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Recovery of 4-chlorophenol from an aqueous solution by ELM: stability of the membrane, modeling, and optimization of the extraction using experimental designs

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ABSTRACT

An emulsified liquid membrane has been developed for the extraction of the 4-chlorophenol (4-CP) from an aqueous effluent. The membrane used was an emulsion of water in oil (W/O), the internal phase was an alkaline solution (NaOH), and the organic phase was a mixture of a surfactant (SPAN 80) and an extractant (TBP) dissolved in an organic solvent (heptane). The only limitation of this technique was the stability of the membrane (swelling, cohesion, and rupture). To optimize the different parameters that have a direct influence on the stability of the membrane, experiments were conducted using a fractional factorial design of Plackett–Burman. The obtained results showed the behavior of the emulsified membrane under different operating conditions. Among the different factors studied, the concentrations of SPAN 80 of TBP and the stirring velocity appeared to be the most important parameters. Indeed, a high yield above 99% almost a total elimination of 4-CP was achieved under optimized operating conditions determined by response surface methodology using a full factorial design.

Keywords: Wastewater; Recovery; 4-chlorophenol; Design of experiment (DOE); Emulsified liquid membrane (ELM)

1. Introduction

The toxicity of chlorophenols is proportional to their degree of chlorination [1]. Chlorophenols that are very used in pesticides production can contaminate the water during their manufacture and use or following the breakdown of other chemicals. Wastewater contaminated by chlorophenols can be treated using destructive methods such as oxidation by ozone, hydrogen peroxide or manganese oxides [2] and biological treatment. Non destructive methods such as adsorption, membrane technology, extraction by solvent or emulsified liquid membrane (ELM), distillation and evaporation can also be used.

The extraction by ELM is the method used in our present work for the elimination of the 4-chlorophenol (4-CP) that is a toxic compound. Extraction with ELM was invented and used for the first time by Norman N. Li (1978) [3]. It is prepared by contacting an aqueous phase (internal phase) with an organic solution consisting of a solvent in which a surfactant and an extractant were dissolved. The surfactant is used to obtain an emulsion that ensures the encapsulation of

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the aqueous phase into the organic phase. The resulting emulsion of water in oil (W/O) is further dispersed as emulsified drops in an external feed phase. The solute studied is then extracted from the external phase and transferred across the membrane into the internal phase.

Several works have emerged since then, as the extraction of heavy metals [4–6] or precious metals [7], the separation of hydrocarbons [8,9], the recovery of organic compounds from aqueous solution like 2-chlorophenol [10], the extraction of heteropolyanion complexes [11] etc. Extractions of different metals have being reported and compared when using ELM extraction processes in the presence of different extractants, surfactants, and feed solutions [12].

The ELM method has been also applied in biochemistry. Citric acid extraction [13], recovery of lactic acid [14,15], penicillin separation [16,17], the removal of cholesterol from blood [18] and separation of amino acids [19–21] have been studied.

The ELM method is used in many industrial installations; for example, the recovery of zinc is applied in Austria (Glanzstoff), in Germany (CFK Schwarz), and in the Netherlands (AKZO/Ede) treating 0.7, 0.2, and 0.2 m^3/h, respectively [18,22].

In Austria galvanic solutions, about 0.15 m^3/h, are treated with ELM, and Ni is extracted in 90%. The initial solution is concentrated to be treated by conventional extraction [23].

Results obtained in a pilot-plant installation showed that uranium recovery is possible with ELM. In this system, 90% of uranium is recovered and concentrated to 6 g/dm^3 [24]. A similar pilot-plant installation was used for copper recovery [25].

An industrial plant for the treatment of wastewater loaded in phenol was built in China in the eighties [26]. It treats 0.5 tons/hour of solution containing 1,000 mg/l of phenol. After treatment, the concentration of phenol decreases to 0.5 mg/l. The pH of the treated water must be less than nine as phenol remains nonionic, because in this state, it is soluble in the membrane. When in contact with sodium hydroxide in the internal phase, a reaction occurs, and the phenol is transformed to sodium phenolate. This last form is not soluble in the membrane, and this phenomenon prevents the return of sodium phenolate in the external phase [27].

The stability of the ELMs is very important and must be optimized before their use. A good stability according to the composition of the membrane has being reported in different studies [11,27,28].

