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Green Emulsified Liquid Membrane for hexavalent chromium extraction: formulation and process optimization

In this paper, the influence of several formulation and operating conditions on hexavalent chromium extraction by Green Emulsified Liquid Membranes (GELM) was studied. The best removal efficiency (99.5 %) was achieved by stirring 5 mL of the green emulsion with 25 mL of the external phase at pH of 1 and at a speed of 400 rpm for 18 min. The optimum GELM formulation in terms of stability was obtained with 4% (v/v) tri-n-octylphosphine oxide (TOPO) as extractant, 4% (v/v) polyglycerol polyricinoleate (PGPR) and 1% (v/v) of polyoxyethylene sorbitan monooleate (Tween 80) as stabilizers in sunflower oil. Optimum GELMs showed a monomodal distribution of sizes around 1.29 µm. Results confimed that the use of a vegetable solvent and PGPR for GELM formulation is a promising alternative to petroleum organic solvents.

Keywords: Chromium, emulsion liquid membrane, extraction, stabilizers, sunflower oil

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1 Introduction

Membrane processes, especially those involving liquid membranes, are gaining importance and emerging as a viable alternative to conventional extraction processes [1-3]. The growing interest in membrane processes is based on its simplicity, the requirement of small quantities of carrier and low energy consumption. The Emulsion Liquid Membrane (ELM) technique has great potential for recovery and removal of hydrocarbons and different metal ions from wastewater in comparison with conventional methods [4]. This technique have been studied for removing phenol [5-7], cadmium [8-10] and chromium [11, 12] from waste solutions.

ELM processes are those involving a selective liquid membrane phase in which simultaneous extraction/stripping occurs. Separation is achieved by solute permeation through this liquid phase from feed to the receiving phase. The feed and receiving phases are normally miscible while the membrane phase is immiscible in both. An ELM can be considered as a double emulsion consisting of three phases: external, membrane and internal phases. Receiving phase is emulsified in an immiscible liquid membrane using surfactants and high-speed agitation. Emulsion droplets range from 1 to 3 μm in diameter, thus providing good stability [13]. The emulsion is then dispersed in the feed solution with constant agitation and mass transfer from the feed to the internal receiving phase takes place.

Recently, the introduction of green solvents such as vegetable oils in the formulation of organic phase to act as membrane phase have drawn the attention of researchers in this field. The innovative applications of green solvents will be helpful in making this process more cost effective and environment friendly [14,15], since till date most of the ELM based extraction processes have used only organic solvents (such as kerosene, hexane, heptane) as the main component of organic phase. These solvents are toxic and volatile in nature, flammable, and uneconomic due to their limited resources [16]. Currently, vegetable oils are viewed as the best alternative to petroleum-based solvents being economic, renewable, nontoxic, inflammable, non-volatile, and biodegradable.

Soybean, palm, rapeseed, and sunflower oils have been explored in previous works: phenol removal [17, 18], Cu(II) extraction [19], Cr(VI) extraction [20-25], the removal and recovery of rhodamine B [26], and textile dye [27]. These studies show a promising potential of vegetable oils in chemical extractive processes which will have an important environmental relevance.

The use of sunflower oil in the formulation of ELM is a good alternative to conventional organic solvents [28,29]. Additionally, the choice of surfactant is very important to have a stable emulsion.

Polyglycerol polyricinoleate (PGPR) is a synthetic emulsifier widely used to stabilize water-in-oil (W_1/O) and water-in-oil-in-water ($W_1/O/W_2$) emulsions. PGPR is commonly used to stabilize double emulsions for their application in food, cosmetic and pharmaceutical industries. The use of these blended surfactants on the oil phase show good efficiency on the stabilization of water/oil interfaces [30, 31].

Cr(VI) receives particular attention because of its high toxicity and presence in industrial applications, e.g., electroplating, metal finishing and corrosion inhibitors [32]. Since the Cr(VI) is carcinogenic, mutagenic and teratogenic in nature, its recovery and concentration from industrial effluents become a necessary task for environmental safety [33-36].

The aim of this work was to characterize in terms of droplet size distribution, stability, zeta potential and visual inspection the GELMs formulated with sunflower oil as green solvent and PGPR and Tween 80 as stabilizers. Moreover, in order to develop a more efficient process, the

effects of various operating conditions such as stirring speed, stirring time, feed phase (W_2) pH value, composition of the stripping phase (W_1) and phases volume ratios were evaluated to increase Cr(VI) extraction.

2 Materials and methods

2.1 Materials

The liquid membrane solution was formulated using two different types of non-ionic surfactants as stabilizers: Tween® 80 (polyoxyethylene sorbitan monooleate), a hydrophilic surfactant from Sigma-Aldrich (USA) with hydrophilic-lipophilic balance (HLB) of 15.0, and the lipophilic surfactant PGPR (polyglycerol polyricinoleate), supplied by Brenntag AG (Germany), with HLB of 3.0. The mobile carrier or extractant used was TOPO (tri-n-octylphosphine oxide) supplied by Alfa Aesar, Germany. Food grade sunflower oil was used as solvent (density = 0.689 g/cm^3, viscosity= 0.044 Pas).

