Effects of Parameters on the Extraction Yield of Acid Orange10 by ELM from an aqueous solution. Application of Plackett-Burman Design

Lynda Bahloul, Djenouhat Meriem, Farida Bendebane, Hazem Meradi, Fadhel Ismail

***Abstract*— The main objective of this study was to optimize the parameters that influence the extraction of a cationic dye acid orange 10 (C16H10N2Na2O7S2) from an aqueous solution, by an emulsified liquid membrane (ELM) consisting of Aliquat336 as the extractant, Span80 as the surfactant and cyclohexane as the diluents. The internal phase used was sulphuric acid. The extraction process parameters were studied using a statistical method of experimental Plackett-Burman design. Effects of parameters on the extraction yield were analyzed statistically and a mathematical model of the yield according to different parameters was developed, Main effects were studied and levels of all parameters correspondent to the best yield were determined. The concentration of span80 and the acidity of the internal, the composition and the proportion of the membrane were the most important factors for the extraction yield of AO10. Under optimized operator conditions deduced from main effects, a validation of the model was carried out; the extraction yields given by the polynomial models according to the coded and uncoded parameters and the extraction yields obtained experimentally, were very close comparatively.**

***Index Terms*— Acid orange10, Design of experiments, Emulsified liquid membrane, Modeling, recovery.**

I. INTRODUCTION

The water pollution is caused by the discharge of dyes from pickling, paper, pulp and dyestuff industries, tanning, printing and textile units etc. [1]. The treatment and disposal of dyes from contaminated wastewaters is one of the most serious environmental problems engendered by the related industries. There are several methods for dye removal; biological treatment [2-4], coagulation/flocculation [2, 5], chemical oxidation and photocatalytic processes [6,7], adsorption [8,9] etc. Emulsion liquid membranes (ELM) are demonstrated to have significant potential as an effective tool for treatment of various industrial wastes since their invention [10,11]. It is one of the potential methods for treatment of industrial wastewater aiming recovery of various inorganic and organic solutes [12,13]. With the invention of the emulsion liquid membrane in late sixties, numerous mathematical models have been developed and applications of these models have been carried out. They were tested for extraction of various metal ions, namely, silver [14], rare earth elements [16], chromium [17], cesium [18], nickel [19], zinc [20], arsenic [21], gold [22] *etc.*

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 some studies [13,23- 26].

Acid Orange 10 ($C_{16}H_{10}N_2Na_2O_7S_2$) is among the most often cationic dyes used in industries. 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 on carrying out a back-extraction (desextration) of the dye. In this study an approach of design of experiment (DOE) [27, 28] was applied to determine the parameters that have influence on the extraction of AO10 from an aqueous solution. The DOE used was the fractional factorial design of Plackett-Burman [29, 30]. The membrane was consisting of SPAN 80 as the surfactant and Aliquat 336 as the extractant. Statistical analysis of experimental results was studied and a modeling of the yield of extraction according to operating conditions was also achieved.

II. EXPERIMENTAL

2.1. Materials and compounds

AO 10 ($C_{16}H_{10}N_2Na_2O_7S_2$) is an anionic dye supplied by Sigma Aldrich (Fig.1) , The emulsified liquid membrane used for the extraction of acid orange 10 consisted of SPAN80 (sorbitan monooleate) as the surfactant, Aliquat 336 as the extractant, cyclohexane as the thinner and sulfuric acid as the internal phase. The cyclohexane produced by Riedel-de Haën was used as a thinner, it was a stable product under ordinary conditions, its role was to improve mainly some physicochemical properties of the extractant and the surfactant, The trioctylmethylammonium chloride (Aliquat 336) (Fig.2) was supplied by Sigma Aldrich. The sorbitan monooleate (SPAN80) (Fig.3) supplied by Sigma Aldrich is a nonionic surfactant type ester with lipophilic character (HLB = 4.3), it was used for the stability of the emulsion. The homogenizer Ultra-Turrax T8 was a mechanical agitator type

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RW20Junk & Kunkel, with a marine propeller; it was used to make the double emulsion W/O/W (water/oil/water).

