Optimization of hexavalent chromium removal by emulsion liquid membrane (ELM) using sunflower oil as eco-friendly solvent

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ABSTRACT

The focus of this study is the extraction of hexavalent chromium (Cr(VI)) from wastewater using emulsion liquid membrane (ELM) in order to contribute to sustainable design by replacing the common synthetic organic solvents to a bio-based solvent. The membrane phase consisted of sunflower oil as solvent and two non-ionic surfactants (Span 80 and Tween 80) as emulsifiers. Tri-n-octylphosphine oxide (TOPO) was used as carrier and Na_2CO_3 aqueous solution (0.5 mol/L) as stripping phase. The extraction of hexavalent chromium by using ELMs with sunflower oil as green solvent was modeled and optimized. The influence of several factors was studied: the volume fraction of the internal aqueous phase (X_1), initial concentration of hexavalent chromium $[Cr(VI)]_0$ (X_2), and the percentage of carrier concentration (X_3). A full 2^3 factorial design was performed to study the influence on the yield of the extraction process of Cr(VI); it provided important information regarding the optimum level of each variable along with its interactions with other variables and their effects on yield. Characterization of the primary water-in-oil (W_1/O) and double emulsions (ELM) are also reported. Results showed that the use of a vegetable solvent in ELMs formulation is a good alternative to petroleum organic solvents reaching Cr(VI) removal efficiency values up to 87.43% using 4% of TOPO at an optimal pH of 1.

Keywords: Chromium; Extraction; Emulsion liquid membrane; Factorial design; Eco-friendly solvent; Sunflower oil

1. Introduction

Hexavalent chromium (Cr(VI)) is widely used in industrial applications, such as electroplating, metal finishing and corrosion inhibition [1] and it must be removed before disposal in discharged industrial wastewaters because of its toxicity under below permissible limits [2]. Unlike other toxic heavy metals, chromates are quite soluble in aqueous phases almost over entire pH range, and thus quite mobile in natural environment.

Several methods have been developed for the removal of Cr(VI) from industrial effluents, such as chemical precipitation, electrochemical precipitation, ion exchange, solvent extraction, adsorption, biosorption and facilitated transport using polymer inclusion membrane [3–8]. Solvent extraction has been widely used for the recovery and/or removal of heavy metals from dilute solutions. A suitable alternative over conventional solvent extraction is the extraction with emulsion liquid membrane (ELM) [9–11].

ELM was developed by Li in 1968 by forming a stable simple water-in-oil (W/O) emulsion between two immiscible phases, followed by further dispersion into a third con-

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tinuous phase to carry out the extraction. The membrane phase is the oil phase that separates the internal aqueous droplets entrapped in the first emulsion from the external continuous phase [12,13].

Kerosene [14] and cyclohexane [15] are the most common solvents used as diluents in the membrane phase in ELM processes. These solvents are toxic, non-renewable, non-biodegradable, flammable and volatile. Moreover, they may cause ecological hazards to the aquatic systems in case of solvent leakages [16].

On the contrary, vegetable oils are potential green solvents that might avoid some of these disadvantages [17,18].

The purpose of this work was to optimizethe ELM extraction of Cr(VI) using TOPO (tri-n-octylphosphine oxide) as carrier and sunflower oil as solvent. As many factors and interactions affect the desired response, i.e., yield of metal extraction, response surface methodology (RSM) was used for process optimization [19–27]. Taking into account preliminary experiments and previous studies, the following operational parameters were selected: external aqueous phase ratio (X_1), the initial concentration of hexavalent chromium $[Cr(VI)]_o$(X_2) and the percentage of carrier concentration (X_3). Both primary water-in-oil (W_1/O) emulsion and the double emulsion (ELM) were characterized in terms of droplet size distribution, stability, zeta potential and visual inspection.

2. Experimental

2.1. Materials

The liquid membrane solution was formulated using two different types of non-ionic surfactants: Tween® 80 (polyoxyethylene sorbitan monooleate), from Sigma-Aldrich(Darmstadt, Germany) with hydrophilic-lipophilic balance (HLB) of 15.0 and Span 80 (sorbitan monooleate), from VWR International Prolabo (Radnor, Pennsylvania, USA), with HLB of 4.3, were chosen as stabilizers for all emulsions. The carrier used was TOPO (tri-n-octylphosphine oxide) supplied by Avocado Research Chemicals Ltd. (London, UK). Sunflower oil was used as solvent (density = 0.689g/cm³, viscosity = 0.044 Pa s).

