacial surface and mass transfer rates of the liquid membrane system. They have fewer negative effects on the environment. They are often biodegradable and less toxic (Talebi, 2012). Bio-diluents act as solvents that facilitate the passage of solutes through the liquid membrane and their extraction from the feed phase to the purification phase. Vegetable oils are an excellent alternative to petroleum-based diluents (Moneer et al., 2024).

Soybean oil can be used in a variety of formulations as an environmentally acceptable and biodegradable diluent. **Table 1** shows the typical composition of crude soybean oil, while **Table 2** shows its physico-chemical characteristics.

Table 1. Typical composition of crude soybean oil (Gasparetto et al., 2022).

Composant	*wt%*
Triacylglycérol[a]	94.4
Phospholipides	3.7
Insaponifiables (stérols, tocophérols et hydrocarbures)	1.3–1.6
Acides gras libres	0.3–0.7
Trace metals (mainly iron and copper)	ppm

[a] Principalement composé d'acide palmitique, stéarique, oléique, linoléique et linolénique.

Table 2. Physico-chemical properties of soybean oil.

Parameters	*Values*
Cematic viscosity	32,09 cst
Density	0,868
acidity index	1,98
pH	6,5
Iron debiris	0
water content	trace
Sediment	0

2.3. Preparation of GELM

The internal phase solution was prepared using H_2SO_4 sulphuric acid (0.05-0.5M) in distilled water. The liquid membrane phase was prepared by dissolving an appropriate amount of Span80 (surfactant) and soybean oil (green diluent) in a beaker (organic phase).

To form the membrane, the internal phase was added drop wise to the organic phase using a pipette. The whole mixture was then stirred using an Ultra-Turrax T8 homogeniser for 30 seconds (optimised time).

The process described was used to make a fresh milky emulsion for each experiment. A Kjank & Kunkel RW20 mechanical shaker was used to disperse this stable emulsion into the external phase, which contained a liquid solution of the dye mixture (Rh-B and MG) at a concentration of 10ppm per pollutant.

The volume ratio of pollutant in the mixture is R([MG]/[[Rh-B]). It is equal to 0.5, at a stirring speed of 250 rpm. A WIW inolab PH 7110 pH meter was used to measure the pH of the external phase.

Figure 3 illustrates the GELM extraction procedure for the extraction of a mixture of malachite green and Rhodamine B dyes.