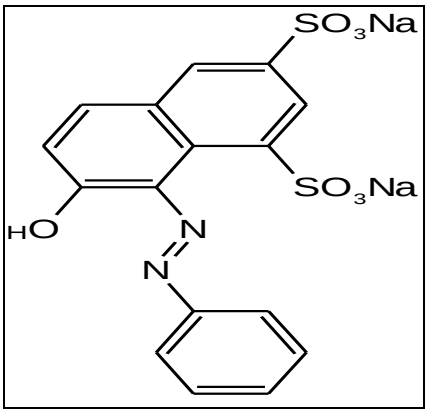

Fig.1 : Acid orange 10

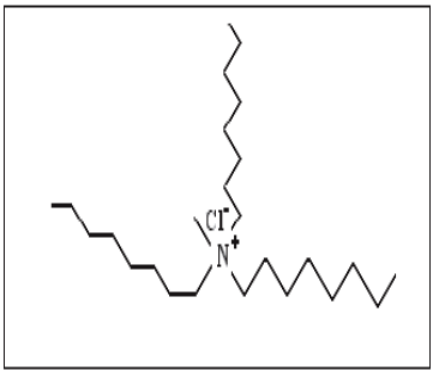

Fig.2 : Aliquat 336

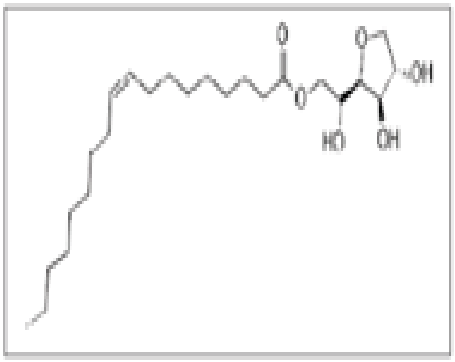

Fig.3 : SPAN 80

2.2. Experimental procedures

To extract the complex ($C_{16}H_{10}N_2Na_2O_7S_2$), the membrane was consisted of Aliquat 336 as the extractant, cyclohexane as the thinner and sorbitan monooleate (SPAN80) as the surfactant. This emulsifier was used to slightly acidic or alkaline and promoted an emulsion (W/O) with marked lipophilicity. The mixture was emulsified at 5000 rpm into a beaker tall form within 5 minutes. Then using a mechanical stirrer at150rpm, this emulsified membrane was dispersed into a beaker containing 150mL of the solution to be treated.

The pH variation of the external phase was monitored using a pH-meter type HANA Hi 8519N. The concentration of the residual complex AO10 at different reaction times ranging from 3 to 15 minutes until equilibrium was determined by up taking samples of 2mL and measuring the absorption intensity using a Jenway (6705UV/VIS) spectrophotometer. The optimal wavelength was determined experimentally and was used in the same conditions. The samples were analyzed to determine the concentration of the residual complex AO10 from a calibration curve carried out at ordinary temperature. The extraction efficiency was calculated by Equation (1).

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

V_{0ext}: initial volume of the external phase
V_{fext}: final volume of the external phase.
C_{0ext}: initial concentration of AY99 in the external phase
C_{fext}: final concentration of AY99 in the external phase.
Y: Extraction yield.

III. RESULTS AND DISCUSSION

3.1. Experimental results

The extraction of AO10 was conducted by varying eight factors simultaneously listed in Table 1. The minimum and the maximum of level for each factor were chosen after a literature review and especially after performing preliminary tests. Table 2 summarizes the different operating conditions of extractions using an emulsified liquid membrane according to a Plackett-Burman experiments design. The experimental results of extraction yields are also presented. All the following statistical studies are based on these experimental data.