Analytical grade hydrochloric acid (HCl), acetone (C_3H_6O), sulphuric acid (H_2SO_4), sodium carbonate ($Na_2CO_3.10H_2O$) and potassium chromate (K_2CrO_4) were supplied from Sigma-Aldrich, (Darmstadt, Germany).

2.2. ELMs preparation

Cr(VI) stock solution(C = 1000 mg/L) was prepared from potassium chromate (K_2CrO_4). Acidic feed solutions were prepared by adding HCl to an aqueous solution containing appropriate amount of Cr(VI) ions.

The sunflower oil containing 4% (v/v) of Span 80, 1% (v/v) of Tween 80 and 4% (w/w) of TOPO was used as the oil phase.

The final ELM was prepared in two emulsification steps. First a water-in-oil emulsion (W_1/O) was prepared by dispersing 9 mL of the stripping aqueous solution (Na_2CO_3, 0.5mol/L) into 30 mL of the oil using high shear mixing in an Ystral X10 mixer (Ystral GmbH, Germany), with a 6mm dispersing tool at 5000 rpm for 20 min.

This W_1/O emulsion was then poured into the external aqueous phase containing the Cr(VI). The system was gently stirred with an orbital agitator (400 rpm). Samples were taken from the external aqueous phase for determination of Cr(VI) concentration by UV-Vis spectroscopy using 1,5-diphenyl carbazide as indicator. The percentage of metal ions permeated to the membrane (%Y), or removed by ELM, was calculated by the following relation:

$$Y(\%) = \frac{\left[Cr(VI)\right]_0 - \left[Cr(VI)\right]_t}{\left[Cr(VI)\right]_0} \times 100 \qquad (1)$$

where $[Cr(VI)]_0$ is the initial concentration (mg/L) in the feed solution and $[Cr(VI)]_t$ is the concentration(mg/L) in the feed solution at time t.

2.3. ELMs characterization

ELMs droplet size distributions were analyzed using laser light scattering technique in a Mastersizer S long bench apparatus (Malvern Instruments Ltd., UK). The refractive index of the ELMs was taken as 1.54. For the primary W_1/O emulsion, the water refractive index (1.33) was used and the samples were dispersed in paraffin oil.

Micrographs of the emulsions were obtained with a light microscope Olympus BX50 (Olympus, Japan) with 10–100x magnification using a UV-Vis lamp. Micrographs were used for emulsions' visual inspection and to confirm the droplet size obtained by laser light scattering.

A Zetasizer Nano ZS (Malvern Instruments Ltd., UK) was used for zeta potential (ζ) measurements of ELMs.

Emulsion stability was determined by measuring backscattering (BS) and transmission (TS) profiles in a Turbiscan Lab apparatus (Formulaction, France). Emulsion samples were placed without dilution in the test cells. Transmitted and backscattered light was monitored as a function of time and cell height for 4 d at 30°C. Turbiscan provides useful information regarding the changes in droplet size distribution, appearance of a creaming layer or a clarification front with time [28].

Three replicate measurements were conducted for each sample.

2.4. Factorial experimental design

Factorial design and analysis of variance (ANOVA) methodology are appropriate and efficient statistical tools, which permit to study the effects of several factors that influence responses by varying them simultaneously within a limited number of experiments [20,21,23–27,29,30]. One of the most common factorial designs is 2^k, in which k factors are considered and each factor have assigned two levels being required 2^k measurements to perform the analysis [31–33].

In this work, three factors were chosen as independent variables: the external aqueous phase ratio V_{ext}/V_{emul} (X_1), initial concentration of hexavalent chromium $[Cr(VI)]_0$ (X_2, mg/L) and percentage of carrier concentration (X_3). The response was expressed as percentage of Cr(VI) removed by ELM, as it was indicated in Eq. (1).

The values of each factor at their respective levels are shown in Table 1. The levels of different factors were chosen on the basis of the preliminary trials and previous published results.

The coded values of X_j were obtained from the following relationship [32,33]:

$$X_j = \frac{Z_j - Z_j^0}{\Delta Z_j}, \quad j = 1, 2, \ldots, k \tag{2}$$

with

$$Z_j^0 = \frac{Z_{j\max} + Z_{j\min}}{2} \text{ and } \Delta Z_j = \frac{Z_{j\max} - Z_{j\min}}{2} \tag{3}$$

where X_j is the coded value of jth variable Z_j, the encoded value of j variable, ΔZ_j^0 the value of Z_j at the center point of investigation domain, and Z_j is the step size. Here $Z_{j\max}$ and $Z_{j\min}$ represent the maximum and the minimum level of factor j in natural unit, respectively.