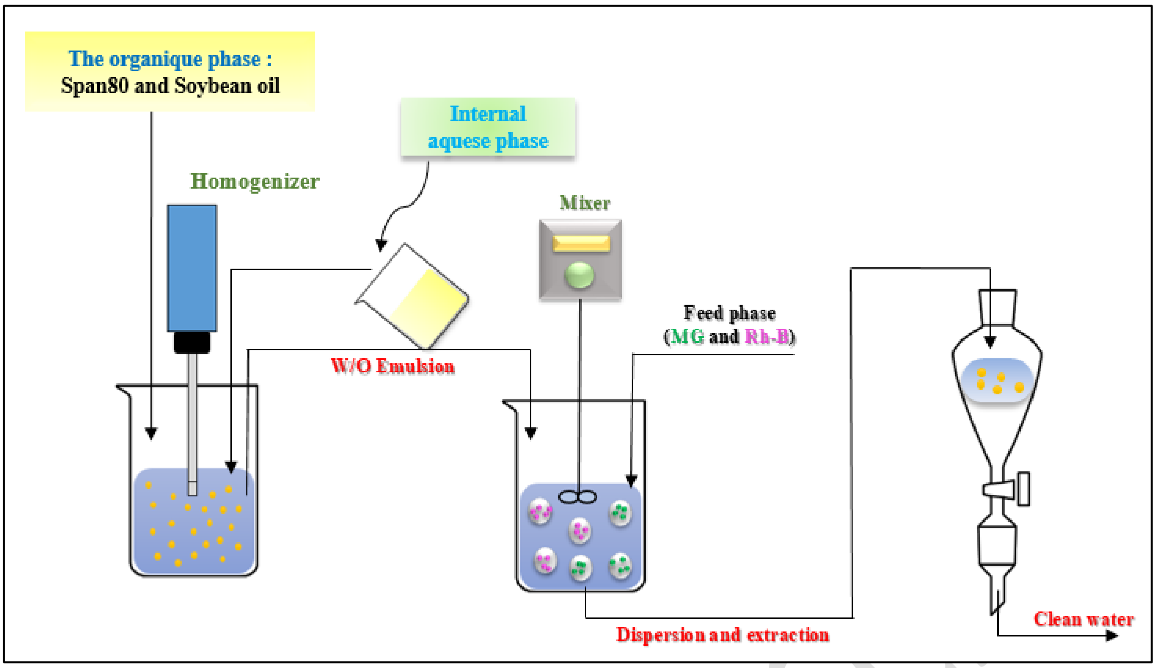


Figure 3. Schematic representation of the mixed extraction of cationic dyes (MG and Rh-B) using the GELM technique.

The concentration of the dye mixture was then monitored using a UV-vis spectrophotometer (Secomam). The extraction percentage of the mixture was calculated using the following equation:

$$Y\,(\%) = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

Where C_0 is the initial concentration of the dye mixture and C: is the concentration of the dye mixture at a certain time after contact with the GELM.

3. Results and Discussion

3.1. Box-Behnken Design

By simultaneously modifying the three variables shown in **Table 3**, the mixture of MG and Rh-B dyes was extracted. Selecting the right parameters is crucial to achieving maximum extraction of the dye mixture.

Table 3. Levels of influential parameters studied.

Parameters	**Unit**	**Level**	
		Low (-1)	**High (+1)**
Span80	%	6	10

$[H_2SO_4]_{int}$	mol/L	0.05	0.5
V_{ext}/V_{em} [a]	-	5	10

[a] Ratio between the volume of the external phase and the volume of the emulsion.

The preliminary tests were followed by the selection of low and high levels for each factor. Following a Box-Behnken experimental design, **Table 4** lists the different operating parameters for extractions using a GELM emulsified liquid green membrane.

It was shown that the mass percentage of Span80, the volume ratio V_{ext}/V_{em} and the concentration of the internal phase were the most important parameters for extracting the mixture of cationic dyes (Rh-B and MG). This can be explained by the fact that these factors plays a crucial role in stabilizing the double emulsion system (W/O/W) by reducing interfacial tension between the oil and water phases, ensuring the integrity of the internal droplets and preventing coalescence. The volume ratio Vext/Vem significantly affects the diffusion kinetics and mass transfer of the dyes, as a proper ratio facilitates optimal contact between the external aqueous phase and the emulsion. The concentration of the internal phase is essential for dye partitioning and solubility, allowing effective encapsulation and selective extraction of the cationic dyes. Together, these parameters directly influence the stability, morphology, and mass transfer efficiency of the system, ensuring high extraction performance for Rhodamine B and Malachite Green.

The other operating parameters were set as follows: extraction time (1h), membrane emulsification time (30s), stirring speed (250 rpm), external phase concentration (mixture of pollutants: $[MG]_0$ = 10ppm and $[Rh\text{-}B]_0$ = 10ppm), volume ratio O/A = 0.5 and temperature (20°C). The experimental results for extraction yields are shown in **Table 4**.

Table 4. Experimental results according to the Box-Behnken design.

N°	Span80	$[H_2SO_4]_{int}$	V_{ext}/V_{em}	Y_{Exp}(%)	Y_{Th} (%)
1	8	0.275	7.5	88.7357	95.597
2	8	0.5	10	45.3989	77.917
3	6	0.05	7.5	90.5414	86.388
4	8	0.05	5	94.5140	86.072
5	8	0.275	7.5	90.4211	95.597
6	6	0.275	5	93.4306	94.228
7	8	0.05	10	51.1772	76.442
8	10	0.275	5	96.3197	84.688
9	6	0.275	10	47.2046	62.448
10	8	0.5	5	95.1159	93.927

11	10	0.05	7.5	89.4580	91.474
12	10	0.5	7.5	87.7727	100.473
13	8	0.275	7.5	90.3007	95.597
14	6	0.5	7.5	86.3281	86.719
15	10	0.275	10	54.3071	90.827

3.1.1. Pareto chart and main effects

The results were presented using the Pareto chart (Fig.4) and the main effects graph (Fig.5).