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

2.2 Methods

2.2.1 ELM preparation

In a 100 mL container, 4% (v/v) Tri-n-octylphosphine oxide (TOPO), 4% (v/v) PGPR and 1% (v/v) of Tween 80 (HLB value of the mixture was 5.4) in sunflower oil were dissolved by stirring; the solution formed was used as oily phase. Then a W_1/O emulsion was prepared by dispersing the stripping aqueous solution (Na_2CO_3, (NaOH) or (($NH_4)_2CO_3$) 0.5 M) into the oily phase at different volume ratios (volume ratio in the range from 2/20 to 20/20) prepared using high shear mixing with in an Ystral X10 mixer (Ystral GmbH, Germany) with a 6 mm stirrer at 5000 rpm for 20 min at 25 ºC, as was previously optimized [29].

2.2.2 Extraction experiments

The acidic external phase was prepared by adding HCl to an aqueous solution containing 50 ppm of Cr(VI). The prepared W_1/O emulsion was mixed under stirring with prepared wastewater (W_2) in order to form GELM while Cr(VI) extraction took place at different volume ratios (volume ratio in the range from 1/10 to 4/10). The contents were stirred by means of a magnetic stirrer at a speed of 150-500 rpm for different time intervals. Once the extraction was done and stirring stopped, the GELM was completely separated by simple decantation in a separator funnel being the external aqueous phase carefully separated in an easy way. Samples were taken from the external aqueous phase for determination of chromium concentration by UV-Vis

spectrophotometry (PG Instruments Ltd., UK) using 1,5-diphenyl carbazide as indicator at 542 nm.

Extraction efficiency (R(%)) was calculated as:

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

where $[Cr(VI)]_0$ is the initial concentration of hexavalent chromium in the external aqueous phase and $[Cr(VI)]_t$ is the concentration of hexavalent chromium at time t.

2.2.3 GELMs characterization

GELMs droplet size distributions were analysed using laser light scattering technique in a Mastersizer S long bench apparatus (Malvern Instruments, Ltd. UK). The refractive index of the ELMs was measured as 1.54. Samples were first diluted with deionized water to prevent multiple scattering effects. Then, they were circulated through the measuring zone using a Hydro SM small volume sample dispersion unit, following the manufacturer's recommendations for this type of emulsion. For the primary W_1/O emulsion, the water refractive index (1.33) was used and the samples were dispersed in paraffin oil, since was previously tested with good results on the determination of water drops on W/O emulsions [37].

Three replicates were obtained for each emulsion. Results were reported as typical droplet size distribution in µm. The mean diameters, volume-weighted mean diameter d_{43} and surface-weighted mean diameter or Sauter diameter d_{32}, were calculated by equations (2) and (3):

$$d_{43} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \qquad (2)$$

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \qquad (3)$$

Where d_i is the droplet diameter and n_i is the number of droplets with diameter d_i.

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 NanoZS (Malvern Instruments Ltd., UK) was used for the zeta potential (ζ) measurements of ELMs. Three replicate measurements were conducted for each sample at a constant temperature of 25 ºC.

Emulsion stability was determined by measuring backscattering (BS) and transmission (TS) profiles in a Turbiscan Lab expert apparatus (Formulaction, France). Emulsions samples (20 mL) were placed without dilution in the test cells. Transmitted and backscattered light was monitored

as a function of time and cell height for 7 days at 30 °C. The optical reading head scans the sample in the cell at different times, providing TS and BS data every 40 □m as a function of the sample height (in mm). These profiles build up a macroscopic fingerprint of the emulsion at a given time, providing useful information about emulsion stability regarding the changes in droplet size distribution, appearance of a creaming layer or a clarification front with time.

3. Results and discussion

3.1 GELMs characterization

The GELMs used in this study were characterized in terms of droplet size distribution, zeta potential, visual inspection and stability with Turbiscan Lab (Formulaction). These measurements allow us to better know the interfacial properties of the system and how they could affect the extraction method with future formulations.

Droplet size distributions of the primary (W_1/O) and double emulsions (GELM) are shown in Fig. 1. The emulsions showed a monomodal droplet size distribution with a d_{32} value of 1.29 ± 0.05 μm for W_1/O emulsions. These results agree with the range found by other authors (d_{32} of 0.3-5 μm) when optimum agitation conditions were used for W_1/O emulsion preparation [29, 38-42].