The study of extraction by ELM is complicated because it depends on several factors. Mathematical models proposed by researchers often lack realism, and in most cases, are specific and can not be generalized. If the transfer through the membrane is a simple diffusion, equation basis will be deducted directly from the second law of Fick [29]. Once we introduce a carrier in the membrane as an extractant, the transfer mechanism will become diffusion reaction in place of simple diffusion [29] and the study will be necessary solving a set of equations that would require an arsenal of mathematical tools. If in addition were taken into account the rupture, the cohesion and the swelling of the membrane, the modeling will become more and more difficult. Therefore, the use of empirical models will be all indicated.

Researchers often conduct a study of a phenomenon using the conventional single factor design method. They set all the parameters and vary only one. Then, they fix this factor at an optimum level vary another parameter and so on. Unfortunately, this technique is not recommended in all situations particularly when the number of parameters is important or there are interactions between them. In this case, the use of design of experiments is imperative. In a full factorial design, the runs are carried out so that all combinations of levels (possible values of parameter) must be made. When the number of parameters increases, the number of runs becomes very high. When the runs of only one part of the complete full factorial design can give enough information, this method is called fractional factorial design. Using this experimental design, we can calculate the coefficients for each parameter and express its importance in relation to the phenomenon studied. We can also calculate the coefficients associated with the interactions between parameters [30].

In this study, an approach of design of experiment [31,32] was applied to determine the parameters that influence on the stability of the membrane using a fractional factorial design of Plackett–Burman [33,34]. The membrane was consisting of SPAN 80 as the surfactant and tri-butylphosphate (TBP) as the extractant. An optimization of operating conditions for the extraction of the 4-CP, using a full factorial design and a response surface methodology [35], was also achieved.

2. Experiment

2.1. Reagents and materials

The TBP $(C_4H_9O)_3$ PO analytical grade and the surfactant SPAN 80 (mono-oleate of sorbitan) were obtained from Aldrich, the n-heptane from Fluka and the 4-CP were received in the form of pure crystals 99% from Merck. Water was bi-distilled. The

spectrophotometer used for measuring the absorbance of 4-CP solutions was a HP8453. The pH was measured with a Hanna pH-meter; the emulsion was prepared with homogenizer Ultra-Turrax T8 IKA. A mechanical agitator (Junk & Kunkel, RW20) with marine propeller was used to make the W/O/W double emulsion.

2.2. Experimental procedures

The membrane was prepared by the dissolution of SPAN 80 and TBP in n-heptane. The internal aqueous phase solution of NaOH was added in a defined relationship to 20 g of the organic phase. Mixture was carried out in a 200-mL long beaker of 30 mm of diameter. The emulsion W/O was made with homogenizer running at 5,000 rpm within 5 min.

In a 500-mL beaker, this emulsion was then dispersed in an external aqueous phase containing 100 mg/L of 4-CP which is the solution to be treated. The pH of the external phase was kept constant at about 6.4 using a buffer solution. The kinetics of extraction was followed with up taking samples of 2 mL per minute. These samples were analyzed by UV spectrophotometer to determine the residual concentration of 4-CP from a calibration curve carried out at pH 6.4 in the range from 0 to 100 mg/L of 4-CP. The wavelength 280 nm was determined experimentally and was used in these conditions.

To measure the rupture rate of the membrane, an emulsion was dispersed in bi-distilled water neutral pH and free from 4-CP. Any change in the pH of the bi-distilled water reflects the breakdown of the emulsion due to the expulsion of NaOH from the internal phase to the external phase.

The preparation of the membrane, the study of its stability, and the extraction of 4-CP were conducted using a simple experimental setup [36].

3. Results and discussion

3.1. Stability of the membrane

According to several works [11,28,37,38], the parameters chosen for the study of the membrane stability were the mass, the concentration of the membrane constituents SPAN 80 and TBP, the volume ratio of the membrane to the internal phase (V_o/V_w), the concentration of the internal phase [NaOH], the volume ratio of external phase to emulsion V_{ex}/V_{em} and the agitation speed SV. Parameters and their levels are listed in Table 1. A fractional factorial design of Plackett and Burman [30,35] was conducted, and the runs are shown in Table 2. The last column in this table represents the response which is the rupture rate T_r, and each row shows a single run. The rupture rate was calculated from a $[OH]^-$ material balance for a stirring time of 4 min. T_r is reflected by the quantity of NaOH expelled into the external phase during the rupture of the membrane on the initial volume of NaOH:

$$T_r = \frac{V_r}{V_i} \times 100 \quad (1)$$

where V_r is the volume of NaOH expelled into the external phase and V_i is the initial volume of the internal phase NaOH.