The experimental data were analyzed by full factorial design (FFD) to fit the following first order polynomial equation:

$$\begin{aligned} \hat{y} &= b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 \\ &\quad + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 \end{aligned} \tag{4}$$

Table 1
Factors and levels in the experimental design (coded and uncoded values)

Independent variables	Range and levels		
	−1	0	1
(X_1)	2.8	4	5.19
$[Cr(VI)]_0 (X_2, mg/L)$	28.2	55	81.7
% extractant (X_3)	1.09	2.55	4

where $\hat{y}$ represents the estimated yield of Cr(VI) extraction, b_0 is the value of fitted response at the center point of design; b_j and b_{ji} are the linear and interaction terms, respectively [34]. The results of Cr(VI) removal using ELMs were analyzed using MINITAB software and the factors were evaluated using main effects plots (X_1, X_2 and X_3), their interactions (X_1X_2, X_1X_3 and X_2X_3) and the median value of the residues. Analysis of variance (ANOVA) and p-value for significant levels were used to check the significance of the studied effect on Cr(VI) removal percentage.

3. Results and discussion

3.1. ELM characterization

Both the primary W_1/O emulsion and the final ELMs used in this study were characterized since it will allow us to better know the interfacial properties of the system and how they could affect the extraction method. Droplet size distributions of the primary (W_1/O) and double emulsions (ELM) are shown in Fig. 1(A). The emulsions showed a monomodal distribution of sizes, and d_{32} value was 1.15 ± 0.05 μm for W_1/O emulsions: these results agree with the range suggested by Li et al. [12] who produced w/o emulsion with $d_{32} = 0.8$–3 μm. For ELM the d_{43} was 154.84 ± 0.10 μm, which indicates a good dispersion of the W/O emulsion in the external phase.

Oil drops containing the inner small aqueous droplets can be clearly identified in Fig. 1(B) confirming the presence of double emulsions. Visual inspection of these micrographs indicates that droplet sizes are in good agreement with experimental data from Fig. 1(A).

The mean ELM zeta potential value was 6.02 ± 3.16 mV. The low zeta potential values at the oil droplets interface facilitate that droplets tend to aggregate, as it was observed in Turbiscan Lab profiles from ELM samples (Fig. 2B).
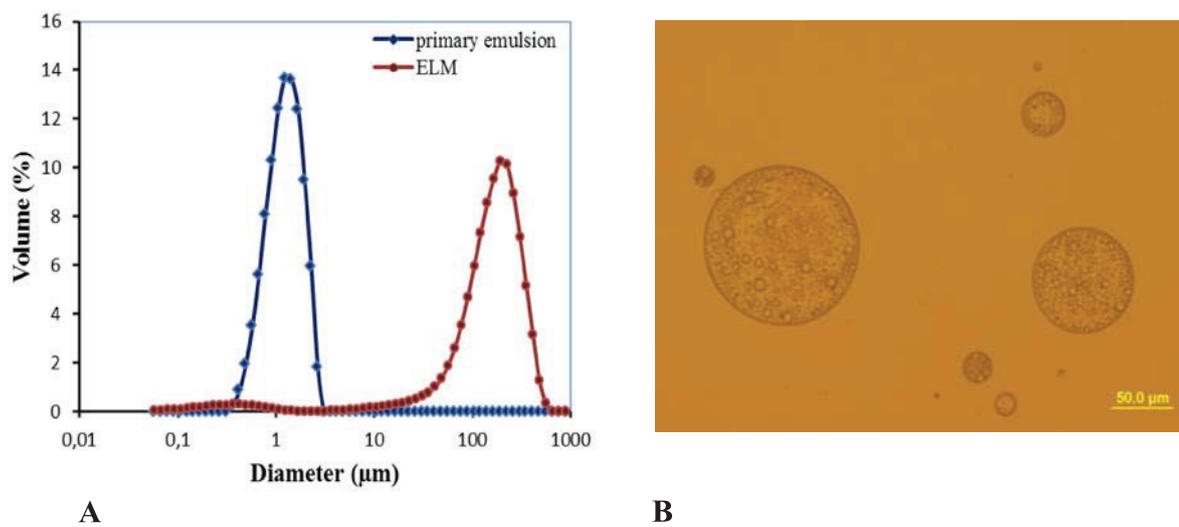
Fig. 1. Droplet size distributions of the primary W_1/O emulsion and the final ELM formulated with 5% of surfactant (Span 80, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase (A); Optical microscopy image of the ELM formulated with 5% of surfactant (Span 80, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase (B).
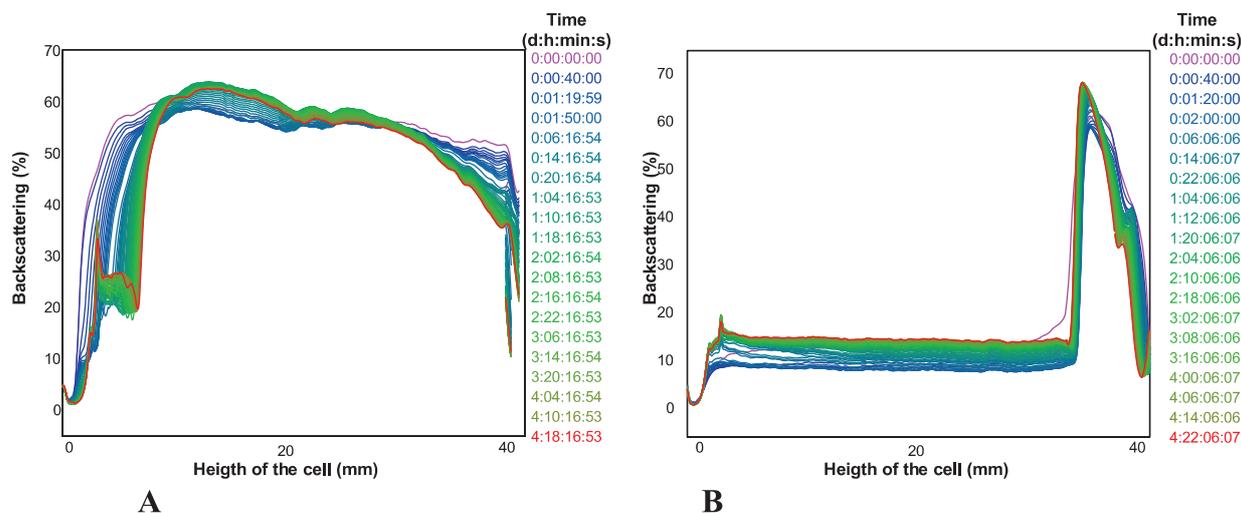
Fig. 2. Backscattering (BS) profiles of emulsions (A) W_1/O; (B) ELM formulated with 5% of surfactant (Span 80, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase.