For GELM the d_{43} was 192.75 ± 0.10 μm, ensuring a good dispersion of the W_1/O emulsion in the external phase that provides the higher extraction efficiency since the large difference between water drops (W_1) and oil drops (O) will ensure that each individual oil drops content a large number of water droplets what enhance contact between phases and therefore the extraction efficiency.
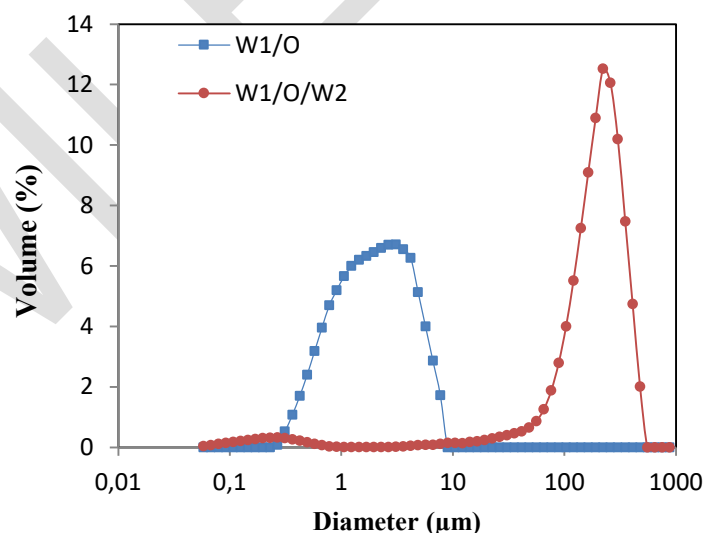

Figure 1. Droplet size distributions of the primary W_1/O emulsion and the final GELM formulated (W_1/O/W_2) with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr (VI) in the external aqueous phase.

Oil drops containing the inner small aqueous droplets can be clearly identified in Fig. 2 confirming the presence of double emulsions. Visual inspection of these micrographs indicates that droplet sizes are in good agreement with experimental data from Fig. 2.
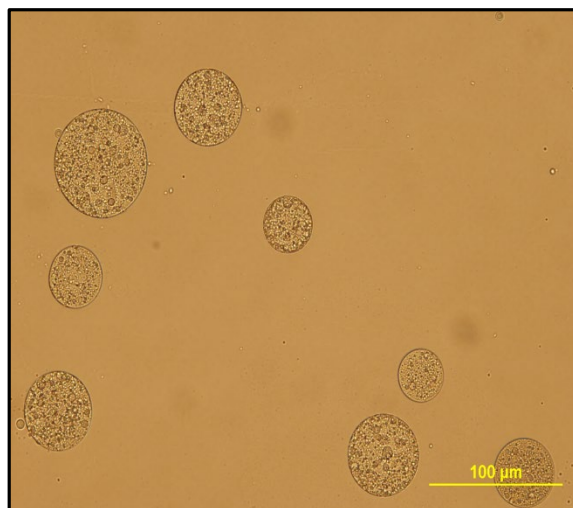

Figure 2. Optical microscopy image of the GELM formulated with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase.

The mean zeta potential value was -0.15 ±3.51 mV. Colloidal stability by ionic charge is typically known to be over ± 30-40 mV [43, 44]. Even, ionic charge is not the only responsible for droplets stability. The low zeta potential values at the oil droplets interface facilitate droplet aggregation and creaming, as it was observed in Turbiscan Lab profiles from GELM samples (Fig. 3B), so the external phase could be carefully separated by simple decantation.

Turbiscan equipment has been widely employed to monitor the stability of emulsions, used either as metal working fluids in industry [45] or as food formulations [46]. The stability of W_1/O emulsions, prepared with PGPR and Spans as emulsifiers, was measured by other authors [31, 46, 47]. In Fig 3A a decrease in BS values with time means an increase of size of water droplets because ofvcoalescence. However, no considerable BS variations (~4%) were measured at the top or bottom of the cell, what means that there were no significant changes in droplet size in the first 24 h. Moreover, after 24 hours a clarification at the bottom part of the cell indicated a sedimentation of water droplets what will encourage emulsion breakage, being a clear advantage from the solvent recovery point of view.
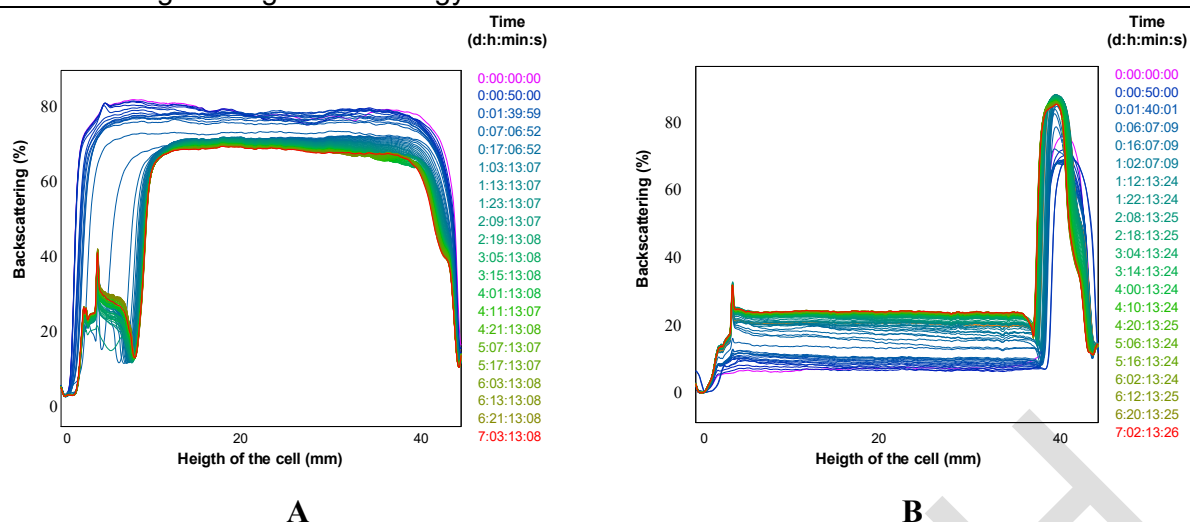
Figure 3. Backscattering (BS) profiles of emulsions (A) W_1/O; (B) GELM formulated with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase.