A Pareto chart of effects is a useful plot for identifying the factors that are important (Fig. 1). It shows the estimated main effect plotted against the horizontal axis. This chart proves that concentrations of SPAN 80 followed by TBP are the most important factors influencing the stability of the membrane.

The main effects plot is most useful when there are several factors (Fig. 2). Changes in the level means can be compared with deduce which factors influence the response the most. For a factor with two levels, it was found that one level increases the mean compared with the other level. This difference is a main effect.

Table 1
Levels and units of parameters

No. run	Parameter	Unit	Level	
			Low (−1)	High (+1)
1	SV	rpm	150	300
2	[NaOH]	mol/L	0.2	0.8
3	V_{ex}/V_{em}	—	5	15
4	V_o/V_w	—	1	3
5	TBP	%	20	30
6	SPAN 80	%	10	20

Table 2
Experimental results for response (T_r) according to Plackett–Burman design

Order	SV (rpm)	[NaOH] (mol/L)	V_{ex}/V_{em}	V_o/V_w	TBP (%)	SPAN 80 (%)	T_r (%)
1	300	0.8	5	1	30	10	**15.43**
2	150	0.2	5	1	20	10	**4.76**
3	150	0.8	5	3	30	20	**4.94**
4	300	0.2	5	3	20	20	**2.49**
5	150	0.8	15	3	20	10	**3.10**
6	150	0.2	15	1	30	20	**1.90**
7	300	0.8	15	1	20	20	**2.08**
8	300	0.2	15	3	30	10	**7.50**

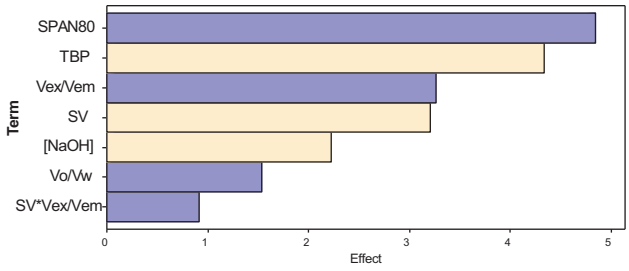

Fig. 1. Pareto chart of effects for T_r as response.

Analysis of variance (ANOVA) is an essential tool for determination of the significance of an effect or of a mathematical model. The term "significance" is used in its restricted sense of statistical significance. In other words, if an effect is significant, there is a high probability (95, 99, or 99.9%) that the effect is "real" [39,40]. The most significant factors can be determined by using a statistical parameter which is P value (Table 3). This value was compared with another value which represents the risk of model. Generally, is equal to 5% of the risk. The coefficients of parameters presented in Table 3 were calculated from the rating of Yates [23]. Algebraic values of the coefficients measure the average change in the rupture rate when the parameters change from level (−1) to level (+1).

The negative sign of the effects and coefficients indicates that the parameter is inversely proportional to the response, and in fact, the growth of the factor causes a decrease in the rate of rupture and this indicates the good stability of the membrane.

The most important effect (−4.845) is those of SPAN 80 whose volume is determinant for the stability of the membrane. It is known that the addition of the surfactant improves stability; this is due to the properties of surfactant favoring emulsions of W/O. An optimization of this parameter will be achieved in a later step (extraction of 4-CP).

The second significant effect (4.33) is of TBP that is another constituent of the membrane. The transition from 20 to 30% in TBP causes a very large destabilization of the membrane. Indeed, as a surfactant, the properties of TBP promote another type of emulsion oil in water. Its presence in the membrane does not improve its stability but facilitates the transport of (4-CP). This factor also must be optimized for extraction in a later stage.

The third significant effect (−3.260) is the V_{ex}/V_{em} ratio. With a certain amount of the emulsion (water/oil) a solution 15 times larger in volume can be treated. Furthermore, the rupture rate T_r is lower than in the case where the V_{ex}/V_{em} ratio is equal to five. The result is interesting as well as the emulsion can handle a volume three times greater, while improving the stability of the membrane.

The fourth factor is the speed of agitation (3.200), the positive sign shows that a high stirring velocity (SV) destabilizes the membrane.