Turbiscan equipment has been widely used to monitor the stability of emulsions, either used as metal working fluids in industry [28] or as food formulations [35–37], since double emulsions present several applications in different fields [13–14,20–25,33–38]. The stability of W_1/O emulsions prepared with PGPR (polyglycerol polyricinoleate) and Spans as emulsifiers was measured by other authors [35–37]. A decrease in BS values with the cell height implies an increase of water droplets size because a coalescence process takes place, resulting in the sedimentation of water droplets at the bottom of the cell. Fig. 2(A) shows the corresponding BS profile of the primary W_1/O emulsion formulated in this study: a BS decrease along the cell height is observed, what means that there is slight coalescence. A corresponding increase in the TS profile was observed at the bottom of the cell in that region (results not shown). However, no considerable BS variations were observed in the middle part of the cell (~4%), what means that there were no significant changes in droplet size, remaining the emulsion region stable.

For ELMs (Fig. 2B), a clarification process was observed along the height of the cell, with a BS decrease at the bottom and an increase at the top, as a result of the lower density of oil droplets which rise towards the top leading to a creaming process. Moreover, BS variations were also caused by flocculation of the oil droplets according to the aforementioned low zeta potential values.

3.2. Extraction mechanism of Cr(VI) with TOPO in the new solvent

The effect of pH on Cr(VI) extraction with the ELM-based sunflower oil was studied in the range from 0.5 to 8. HCl and NaOH solutions were used to get the desired pH in each case. The evolution of the extraction yield as a function of pH is depicted in Fig. 3.

The graph showing the evolution of the Cr(VI) extraction efficiency as a function of pH of the feed phase (Fig. 3), allow us to distinguish three zones: i) pH from
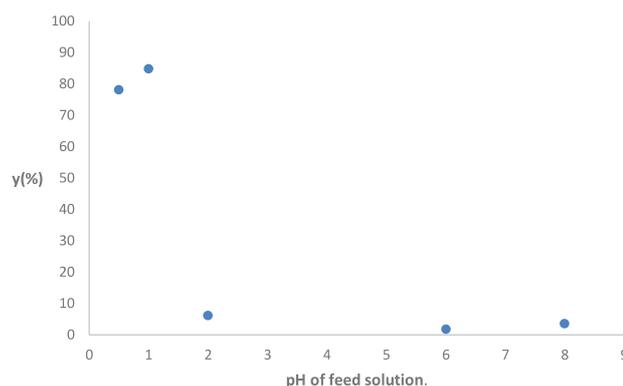
Fig. 3. Effect of pH of feed solution on the yield extraction of Cr (VI). Sunflower oil; 5% of surfactant (Span 80, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio V_{int}/V_{org} = 0.3; feed solution: $[Cr(VI)]_0$ = 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio V_{emul}/V_{ext} = 5.