In the case of ELMs (Fig. 3B), a clarification process was observed along the height of the cell, revealed by a decrease in BS measurements at the bottom and an increase at the top of the cell, due to the lower density of oil droplets which rise towards the top and resulting in a creaming process. Moreover, BS variations were also caused by aggregation of the oil droplets according to the aforementioned low zeta potential values.

It is important to point out, that during extraction process the ELM was continuously stirred and hence the migration of water droplets was avoid. Moreover, to easily separate the purified aqueous effluent (W_2) from the W_1/O emulsions, it is an advantage that the emulsion will be easily separated by just common sedimentation.

3.2 Analysis of parameters affecting the chromium recovery

3.2.1 Effect of the extraction time

Fig. 4 shows the evolution with time of Cr(VI) removal. The Cr(VI) removal increases during the first 18 min (56–99.5%) and from the on, a plateau is observed. This plateau indicates the equilibrium condition, so from them on it can be considered that after this point the receiving phase is saturated . In the following experiments, the extraction time for Cr(VI) removal was fixed to t = 18 min and the effect of different operating ELM conditions on hexavalent chromium removal performance was studied: stirring speed, type and concentration of internal phase, volume ratio of internal phase to membrane phase, volume ratio of emulsion to external phase and pH of feed phase. Similar saturation times were observed by other authors when uranium is extracted by

liquid membranes, which use a liquid membrane with a $d_{3,2}$ diameter of the water droplets of 1-1,5 µm [48]. However, larger reduction time (around 2 minutes) are obtained by other authors who recover Cobalt (II) by a liquid membrane with a d3,2 diameter of the water droplets of around 0.3-0.7 µm, which could be the responsible of larger interfacial area and hence faster metal transfer [41].
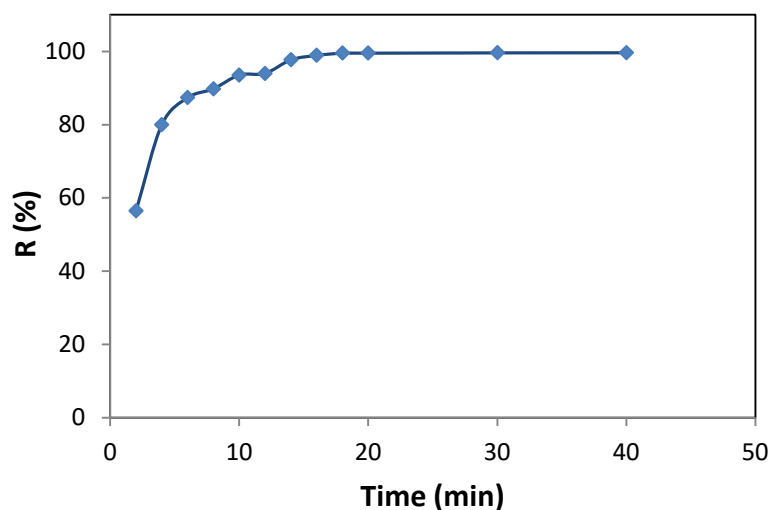

Figure 4. Effect of extraction time on the Cr(VI) removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio V_{int}/V_{org} = 0.3; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio V_{emul}/V_{ext} = 5.

3.2.2 Effect of stirring speed

The effect of the stirring speed during the extraction process was studied at 150, 300, 400 and 500 rpm. The results obtained are shown in Fig. 5. It was observed that the agitation speed improves significantly the extraction efficiency from 150 rpm to 400 rpm increasing from 47.2-72.3% to 95.9-99.6%. This effect can be explained by the fact that the number of emulsion globules increases at high stirring speed, which leads to an increase in the surface area of membrane and thus enhancing the Cr (VI) mass transfer. Not significant differences were obtained when higher agitation speeds were used. Indicating that higher speed do not significantly reduced the oil droplet size. Cr(VI) recovery of 99% were obtained for 400 and 500 rpm after 10 min.

When 300 rpm as used, similar recovery values were registered but, in that case, more time (14 min) is required to arise the equilibrium, what agrees with the fact that the lower interfacial area leads to a slower mass transfer.