The fifth factor is the concentration of sodium hydroxide [NaOH] (2.225), the positive sign means that high concentrations destabilize the membrane, but may be favorable for extraction. The role of [NaOH] is to transform the phenol function to the phenolate function, and then, we must be satisfied with the minimum of concentration that is sufficient to transform the entire amount of 4-CP trapped by the emulsion.

The 6th factor V_o/V_w has no remarkable effect (−1.535), and therefore, a negative sign ratio of three is more favorable

The last factor is the combination effect of the SV and the volumetric ratio V_{ex}/V_{em}. This effect is negligible. Mathematical models of the rupture rate T_r according to the coded and uncoded process parameters given by Eqs. (1) and (2), respectively, were determined with the regression coefficients presented in Table 3.

$$T_r(\%) = 5.275 - 2.422 \times \text{SPAN}\,80 + 2.167 \times \text{TBP} - 1.630 \times V_{ex}/V_{em} + 1.600 \times SV + 1.112 \times [\text{NaOH}] - 0.768 \times V_o/V_w. \quad (2)$$

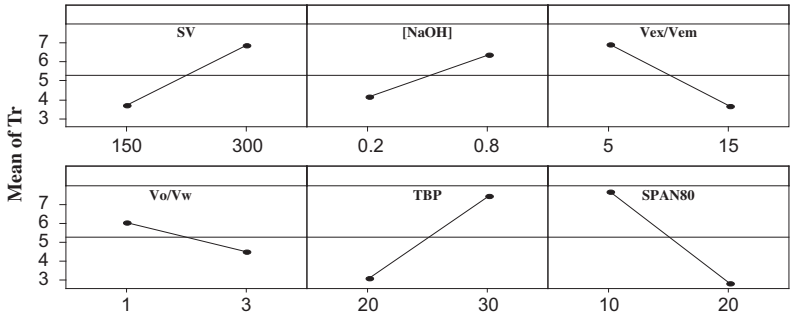

Fig. 2. Main effects plot (data means) for T_r.

Table 3
Effects and estimate coefficients for response (T_r)

Term	Effect	Coefficient		T-value	p-value
		Coded unit	Uncoded unit		
Constant	—	5.275	−0.1542	11.59	0.055
SV	3.200	1.600	0.0213	3.52	0.176
[NaOH]	2.225	1.112	3.7083	2.45	0.247
V_{ex}/V_{em}	−3.260	−1.630	−0.3260	−3.58	0.173
V_o/V_w	−1.535	−0.768	−0.7675	−1.69	0.341
TBP	4.335	2.167	0.4335	4.76	0.132
SPAN 80	−4.845	−2.422	−0.4845	−5.32	0.118

$$T_r(\%) = -0.1542 - 0.4845 \times \text{SPAN 80} + 0.4335 \times \text{TBP} - 0.326 \times V_{ex}/V_{em} + 0.0213 \times SV + 3.7083 \times [NaOH] - 0.7675 \times V_o/V_w. \quad (3)$$

3.2. Extraction of 4-CP

From results obtained above, it is clear that SPAN 80 as a surfactant, and TBP as an extractant are the most important parameters for the stability of the membrane. To extract 4-CP from water using this emulsified membrane, these parameters are probably very important and they must be considered. The stirring speed, which destabilizes the membrane, can be justified by the kinetics of extraction. The extraction of 4-CP was carried out according to these three important parameters. The ratios V_{ex}/V_{em}, V_o/V_w and the concentration [NaOH] are maintained at 15, 1, and 0.2 M, respectively. A full factorial design was used to optimize the extraction of 4-CP (Table 4). The last column in this table shows the efficiency of extraction.

A Pareto chart of effect was used for identifying the importance of factors (Fig. 3). This chart proves

Table 4
Experimental results for response (yield) according to full factorial design

Run order	TBP (%)	SPAN 80 (%)	SV (rpm)	Yield (%)
1	30	16	250	72.00
2	30	8	250	98.37
3	20	8	150	90.90
4	20	16	250	94.63
5	30	16	150	84.97
6	20	8	250	86.17
7	30	8	150	97.21
8	20	16	150	99.59

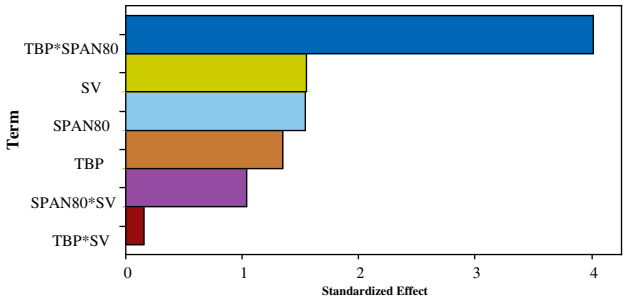

Fig. 3. Pareto chart of the standardized effects, (response is yield, Alpha = 0.50).