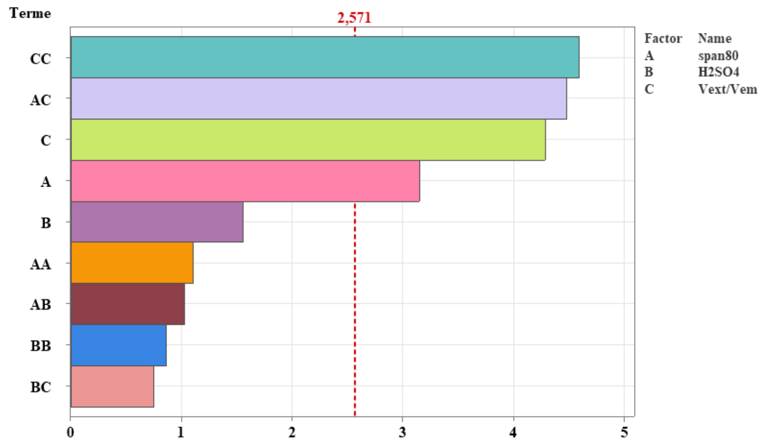


Figure 4. Pareto chart of standardised effects for extraction of the dye mixture by the GELM process.

Figure 4 shows that the factors span80, V_{ext}/V_{em} and the interaction spn80×V_{ext}/V_{em} and the square of the ratio of the volume of the external phase to the volume of the emulsion $(V_{ext}/V_{em})^2$ have a significant effect on the extraction of the dye mixture (MG and Rh-B).

We can deduce the influence of each factor from the variations of each factor in the study area. These impacts can be favourable (positive) or unfavourable (negative) on the chosen response.

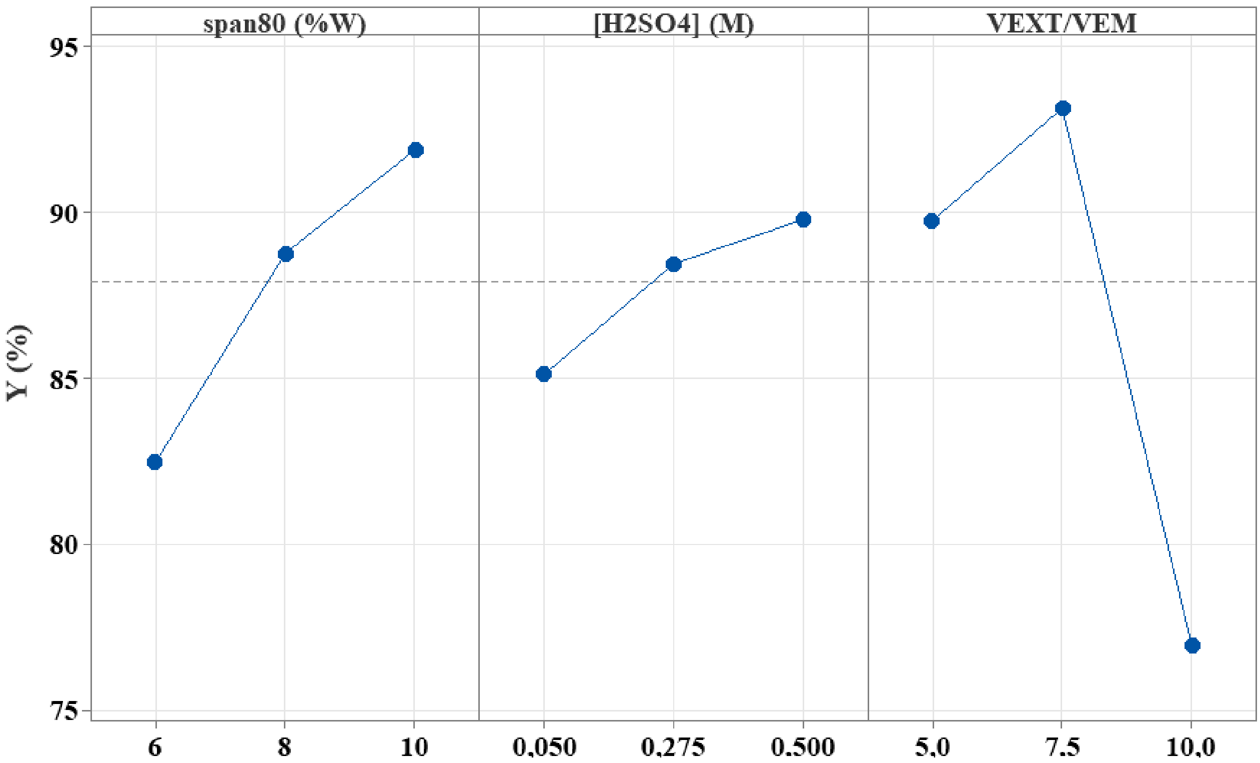


Figure 5. Diagram of the main effects of the parameters for the extraction yield of the dye mixture.