Some works found that an intermediate agitation speed value which led to a maximum extraction capacity [40, 49-53]. These studies reported that when working at lower agitation speed range, the extraction efficiency increases when agitation speed increases, due to the mentioned reduction in oil droplets size. However, a maximum extraction efficiency was found for an intermediate agitation speed, since when agitation speed increases extraction efficiency started to increase due to the swelling of water molecules from the external aqueous phase into the inner aqueous phase. However, this maximum was frequently found at larger agitation speeds than the ones used in the present work.

In the present work 400 rpm was considered the optimum agitation speed to provide a good dispersion of emulsion globules along with a high extraction yield in short periods of time.
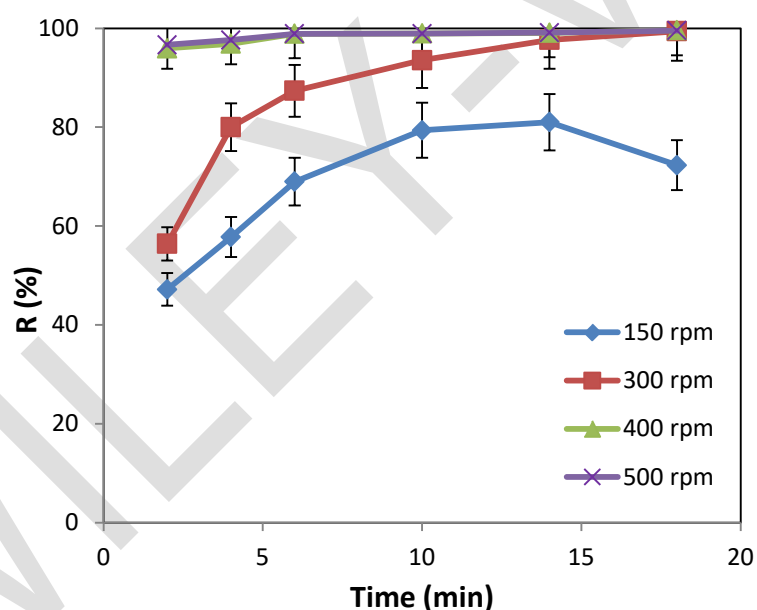

Figure 5. Effect of stirring speed on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio $W_1/O = 6/20$; feed solution: $[Cr(VI)]_0 = 50$ ppm, pH = 1; the volume ratio $W_1/O/W_2 = 2/10$.

3.2.3 Effect of different type of internal phase

Although in the preliminary experiments sodium carbonate solutions ($Na_2CO_3.10\ H_2O$) were used as internal aqueous phase, other alkaline solutions were also tested. Three different stripping solutions were selected: sodium carbonate ($Na_2CO_3.10\ H_2O$), sodium hydroxide (NaOH) and ammonium carbonate (($NH_4)_2CO_3$), which had been shown satisfactory results on chromium extraction processes in previous works [54, 55], all of them at a concentration of 0.5 M, as internal phase on the extraction of chromium is presented in Fig. 6.

The three internal phases tested showed similar recoveries values after 6 min. However, before this time, ammonium carbonate showed lower recovery, while not significant changes were observed between sodium carbonate and sodium hydroxide. Similar results were obtained by other authors when Na_2CO_3. and (($NH_4)_2CO_3$) solutions were used as stripping phase [55]

For the rest of experiments sodium carbonate solutions was used, since not significantly improvement was observed by the other solutions tested.
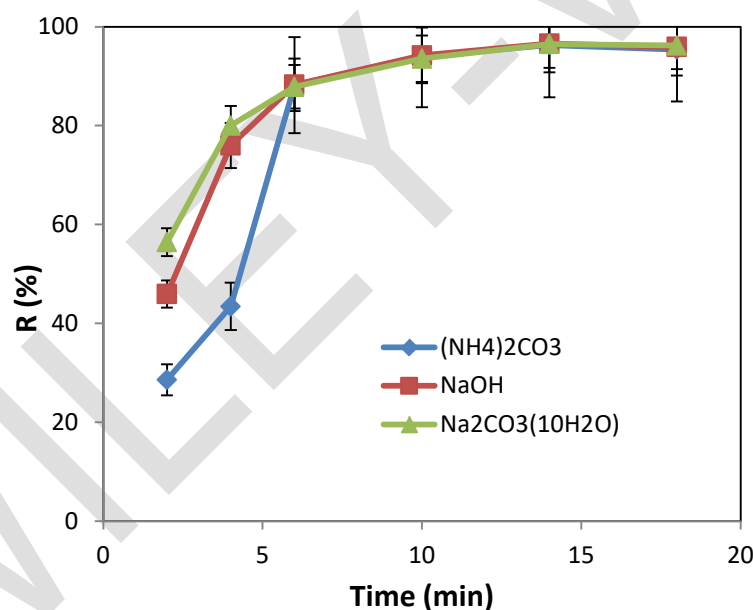

Figure 6. Effect of type of internal phase on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

3.2.4 Effect of internal phase concentration

The effect of Na_2CO_3 concentration in the stripping solution on the extraction efficiency of Cr (VI) was also investigated in the range of 0.1–1 M and the results are shown in Fig. 7.