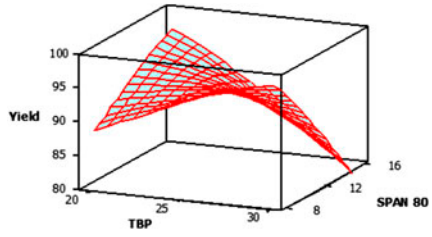

Fig. 4. Surface plot of yield vs SPAN 80; TBP.

that SPAN 80, TBP, and SV have separately comparative effects but the product TBP*SPAN 80 presents the most important effect influencing the yield of 4-CP extraction. This means that each of these two factors (TBP and SPAN 80) has an effect on each other and that their interaction becomes very important. This phenomenon can be seen in the surface plot (Fig. 4) and contour plot (Fig. 5) which give the yield according to these two factors, in fact, the extraction efficiency is high in both combinations representing a low concentration for one factor against a high concentration for the other factor and vice versa.

TBP may form complexes with the 4-CP at the interface, external phase/organic phase; a hydrogen bonding can occur between the oxygen in the phosphoryl group of TBP and the hydrogen atom of the

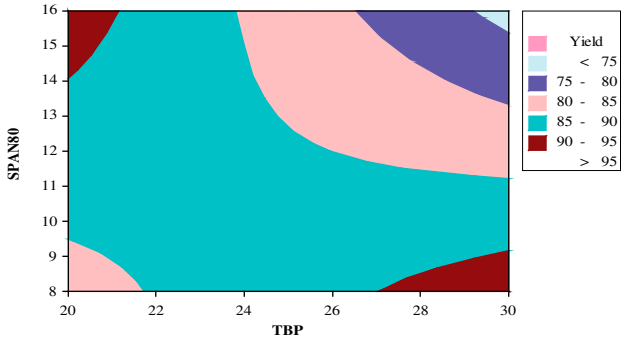

Fig. 5. Contour plot of yield vs. SPAN 80; TBP.

Table 5
Effects and estimate coefficients for response (yield)

Term	Effect	Coefficients coded unit	*T*-value	*p*-value
Constant	—	90.480	50.07	0.012
TBP	−4.685	−2.343	−1.35	0.406
SPAN 80	−5.365	−2.683	−1.54	0.366
SV	−5.375	−2.688	−1.55	0.365
TBP*SPAN80	−13.940	−6.970	−4.01	0.156
TBP*SV	−0.530	−0.265	−0.15	0.904
SPAN 80*SV	−3.590	−1.795	−1.03	0.490

chlorophenol radical hydroxide. Thus, TBP may also be used as carrier for the extraction of the chlorophenol from the external phase through the organic phase of the membrane, to the internal phase. In alkaline water, chlorophenol is ionized and forms sodium 4-chlorophenolate thus, TBP which releases the chlorophenol in the internal alkaline phase, stays always maintained in the organic phase.

The interaction TBP*SPAN 80 is very important: SPAN 80 improves the stability of the membrane but it constitutes also a barrier against the transport of 4-CP with TBP. In another hand, TBP, which destabilizes the membrane, is necessary to extract 4-CP as mentioned above.

ANOVA determines the most significant factors by using the statistical parameter *p*-value (Table 5). The coefficients of parameters presented were calculated from the rating of Yates [23]. Algebraic values of the coefficients measure the average change in the yield when the parameters change from level (−1) to level (+1).