Figure 5 shows that the factors that have a positive effect on extraction yield are Span80, the concentration of the internal phase and the volume ratio of the external phase to the emulsion volume in the range (5-7.5). In other words, the extraction of the mixture (MG and Rh-B) increases with the concentration of the internal phase and the percentage by weight of surfactant. (Bouranene et al., 2003), (Bendebane et al., 2021), (Kasaini et al., 1998), (Djenouhat et al., 2008a), (Bahloul et al., 2015), (Djenouhat et al., 2008b). This indicates that these two parameters play a crucial role in enhancing the efficiency of the GELM process.

It was observed that extraction efficiency increased from 82.44% to 91.87% at the maximum surfactant concentration (Manzak & Tutkun, 2005). Surfactant was introduced as an emulsifier for the liquid membrane. It prevents emulsion leakage by acting as a barrier between the internal and external phases. Due to incomplete coverage of the membrane interface caused by low surfactant concentrations, removal efficiency decreased below 10%. (Chaouchi & Hamdaoui, 2014), (Peng and al., 2012), (Dâas & Hamdaoui, 2010), (Manzak & Tutkun, 2005).

On the other hand, only one factor has a negative effect on extraction yield: the V_{ext}/V_{em} ratio in the range (7.5-10).

3.1.2. Analysis of variance (ANOVA)

The model and the relationship between response values and one or more independent variables are examined using analysis of variance (ANOVA). In fact, ANOVA can be used to test the effectiveness of parameters (Daraei and al., 2019). **Table 5** shows that four terms (Span80, V_{ext}/V_{em}, $(V_{ext}/V_{em})^2$, span80×V_{ext}/V_{em}) were statistically significant.

Table 5. ANOVA results for the model obtained.

Source	***DF***	***Adj SS***	***Adj MS***	***F-Value***	***P-Value***
Model	9	1329.65	147.739	8.26	0.016
Linear	3	549.71	183.237	10.24	0.014
span80	1	177.46	177.463	9.92	**0.025**
H_2SO_4	1	43.52	43.519	2.43	0.180
V_{ext}/V_{em}	1	328.73	328.729	18.38	**0.008**
Square	3	391.51	130.502	7.30	0.028
span80×span80	1	21.94	21.941	1,23	0.318
H_2SO_4×H_2SO_4	1	13.27	13.273	0.74	0.428
V_{ext}/V_{em}×V_{ext}/V_{em}	1	377.54	377.542	21.11	**0.006**
2-Way Interaction	3	388.43	129.478	7.24	0.029
span80×H_2SO_4	1	18.78	18.781	1.05	0.352
span80×V_{ext}/V_{em}	1	359.48	359.476	20.10	**0.007**
H_2SO_4×V_{ext}/V_{em}	1	10.18	10.177	0.57	0.485
Error	5	89.43	17.886		
Lack-of-Fit	3	89.43	29.810	*	*
Pure Error	2	0.00	0.000		
Total	14	1419.08			

3.1.3. Polynomial regression

The second-order mathematical model links the different components, their squares and their interactions to the extraction yield of the dye mixture.

Equation 2 shows the regression of the Y response in coded units as a function of all the variables, while equation 3 shows the regression in uncoded units.

$$Y\% = 95,60 + 4,71 span80 + 2,33 H_2SO_4 - 6,41 \frac{V_{ext}}{V_{em}} - 2,44(span80)^2 - 1,90(H_2SO_4)^2 - 10,11\left(\frac{V_{ext}}{V_{em}}\right)^2 + 2,17 span80 \times H_2SO_4 + 9,48\, span80 \times \frac{V_{ext}}{V_{em}} - 1,60 H_2SO_4 \times \frac{V_{ext}}{V_{em}} \quad \textbf{(2)}$$

$$Y\% = 78,8 - 3,44\, span80 + 13,7 H_2SO_4 + 7,32 \frac{V_{ext}}{V_{em}} - 0,61(span80)^2 - 37,5(H_2SO_4)^2 - 1,62\left(\frac{V_{ext}}{V_{em}}\right)^2 + 4,82 span80 \times H_2SO_4 + 1,90 span80 \times \frac{V_{ext}}{V_{em}} - 2,84 H_2SO_4 \times \frac{V_{ext}}{V_{em}} \quad \textbf{(3)}$$

3.1.4. Response surface and contours

The response surface establishes the ideal circumstances for obtaining the best response by representing the interaction between the factors. From the mathematical model used to plot the response surfaces, it should be noted that the objective is achieved with the maximum extraction efficiency in the study area. This is represented by a maximum in the response surfaces (**Fig.6**) or by the red contour (**Fig.5**).