0.5 to 1, where the extraction yield increases to an optimum value, 84.9%, when using the plant solvent; ii) at a pH between 1 and 2, where the extraction yield decreases sharply, and iii) at pH beyond 2 there is no more noticeable extraction. Therefore, the extraction of Cr(VI) using the TOPO is optimal for a pH = 1. Based on these results, and taking into account that the distribution of chromate species is a function of pH and the concentration of Cr(VI), we can conclude that the transport of Cr(VI) is carried out by an ion mechanism of association of a pair $(H^+, HCrO_4^-)$ with the TOPO, according to the reaction mechanism given by the following equation:

$$(H^+, HCrO_4^-) + TOPO \leftrightarrow H_2CrO_4TOPO \qquad (5)$$

Kumbazar [14] suggested a similar transport mechanism in the case of extraction of the hexavalent chromium by the TOPO using kerosene as solvent.

Sunflower oil acts as an ordinary solvent and has no effect on the transport mechanism that is provided by carrier (TOPO). This carrier is easily soluble in the solvent again.

3.3. ELM Application and analysis of three parameters affecting the chromium recovery using factorial experimental design

The experimental design was done with replicate runs performed in random way. Table 2 shows the design matrix of coded values for the studied factors and the response in terms of Cr(VI) removal percentage.

Table 3 displays the main effects and their interactions, the model coefficients, probability, as well as Student's t-test values. The significance of the regression coefficients was

Table 2
2^3 full factorial design and replicate runs

Runs no.	X_1	X_2	X_3	Yield, y (%)
1	–1	–1	–1	75.88
2	1	–1	–1	79.78
3	–1	1	–1	50.67
4	1	1	–1	37.45
5	–1	–1	1	84.11
6	1	–1	1	85.1
7	–1	1	1	83.88
8	1	1	1	79.35
9	0	0	0	44.54
10	0	0	0	48.18
11	0	0	0	41.81
12	0	0	0	44.09
13	0	0	0	43.18
14	0	0	0	45.81
15	0	0	0	44.00
16	0	0	0	47.45
17	0	0	0	43.61

Table 3
Estimated effects and coefficients for Cr(VI) removal percentage (coded units)

Term	Effect	Coefficient	Standard error coefficient	t	P
		72.03	0.8371	86.05	0.000
X_1	–3.22	–1.61	0.8371	–1.92	0.087
X_2	–18.38	–9.19	0.8371	–10.98	0.000
X_3	22.17	11.08	0.8371	13.24	0.000
X_1X_2	–5.66	–2.83	0.8371	–3.38	0.080
X_1X_3	1.44	0.72	0.8371	0.86	0.410
X_2X_3	15.39	7.69	0.8371	9.19	0.000
CtPt		–27.29	1.1504	–23.72	0.000

S = 2.36756, PRESS = 1119.04, R² = 99.07%, R²(adjusted) = 98.35%, R² (predicted) = 79.37%; CtPt: central point

determined by applying a Student's t-test. All factor effects were significant with 95% confidence level, except factor X_1 (p = 0.087) and the interaction X_1X_3 (p = 0.410). The R² indicated that the first-order model explained 99.07% of the variability of Cr(VI) removal percentage. The model also presented a high adjusted square correlation coefficient R² of 98.35%.

Therefore, Cr(VI) removal by ELM could be expressed with the following equation:

$$y(\%) = 72.03 - 9.19X_2 + 11.08X_3 - 2.83X_1X_2 + 7.69X_2X_3 \quad (6)$$

Eq. (6) shows the presence of interactions between the X_1 and X_2 and also between X_2 and X_3.