Mathematical model of the Yield according to the coded process parameters which is given by Eq. (3) was determined with the regression coefficients presented in Table 5. This model was simplified according to the most important factors determined by Pareto Chart only (Fig. 3). The application of this model compared with the experimental results is presented below in Table 6. From modeling, results show that 100% of yield can be obtained in the best conditions corresponding to Run Order seven. This was confirmed with response surfaces and contour plots in the followed section.

$$\text{Yield}\ (\%) = 90.480 - 2.343 \times \text{TBP} - 2.683 \times \text{SPAN}\,80 - 2.688 \times \text{SV} - 6.970 \times \text{TBP}^{*}\text{SPAN}\,80 \quad (4)$$

3.3. Optimization of the extraction

Because of the interaction between the two most important factors, the extraction efficiency is not a direct function of either the TBP or SPAN 80. Therefore, classical optimization by varying one parameter at a time cannot give good results, and hence, using an experimental design as described in this work is therefore required. In this study, when the concentration of TBP or SPAN 80 increases, the extraction efficiency may decrease as it may also increase and this can be seen in the response surface and contour plot expressing yield as a function of TBP of SPAN 80 (Figs. 4 and 5).

By cons, the third factor which is the speed of agitation can be easily followed, in effect, when the speed increases the extraction efficiency decreases as can be seen in Figs. 6–9. This decrease is probably due to the destabilization of the membrane as it begins to break down at higher stirring speed.

Once the SV is set, we must now follow the other two factors simultaneously. Fig. 10, which gives the

Table 6
Comparison of results obtained from model with experimental

Run order	TBP		SPAN 80		SV		Yield	
	(%)	Code	(%)	Code	(rpm)	Code	Experimental (%)	Modelled (%)
1	30	1	16	1	250	1	72.00	75,796
2	30	1	8	−1	250	1	98.37	95,102
3	20	−1	8	−1	150	−1	90.90	91,224
4	20	−1	16	1	250	1	94.63	94,422
5	30	1	16	1	150	−1	84.97	81,172
6	20	−1	8	−1	250	1	86.17	85,848
7	**30**	**1**	**8**	**−1**	**150**	**−1**	**97.21**	**100,478**
8	20	−1	16	1	150	−1	99.59	99,798

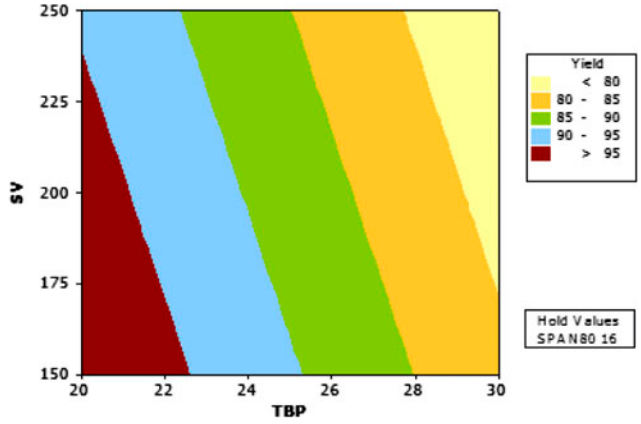

Fig. 6. Contour plot of yield vs. SV; TBP.

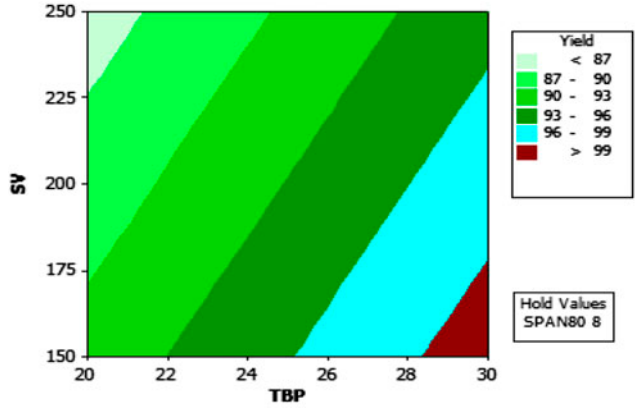

Fig. 7. Contour plot of yield vs. SV; TBP.

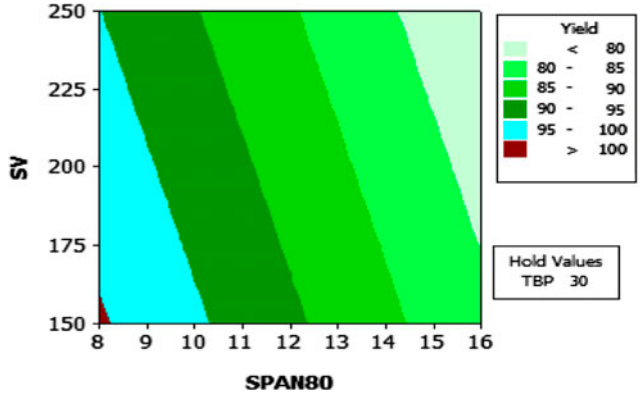

Fig. 8. Contour plot of yield vs. SV; SPAN80.