The 3D curve in Figure 10 illustrates how changing two parameters, with the third remaining constant, affects the extraction yield of the dye mixture.

Figure 5 shows that the best yields are obtained when the volume ratio of the external phase to the emulsion is between (6-9) and between 0.3 and 0.5M in $[H_2SO_4]_{int}$.

At a span80 mass percentage of 10%, the response surface is convex (**see Fig.6**).

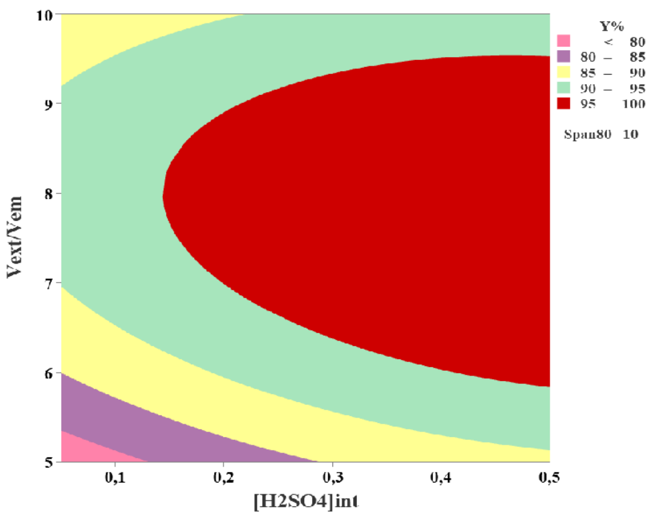


Figure.5. Contour area of yield as a function of $[H_2SO_4]_{int}$-V_{ext}/V_{em} at 10% span80.

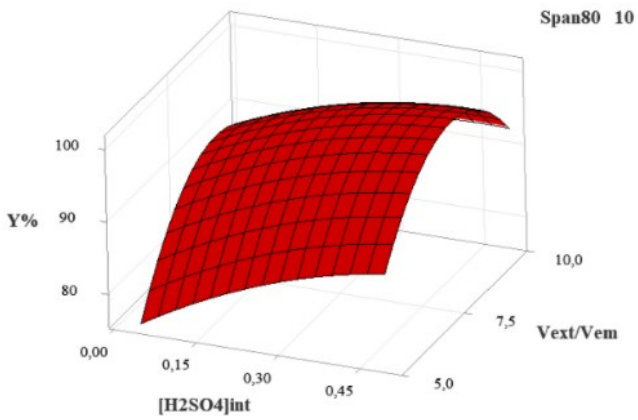


Figure.6. Performance response surface as a function of $[H_2SO_4]_{int}$-V_{ext}/V_{em} at 10% span80.

This work has improved the GELM for the transport of MG and Rh-B dyes without the presence of an extractant. The dye mixture is sufficiently dissolved in the oil phase to function as a membrane body and crosses the membrane by direct transport (Shokri and al., 2020).

Because of its hydrophobic aromatic rings, the dye molecules can dissolve in the oil and diffuse towards the membrane to enter the internal aqueous system, which is the phase that contains its counterion ($SO4^{-2}$).

The main ingredient in applied soybean oil, triglycerides, essentially functions as a complexing agent (Badgujar & Rastogi, 2011), binding to the dye molecules and dissolving them as they transfer to the internal phase (aqueous phase).

3.1.5. Optimization

To determine the performance of the prepared GELM, a statistical optimization of all the influential parameters was conducted using the design of experiments (DoE) approach. The optimization process was carried out using MINITAB 21 software, employing Response Surface Methodology (RSM) to analyze the effects of the three factors: Span80 concentration, internal phase concentration, and Vext/Vem ratio. The software generated a predictive model, identifying the optimal conditions for maximum extraction efficiency. **Figure 7** presents these conditions: a Span80 concentration of 10%, an internal phase concentration of 0.5 M, and a Vext/Vem ratio of 7, yielding a predicted extraction efficiency of 99.77% with a desirability of 0.97.