The main effects plots are shown in Fig. 4(A). It can be seen that X_2 has a negative effect on the extraction yield, while X_3 has a positive effect being both significant. No effect was observed for the external aqueous phase ratio X_1. Fig. 4(B) shows the interaction plot for Cr(VI) removal. As it was just aforementioned, it can be seen that there is a strong interaction effect between X_1 and X_2 and also between X_2 and X_3. Alternatively, the interaction between X_1 and X_3 was not relevant.
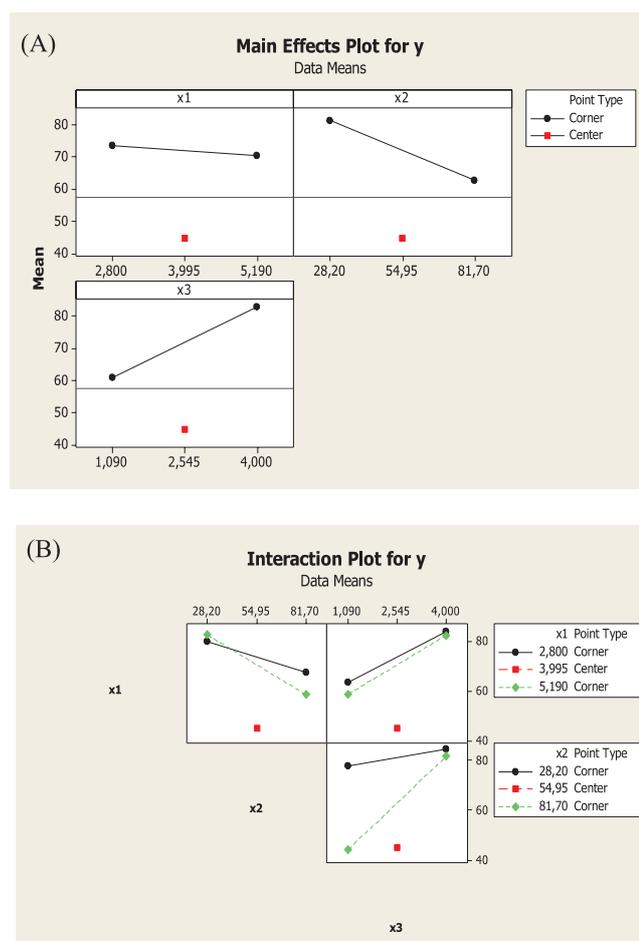
Fig. 4. Main effects plot for Cr(VI) removal by ELM using sunflower oil as solvent A); Interaction effect plot for Cr (VI) removal by ELM B).

Table 4
Analysis of variance (ANOVA) for % removal (coded units)

Source	d_f	Seq SS	Adj SS	Adj MS	F	P
Main effects	3	1678.90	1678.90	559.63	99.84	0.000[a]
2-way interaction	3	341.95	541.95	180.65	32.23	0.000[a]
Residual error	9	50.45	50.45	5.61		
Lack of Fit	1	16.82	16.82	16.82	4.00	0.080[ns]
Pure error	8	33.63	33.63	4.20		
Total	16	5424.67				

d_f = degrees of freedom, Seq SS = sequential sum of squares, Adj SS = adjusted sum of squares, Adj MS = adjusted mean sum of squares, F = factor F, P = probability
[a]Significant at 5% level; ns: Not significant.

The contribution of each factor was estimated by a statistical analysis of variance (ANOVA). Table 4 shows the sum of squares being used to estimate the factors' effect and the F ratios, which are defined as the ratio of the respective mean-square-effect to the mean-square-error. From the p value, defined as the lowest level of significance leading to the rejection of the null hypothesis, it can be noticed that the main factors, two and three-way interactions were all significant at 5% of probability level ($p < 0.05$).

The relative importance of the main effects and their interactions is shown in the Pareto chart given in Fig. 5. It was observed that for a 95% confidence level and eight freedom degrees, the t value was equal to 2.306. It can also be seen that the carrier concentration had the greatest effect on the Cr(VI) removal percentage. The second factor affecting the Cr(VI) removal percentage was X_2 followed by the X_2X_3 interaction and finally X_1X_2 interaction.

The suitability of the model was also evaluated by the residuals, i.e., difference between the experimental and predicted values, which are shown in Table 5. The median value of the residues is of the order of 5.88235E-06. According to this value, the reliability of the model can be confirmed.