Table 1: Parameters and levels

N° run	Parameter	Unit	Level	
			Low (-1)	**High (+1)**
1	SPAN 80	%	6	10
2	Aliquat336	%	2	6
3	SV	rpm	150	250
4	[H2SO4] int	Mol/L	0.1	0.5
5	O/A	_	1	4
6	Vex/Vem	_	3	6
7	$[AO10]_0$	ppm	10	50
8	[H2SO4] ext	Mol/L	0.1	0.5

Table 2: Experimental results according to P-B Design

Run Order	SPAN80 (%)	Aliquat336 (%)	SV (rpm)	[H2SO4] int (Mol/L)	O/A	Vex/Vem	[AO10]0 (ppm)	[H2SO4] ext (Mol/L)	Y (%)
1	6	2	150	0.1	1	3	10	0.1	**94.44**
2	10	2	150	0.1	4	6	50	0.1	**82.11**
3	10	2	250	0.1	1	3	50	0.5	**88.99**
4	6	6	250	0.5	1	6	50	0.1	**94.25**
5	6	6	150	0.1	1	6	50	0.5	**97.96**
6	10	2	250	0.5	1	6	10	0.1	**89.62**
7	6	2	150	0.5	4	6	10	0.5	**96.18**
8	10	6	150	0.5	4	3	50	0.1	**89.74**
9	10	6	250	0.1	4	6	10	0.5	**82.68**
10	6	2	250	0.5	4	3	50	0.5	**96.49**
11	10	6	150	0.5	1	3	10	0.5	**98.96**
12	6	6	250	0.1	4	3	10	0.1	**90.73**

3.2. Pareto chart

The Pareto chart of effects is a useful field to identify the most important factors. It shows the estimated main plot against the horizontal effect. From Figure 4 we can see that the most important factors in the decreasing order are the quantity of SPAN80, the acidity of the internal phase, the O/A ratio and the acidity of the external phase. The stirring velocity and the volume ratio Vex/Vem have a low effect. The extractant and the initial concentration of dye are the less important parameters.

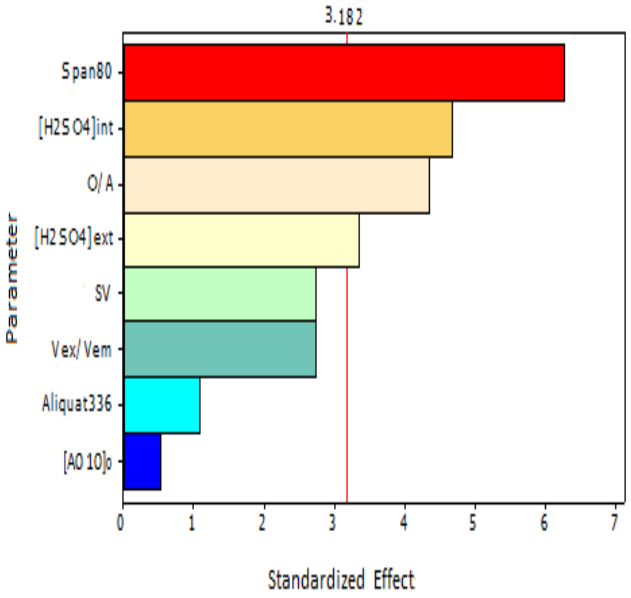

Fig.4: Pareto Chart of the Standardized Effects for Y(%) as response (Alpha = 0.05)

3.3. Main effects

The main effects plot is the most useful when there are several factors (Fig.5). From level changes, we can deduce the influence of all factors on the extraction yield (Y). These effects may be positive or negative according to the slopes of the linear curves.

3.4. Effects and interactions for Y(%)

The achieved yields with the different interactions are presented in the figure 6. The emulsifier Span 80 does not present any interaction with the other parameters and its low concentration enhances the extraction yield. On the other hand, the extractant Aliquat336 and the stirring velocity present interactions with all parameters. Their optimal values must be determined according the other parameters. There are no interactions between the other parameters except for the couple $[AO\ 10]_0$-$[H_2SO_4]_{ext}$.