To validate the statistical model, experimental verification was carried out under these optimal conditions. The same experimental setup and procedure were used as described in the initial extraction process. The results confirmed the accuracy of the model, with the extraction yield of the dye mixture (Rh-B and MG) reaching 99.91%, closely matching the predicted value.

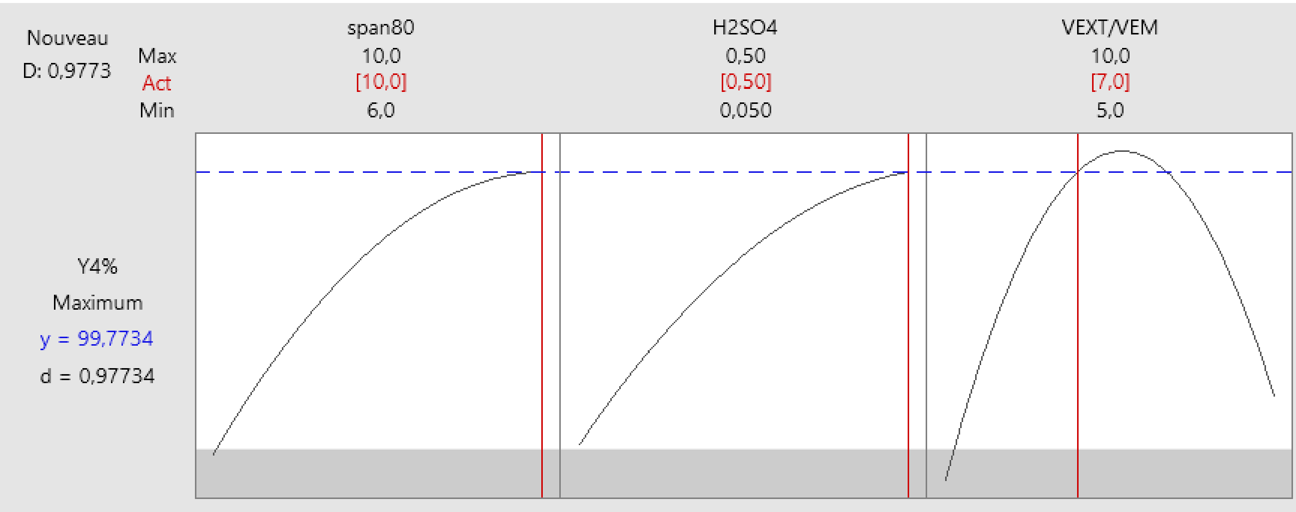


Figure 7. Plot of the optimizer for extracting the dye mixture using the GELM process.

4. Conclusion

A new green emulsion liquid membrane system, abbreviated GELM, made from crude soya oil has been introduced for the treatment of coloured wastewater. According to the results, three parameters, namely the mass percentage of span80, the concentration of the internal phase and the volume ratio between the external phase and the emulsion (V_{ext}/V_{em}), were varied to study the extraction of the mixture of cationic dyes (Rh-B and MG).

The optimal values of each parameter to achieve the highest removal of the dye mixture. The model suggested 10 wt % for span80, a 0.5M H_2SO_4 solution as the internal phase and the ratio V_{ext}/V_{em} = 7, for a dye mixture removal of **99.91%**. Experimental and **99.77%** theoretical.

According to the regeneration results, the use of soybean oil as a non-toxic, edible, inexpensive and widely available diluent enabled decolourisation of the external phase using the same membrane. The green liquid membrane was used more than eight (08) times to extract the mixture of MG and Rh-B dyes.

In addition, the high bleaching efficiency of GELM was achieved without the need for extractant. Finally, the results of the study suggest that there may be safe and affordable substitutes to the GELM technique that use non-renewable organic solvents from the many types of edible vegetable oils to apply GELM in water decolourisation with impeccable performance.

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Conflict-of-Interest Statement: The authors declare that they have no conflict of interest.

Author Contributions: Sonia Khelifa (Ph.D. student) conducted all the experiments. Salima Bendebane (Assistant Professor) and Farida Bendebane (Professor) were involved in interpreting the results and writing the manuscript.

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