3.4. Optimization of process parameters

3.4.1. Interaction between the volume ratio V_{ext}/V_{emul} (X_1) and the initial concentration of Cr(VI) (X_2)

In order to study the interaction between X_1 and X_2, the carrier concentration (X_3) was fixed at its maximum value (4%). The plots of the response surface (Fig. 6A) show that a maximum yield of 87.43% was obtained for a X_1 value of 5.19 and X_2 of 28.2 mg/L. It can be noticed that, at high Cr(VI) concentrations, the extraction yield increases slightly with decreasing volume ratio. This can be explained by the fact that at high Cr(VI) concentrations it is necessary to use larger volume of emulsion since the required carrier amount is a function of the Cr(VI) to be transported. Similar behavior was observed by Hasan et al. [15] for Cr(VI) extraction by ELM using TOPO. They stated that increasing emulsion volume both the number of globules and active sites on the membrane surface increased leading to higher total surface area available for the extraction process. But the opposite trend was observed at low Cr(VI) concentrations since the extraction yield increased with increasing volume ratio being in good agreement with pre-
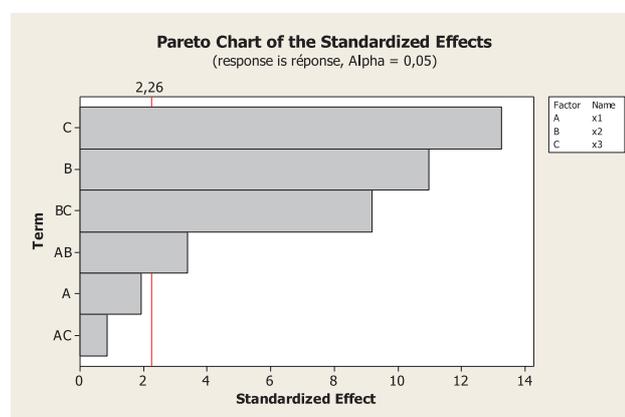
Fig. 5. Pareto chart of statistical effects on the removal of Cr (VI) at P = 0.05.

Table 5
Difference between the experimental and the predicted values (residuals)

Obs.	Experimental values	Predicted values	Residual
1	75.8800	77.3300	−1.4500
2	79.7800	78.3300	1.4500
3	50.6700	49.2200	1.4500
4	37.4500	38.9000	−1.4500
5	84.1100	82.6600	1.4500
6	85.1000	86.5500	−1.4500
7	83.8800	85.3300	−1.4500
8	79.3500	77.9000	1.4500
9	44.5400	44.7411	−0.2011
10	48.1800	44.7411	3.4389
11	41.8100	44.7411	−2.9311
12	44.0900	44.7411	−0.6511
13	43.1800	44.7411	−1.5611
14	45.8100	44.7411	1.0689
15	44.0000	44.7411	−0.7411
16	47.4500	44.7411	2.7089
17	43.6100	44.7411	−1.1311
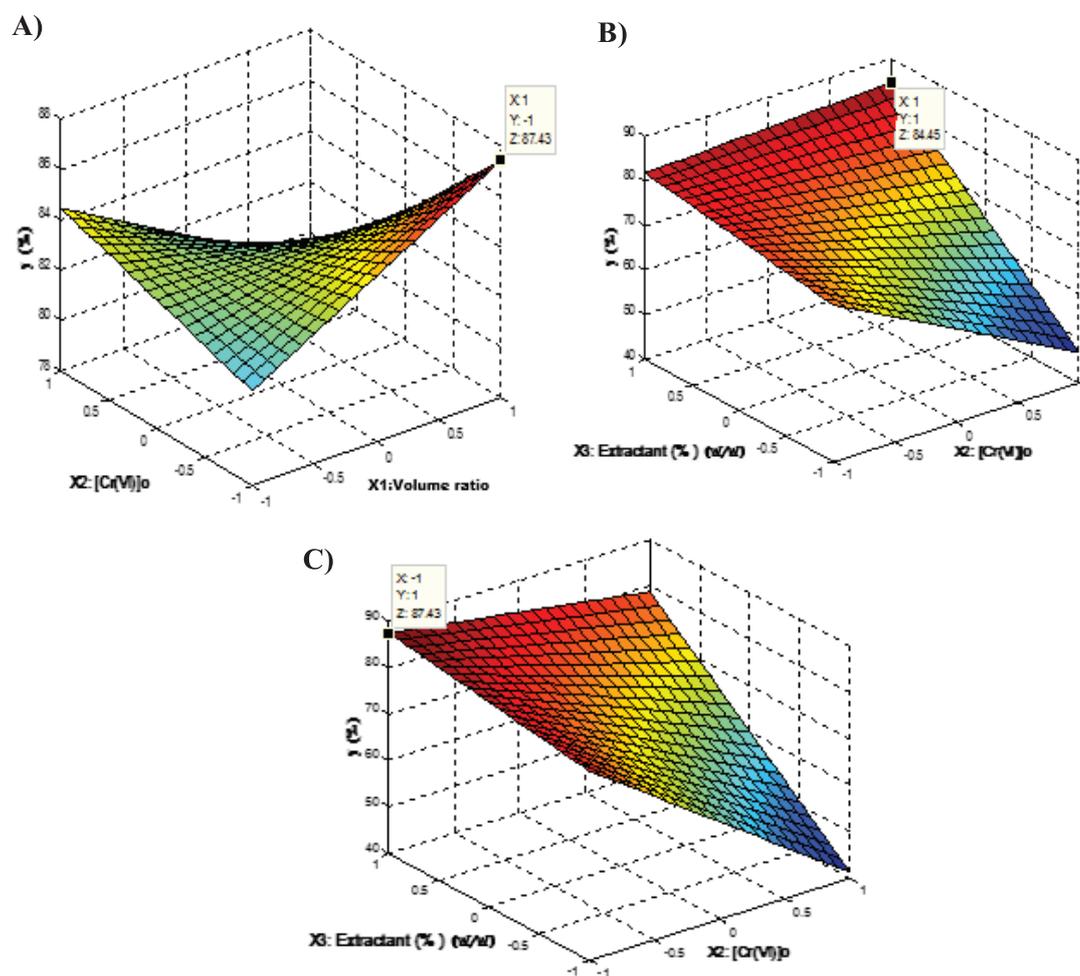
Fig. 6. Response surface plot for Cr (VI) yield, the interaction between the volume ratio V_{ext}/V_{emul} and the initial concentration of Cr (VI) (A); the interaction between the initial concentration of Cr(VI) and the carrier % (w/w), the volume ratio $X_1 = -1$ (B), the volume ratio $X_1 = +1$ (C).