extraction efficiency as a function of TBP extractant and SPAN 80 emulsifier, shows that this yield is quite high and above 95% in two antagonistic regions corresponding to 8% of SPAN 80 and 30% of TBP on the one hand and 16% of SPAN 80 and 20% of TBP on the other. The yield reaches 100% in one of these two

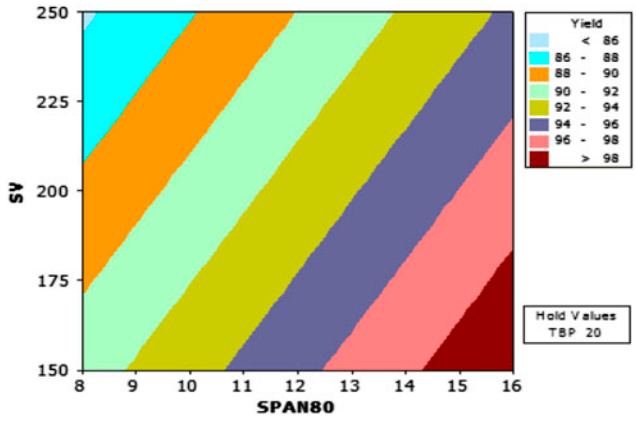

Fig. 9. Contour plot of yield vs. SV; SPAN80.

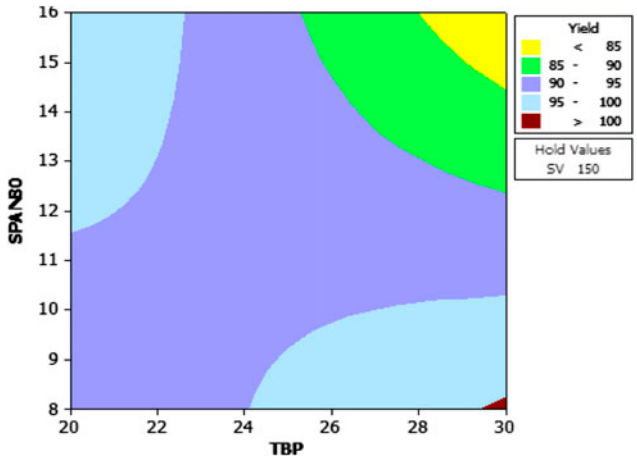

Fig. 10. Contour plot of yield vs. SPAN80; TBP.

regions corresponding simultaneously to a low concentration of SPAN 80 and a high concentration of TBP. The extraction is lower when the concentrations of the emulsifier and the extractant are also high. Results obtained from this final contour plot concord well with the modeling.

4. Conclusion

The extraction of 4-CP from pure 4-CP solution using an emulsified membrane is a technique that could give industrial success. The membrane used in this study was composed of Span 80 as an emulsifier, TBP as an extractant in a basic medium. The stability of the emulsified membrane has a very important role in the extraction. In this context, a study of the effects of different membrane components and process parameters was conducted using an experimental design of Plackett–Burman. A mathematical model showing the rupture rate of the membrane as a

function of various factors was developed. Among the eight factors studied, the concentrations of surfactant, extractant, and the stirring speed proved to be the most important factors for the stability of the membrane. The extraction of 4-CP was optimized by studying the effects of these three important factors using a full factorial design. This design of experiment showed the effects of factors on each other when they vary simultaneously and deduced a mathematical model showing the performance against the most important parameters. Indeed, it was found that TBP extractant and the surfactant SPAN 80 have a combined effect on the extraction and a high stirring speed decreases its performance. In this study, the extraction of 4-CP from aqueous solution containing initially 100 mg/L was performed with a 100% yield under the following conditions: The reports V_{ex}/V_{em}, V_o/V_w and The concentration [NaOH] were maintained at 15, 1, and 0.2 M, respectively. The pH of the external phase constant was kept between 5 and 6.4 using a buffer solution, the stirring speed was 150 rpm and concentrations of TBP and SPAN 80 were optimized at 30 and 8%, respectively. This work will be continued by a desextraction of 4-CP and the products formed in the process. The waste product will probably be concentrated in a controlled environment and the components of the membrane will be regenerated.

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