The extraction efficiency increased with the stripping solution concentration from 0.1 to 0.5 M. As a general trend, it can be observed that at higher Na_2CO_3 concentration the extraction capacity increased, due to their capacity to form Na-Cr complexes. Similar results were registered when Na(OH) was tested as a tripping phase for Cr(VI) extraction [54]

The maximum extraction of Cr (VI) occurred at a concentration of 0.5 M Na_2CO_3. For higher concentrations, extraction efficiency decreased because the emulsion was unstable due to interaction of stripping solution with surfactant [56]. Moreover, the pH difference between internal phase and feed phase induces a significant amount of osmotic pressure that was responsible for the swelling of the emulsion, which lead to the emulsion breakage reducing the extraction efficiency [57, 58].
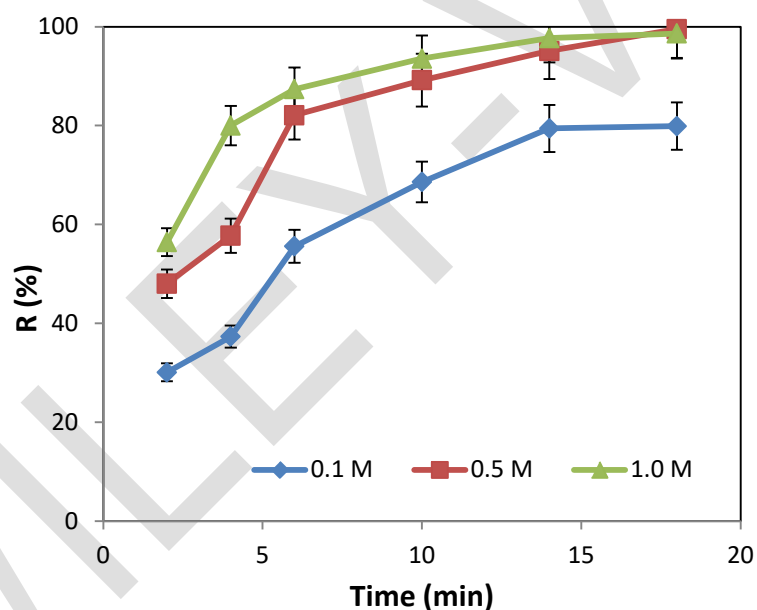

Figure 7. Effect of internal phase concentration on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3; the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

3.2.5 Effect of volume ratio of internal phase to membrane phase

To investigate the effect of volume ratio of internal phase to organic phase on the extraction of Cr (VI) by GELM, this ratio was varied in the range from 2/20 to 20/20. The results are shown in Fig. 8.

It was observed that the extraction efficiency increased from 91.4 to 99.5% with increasing volume ratio from 2/20 to 6/20, probably due to the increase of stripping sodium which favors complex chromium formation. However, a decrease to 95.74% with volume ratio of internal phase to membrane of 10/20 was registered, and even larger reduction was observed when the same volume in both phases (20/20) was used, extraction efficiency decreased until 24.6%.

This larger reduction observed at higher internal phase can be attributed to the lower emulsion stability. The higher water droplets concentration could produce potential instability since could easily coalesce reducing its extraction efficiency because of the interfacial area reduction and resulting mass transfer decrease.

Similar results were also observed by other authors [54 ,59]. Therefore, the volume ratio of internal phase to membrane phase of 6/20 was considered as the best ratio.
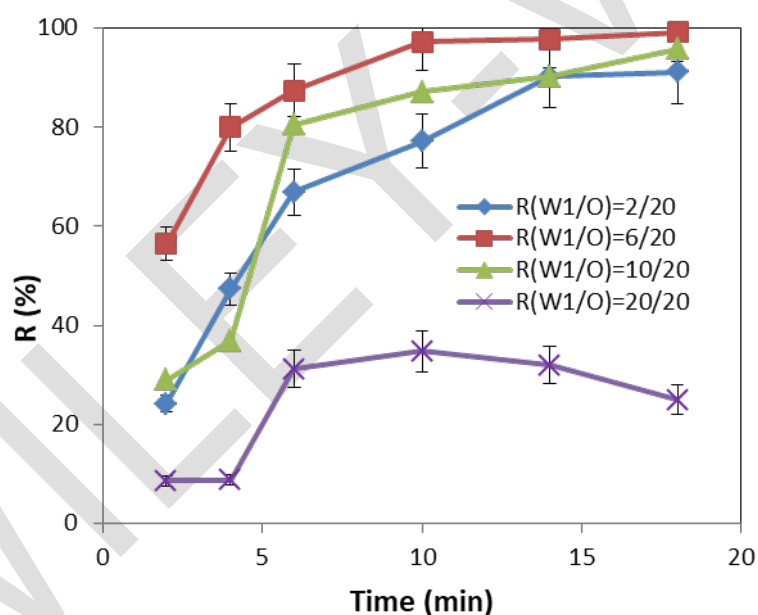

Figure 8. Effect of volume ratio of internal phase to membrane phase on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

3.2.6 Effect of volume ratio of emulsion to external phase

The volume ratio of the emulsion (W_1/O) to the external phase controls interfacial mass transfer and plays an important role in determining the efficiency of ELMs [60]. The effect of the volume ratio of emulsion to external phase on the extraction efficiency was studied in the range from 1/10 to 4/10, and the results are shown in Fig. 9.