vious studies in which Cr(VI) was removed by ELM using TOMAC (tri-n-octyl methyl ammonium chloride) [39]. In that study, it was reported that higher treat ratios reduced the ELM swelling and breaking increasing the concentration of Cr(VI) per globule and therefore enhancing Cr(VI) extraction. It was also previously reported by other authors that the extraction process by ELM was non-linear with respect to the total Cr(VI) concentration [40].

3.4.2. Interaction between the initial concentration of Cr(VI) (X_2) and the carrier concentration (X_3)

To study the interaction between X_2 and X_3, the volume ratio X_1 was set to its optimal values (+1) and (–1). Plots of the response surface in the plane X_2–X_3 (Fig. 6B and 6C) show that when the volume ratio X_1 is at the minimum level an extraction rate of 84.45% was achieved.

At high concentrations of Cr (VI), the extraction yield increases with increasing amount of carrier. Similar behavior was reported by other authors when TOPO was used for Cr(VI) removal with ELM [14,15]. Extraction rates up to

87.43% were obtained by increasing the amount of carrier up to 4% (w/w) whatever the initial concentration of Cr(VI). The same carrier concentration was selected as optimal for Cr(VI) extraction by ELM using TOPO in previous studies [14].

Therefore, the maximum removal of Cr(VI) by ELM using sunflower oil as solvent at the optimum conditions (X_1 = 5.19, X_2 = 28.2 and X_3= 4) was 87.43%. In previous studies reported in the literature, the removal percentage of chromium was 97% for the extraction of Cr(VI) with ELM using kerosene as solvent [14] and 98% for cyclohexane as solvent [15]. Although the removal efficiency obtained in this work is relatively lower compared to the ELM extraction with organic solvents, the sunflower oil is a good alternative as a green solvent.

4. Conclusions

The present study allow us to say that the use of sunflower oil as solvent in the formulation of ELM used for Cr(VI) removal by extraction with TOPO is a good alternative compared to those using conventional solvents.

Statistical analysis of variance (ANOVA) of the results obtained from a full 2^3 factorial design showed that the carrier concentration (X_3) had the greatest effect on the removal percentage of Cr(VI) by ELM. The second factor affecting the Cr(VI) removal percentage was the $[Cr(VI)]_0$ (X_2) followed by the interaction between X_2 and X_3 and finally the interaction between the external aqueous phase ratio (X_1) and X_2.

At high Cr(VI) concentrations the extraction yield increased slightly with decreasing volume ratio $V_{ext}/V_{emul,}$ but the opposite trend was observed at low Cr(VI) concentrations. The initial concentration of Cr(VI) in the feed phase influences negatively the extraction yield, while the amount of carrier used has a positive effect.

Extraction yields up to 87.43% were obtained by increasing the amount of TOPO up to 4% (w/w) whatever the initial concentration of Cr(VI) in the range studied at an optimal pH of 1.

Acknowledgements

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