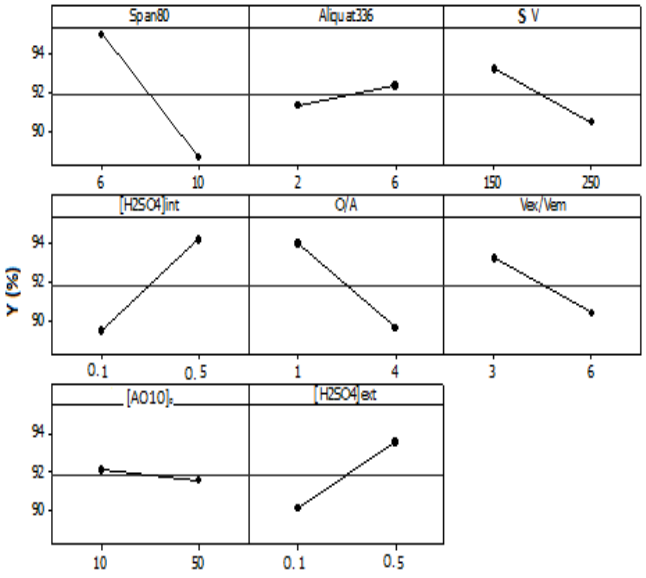

Fig.5: Main Effects Plot of parameters for Y(%)

3.5. Polynomial regression

From ANOVA (Analysis of variance), if the effect of a parameter is significant it is high probability (95%, 99%, or 99.9%) that the effect is "real" [31, 32]. P-value is a statistical parameter which indicates the importance of a parameter. The coefficients of the parameters presented in Table 3 were calculated from the Yates' rating [33]. The algebraic values of the coefficients measure the average change in extraction yield when the parameters change from level (-1) to level (1).

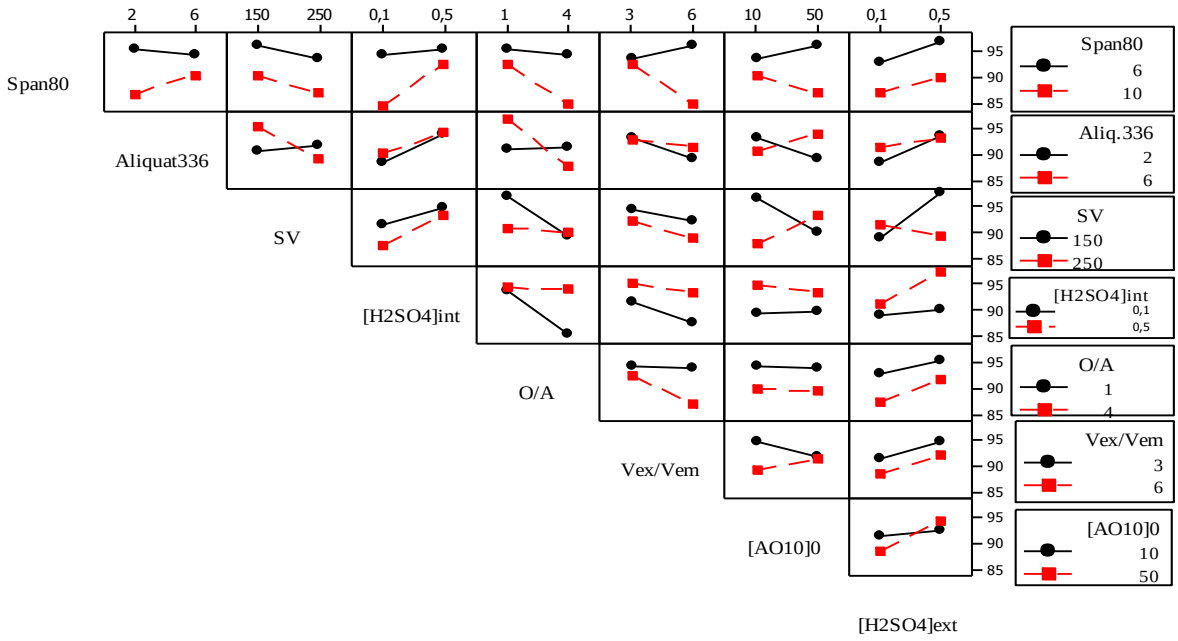

Fig.6: Interaction plot of parameters for Y(%)

Table 3: Effects and coefficients of the estimated yield (coded units).