It was found that when the volume ratio of the emulsion to the external phase was increased from 1/10 to 2/10, the extraction efficiency increased significantly. Similar behavior was also observed by Hasan *et al* [61] 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, so it can be assumed that for a ratio 1/10 there is not enough liquid membrane to extract the Cr(VI) on the feed aqueous phase. Beyond 2/10, the extraction efficiency kept constant. Since the Cr(VI) concentration and volume of feed phase was constant, it can be assumed that at the ratio of 2/10 there is enough emulsion to arise the equilibrium conditions. Other works found that extraction efficiency decreases as the ratio between emulsion and feed phase increases [54].
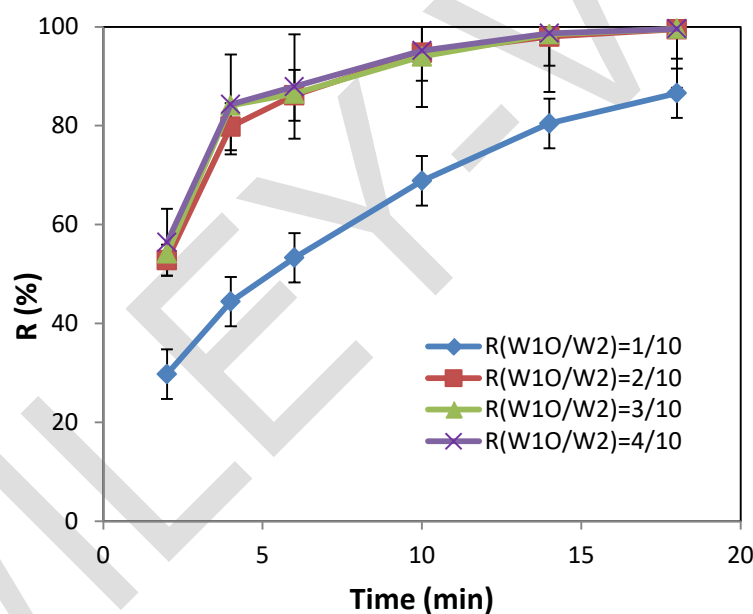

Figure 9. Effect of volume ratio of emulsion to external phase on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm.

3.2.7 Effect of pH of the feed phase

An acidic feed effluent is required to ensure chromium extraction from feed solutions according to previous studies [53-55]. Chromate ions can exist in different forms depending on the feed pH, H_2CrO_4 is the present form in which chromium ions can be present at really low pH (pH≤1)., while at pH between 2 and 6 two different species can be present $Cr_2O_7^{2-}$ and $HCrO_4$ and under pH > 8 chromate anion is the predominantly specie [62,63].

In the present study the effect of the feed phase pH on the extraction of Cr(VI) was studied in the range from 0.5 to 7. HCl and NaOH solutions were used to adjust the pH in each case. The experimental results are depicted in Fig. 10.

As it can be observed extraction efficiency was more than double when pH goes from 2.0 to 1.0. Similar results were registered for a pH range from 3.0 to 7.0. indicating that chromium as a $Cr_2O_7^{2-}$ and $HCrO_4$ species do not efficiently form complexes with the extracting agent, producing low extraction efficiencies (lower than 10%). Values of extraction efficiency increased up to 30% for pH 2.0. For pH 1.0 and 0.5 extraction efficiency arise values between 98.0-99.5% without significant differences between both pHs. It can be concluded that the transport of Cr(VI) is carried out by an ion mechanism of association of H_2CrO_4 with TOPO.

Previous studies [57] suggested a similar transport mechanism in the case of Cr(VI) extraction with TOPO dissolved in kerosene, using ACE 4360J as surfactant and ammonium carbonates as the receptor phase. However, other authors [54] found optimum values of extraction efficiency at pH around 0.45, obtaining values lowers than 50% at pH 0.75. this difference can be attributed to the use of tridodecylamine extractant instead of TOPO.