Term	Effect	Coef Coded units	Coef Uncoded units	T	P
Constant		91.846	111.043	181.64	0.000
SPAN 80	-6.325	-3.162	-1.58125	-6.25	0.008
Aliquat336	1.082	0.541	0.270417	1.07	0.363
SV	-2.772	-1.386	-0.0277167	-2.74	0.071
[H2SO4] int	4.722	2.361	11.8042	4.67	0.019
O/A	-4.382	-2.191	-1.46056	-4.33	0.023
Vex/Vem	-2.758	-1.379	-0.919444	-2.73	0.072
$[AO10]_0$	-0.512	-0.256	-0.0127917	-0.51	0.648
[H2SO4] ext	3.395	1.697	8.48750	3.36	0.044

To enable the prediction of response and system optimization, the method of experiment design on both its design and structure allows a mathematical representation of the response (yield) according to all factors. The regressions are represented by polynomial equations 2 and 3 corresponding to the coded and uncoded parameters respectively.

$$Y\ (\%) = 91{,}846 - 3{,}162\ (Span80) + 0{,}541\ (Aliquat336) - 1{,}386\ (SV) + 2{,}361\ (H_2SO_4)_{int} - 2{,}191\ (O/A) - 1{,}379\ (Vex/Vem) - 0{,}256\ (AO10) + 1{,}697\ (H_2SO_4)_{ext} \quad (2)$$

$$Y\ (\%) = 111{,}043 - 1{,}58125\ (Span80) + 0{,}270417\ (Aliquat336) - 0{,}0277167\ (SV) + 11{,}8042\ (H_2SO_4)_{int} - 1{,}46056\ (O/A) - 0{,}91944\ (Vex/Vem) - 0{,}0127917\ (AO1O)_0 + 8{,}48750\ (H_2SO_4)_{ext} \quad (3)$$

According to models deduced above, estimated yields were determined and compared to the experimental yields. Results were very close and this indicates that the model is very representative of the extraction process studied (Table 4).

Table 4: Comparison between estimated and experimental yields

Run Order	Y(exp.) (%)	Y(est.) (%)
1	**94.44**	**95.6208**
2	**82.11**	**81.6442**
3	**88.99**	**89.4075**
4	**94.25**	**95.3825**
5	**97.96**	**96.8275**
6	**89.62**	**88.4875**
7	**96.18**	**96.5975**
8	**89.74**	**90.2058**
9	**82.68**	**83.8608**
10	**96.49**	**96.0725**
11	**98.96**	**98.4942**
12	**90.73**	**89.5492**

3.7. Optimization of the model

From main effects of the extraction yield. a primary optimized conditions can be deduced for an extraction yield of about 100% . These conditions are summarized as below:

- $[\ H_2SO_4\ ]_{int}$ = 0.5 Mol/L in the internal phase
- $[\ H_2SO_4\ ]_{ext}$ = 0.5 Mol/L in the external phase
- V_{ext} / V_{em}= 3
- $[AO10]_0$ = 10 mg / L
- Aliquat 336 = 6 %
- Span80 = 6 %
- Dilute cyclohexane = 88 %
- Emulsification time = 5 min

- O/A = 1
- Contact time = 10 min
- Stirring Velocity = 150 rpm

IV. CONCLUSION

The extraction of the anionic dye acid orange 10 ($C_{16}H_{10}N_2Na_2O_7S_2$) was the subject of this work. The study of an emulsified liquid membrane consisting of Span80 and aliquat336 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. Using a Plackett-Burman design the extraction of AO10 (anionic dye) was carried out varying different operator parameters simultaneously. Effects of parameters on the extraction yield were analyzed statistically and a mathematical model of the yield according to different parameters was developed. Main effects were studied and levels of all parameters correspondent to the best yield were determined. The concentration of Span80 and the acidity of the internal, the composition and the proportion of the membrane were the most important factors for the extraction yield of AO10.

Under optimized operating conditions deduced from main effects. a validation of the model was carried out; the extraction yields given by the polynomial models according to the coded and uncoded parameters and the extraction yields obtained experimentally was higher than 99.9%. 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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