In the present study, the extraction of Cr(VI) using TOPO is considered to be optimal for pH =1, since lower pHs do not offer significantly improves on extraction efficiency. However, not satisfactory results are obtained at intermediate pHs (3-7), indicating that frequently a pH adjustment of most of industrial wastewaters will be required for Cr(VI) by ELMs.
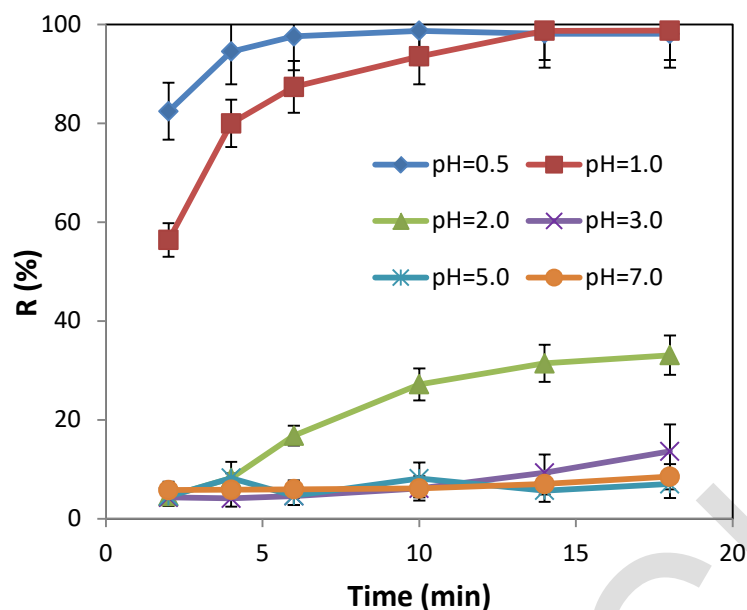
Figure 10. Effect pH of feed phase on the chromium removal, Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

4 Conclusions

The removal of more than 99% of Cr(VI) from the external feed solution by the use of GELM using PGPR and Tween80 as surfactants, TOPO as carrier and sunflower oil as organic phase was performed at optimum operating conditions, being: surfactant concentration: 5%(v/v); TOPO concentration: 4% (v/v); volume ratio of internal phase to organic phase: 6/20 and Na_2CO_3 internal phase concentration: 0.5 M; stirring speed: 400 rpm; volume ratio of internal emulsion W_1O to external phase W_2: 2/10; and pH of feed phase (W_2): 1.0.

The use of sunflower oil as solvent and PGPR as inner emulsifier in the formulation of GELM is a good alternative with respect to conventional formulations based on an organic solvent.

Disclosure

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

Acknowledgements

Symbols used

$[Cr(VI)]_0$ initial concentration of hexavalent chromium in the external aqueous phase

$[Cr(VI)]_t$ concentration of hexavalent chromium at time t

W_1/O water in oil emulsion

$W_1/O/W_2$ water in oil in water double emulsion

Abbreviation

Cr(VI)   hexavalent chromium

ELM   Emulsion Liquid Membrane

PGPR   Polyglycerol polyricinoleate

R   Extraction efficiency

TOPO   tri-n-octylphosphine oxide

Tween 80   polyoxyethylene sorbitan monooleate

Sub- and superscripts

0   initial

t   at time t

i   particle i

1   first water phase

2   second water phase

Greek letters

d_i droplet diameter

d_{43} volume-weighted mean diameter

d_{32} surface-weight diameter or Sauter diameter

n_i number of droplets with diameter d_i

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Table of contents

Single and double emulsions were prepared and characterized in terms of particle size and stability, using as organic phase a green solvent (sunflower oil) that was been previously demonstrate to have viability to produce Cr(VI) extraction.

Several stabilizer were used, their suitability to be used for the formulation of liquid membranes (double emulsions) is tested, regarding their physical properties and their extraction capacity.

Several formulation parameters were tested such as the presence of different alkaline solutions as internal aqueous phase, different pHs, and several ratios between the different aqueous and

oil phases. Moreover, the effect of stirring velocity during extraction process was tested and optimized.

Figure legends

Figure 1. Droplet size distributions of the primary W_1/O emulsion and the final ELM formulated ($W_1/O/W_2$) with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr (VI) in the external aqueous phase.

Figure 2. Optical microscopy image of the ELM formulated with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase.

Figure 3. Backscattering (BS) profiles of emulsions (A) W_1/O; (B) ELM formulated with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase.

Figure 4. Effect of extraction time on the Cr(VI) removal. Sunflower oil; 5% of surfactant (PGPR, 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.

Figure 5. Effect of stirring speed on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; the volume ratio $W_1/O/W_2$ = 2/10.

Figure 6. Effect of type of internal phase on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

Figure 7. Effect of internal phase concentration on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3; the volume ratio W_1/O = 6/20; feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

Figure 8. Effect of volume ratio of internal phase to membrane phase on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); feed solution: $[Cr(VI)]_0$= 50 ppm, pH = 1; Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2$ = 2/10.

Figure 9. Effect of volume ratio of emulsion to external phase on the chromium removal. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio W1/O = 6/20; feed solution: [Cr(VI)]0= 50 ppm, pH = 1; Stirring speed = 300 rpm.

Figure10. Effect pH of feed phase on the chromium removal, Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); the volume ratio $W_1/O = 6/20$; feed solution: $[Cr(VI)]_0 = 50$ ppm, Stirring speed = 300 rpm; the volume ratio $W_1/O/W_2 = 2/10$.