

Effect of temperature on the heat treatment to recover green solvent from emulsion liquid membranes used in the extraction of Cr(VI)

Katia Anarakdim^a, María Matos^{b,*}, Angel Cambiella^b, Ounissa Senhadji-Kebiche^a Gemma Gutiérrez^b

^aLaboratoire des Procédés Membranaires et des Techniques de Séparation et de Récupération, Département de Génie des Procédés, Université de Bejaia, Algérie.

^bDepartment of Chemical and Environmental Engineering, University of Oviedo, Julián Clavería 8, 33006 Oviedo, Spain.

*Corresponding author. Tel: +34 985 103665; Fax: +34 985 103434

E-mail address: gutierrezgemma@uniovi.es (Ph D Gemma Gutierrez)

Abstract

One of the main difficulties to achieve a good performance with the emulsion liquid membranes technique for metal extraction is the solvent phase recovery. In the present work, heating is proposed as an efficient and easy method to destabilize extraction liquid membranes (ELM) used to recover Cr(VI) from wastewaters. The formulated ELM consists of sunflower oil as vegetable green solvent, PGPR and Tween 80 as surfactants, tri-n-octylphosphine oxide (TOPO) as an extractant and a sodium carbonate Na₂CO₃ (0.5M) solution as the internal water phase.

The effect of the temperature during demulsification process was investigated. The membrane phase was successfully demulsified by heating at 80 °C during 2 hours, with a water content less than 4%. Emulsion were reformulated with recovered oil up to four times to extract Cr(VI) with an extraction efficiency (EE) up to 99 %. Physical properties of water-in-oil (W₁/O) and ELMs formulated, using fresh and recovered oil, were characterized by dynamic light scattering (DLS) and multiple light scattering (MLS). Emulsions reformulated with recovered sunflower demonstrated to have not oil degradation, evaluated by dynamic scanning calorimetry (DSC) and Fourier transform infrared (FTIR), and were appropriate to form stable W₁/O with high Cr(VI) removal capacity.

Keywords: demulsification; heat treatment; recovered oil; Cr(VI) extraction; Extraction liquid membranes

33 **Introduction**

34 Traditionally, a special attention has been paid to the removal of Cr(VI) ions from waste
35 effluents due to its high toxicity and numerous industrial applications. Cr (VI) is classified as
36 a carcinogenic, mutagenic and teratogenic compound. Therefore, its recovery and
37 concentration from industrial effluents become a necessary task for environmental safety
38 [1,2].

39 One of the main problems that present Cr (VI) recovery is its usual low concentrations in
40 wastewater effluents. In this way, liquid-liquid extraction using liquid membranes (ELMs) has
41 been reported as a promising technique since ELMs showed good performance recovering
42 metal ions such as cadmium, chromium and nickel and pollutants of other nature as dyes and
43 acetic acid from industrial wastewaters [3-13]. ELMs presents high metal extraction
44 efficiency, easy installation and process economy. However, frequently toxic organic solvents
45 are used [14, 15] even some recent works use alternative solvents such as ionic liquids [16].

46 Extraction with ELMs consists of four steps. (i) firstly, a stable water in oil (W_1/O) emulsion
47 is prepared [17-22], (ii) W_1/O emulsion is mixed with the wastewater which will act as an
48 external aqueous phase of a water-in-oil-in-water ($W_1/O/W_2$) emulsion. The mixture is
49 continuously stirred to enhance the metal extraction. (iii) The low stability of the external
50 interface oil-water makes that, once the stirring is stopped, a phase separation takes place
51 immediately, a W_1/O emulsion in the upper part and a purified aqueous phase at the bottom.
52 (iv) The W_1/O emulsion should be destabilized in order to obtain the new highly concentrated
53 waste effluent and, if possible, to reuse the oily phase. Figure 1 schematically describes the
54 processes mentioned.

55 **FIG 1**

56 For economic and environmental considerations, the reuse of the organic membrane solution
57 is one of the most critical factors for developing a commercially viable ELM process, since
58 extractant and stabilizers are more expensive than other chemicals used herein. Moreover,
59 solvents need specific and frequently expensive treatments to ensure environmental
60 requirements before its disposal. In that sense, solvent reuse will perform a clear economic
61 and environmental advantage on process operation.

62 W/O demulsification from ELMs after pollutant extraction had been investigated [23,24].
63 However, the destabilization of W/O emulsion from petroleum industry had been widely

64 studied by several techniques such as coalescence by surfactants or coagulation agents,
65 gravity settling, heating, microwave, ultrasounds, freeze/thaw, magnetic field application,
66 membrane processes or the combination of several of them [15, 25-34]. Normally, this
67 destabilization process requires a variety of chemicals and the recovered water phase needs a
68 secondary purification, involving additional energy and equipment requirements.

69 Heating treatment demulsification is a simple process to be industrialized and scaled up, but
70 the process is mainly influenced by some physical characteristics of internal droplet size and
71 the oil properties such as their nature and viscosity, which make their application not always
72 possible. In this case, heat capacity of sunflower oil is slightly higher than other solvents
73 frequently used in extraction process, such as kerosene or toluene, which could lead to an
74 increase of around 10% of the energy required to warm up the system and makes necessary to
75 optimize the temperature and time required to ensure a satisfactory demulsification. However,
76 this type of solvent does not produce potential toxic vapours from other aforementioned
77 solvents. The main economic advantage of heating demulsification is that the separation can
78 be easily made by settling, no needing expensive equipment and lowering investment and
79 operation costs. Moreover, is also important to point out that other demulsification techniques
80 require also high temperatures in order to achieve significant efficiency [24, 34].

81 One of the most important factors affecting emulsion stability and instability is drop diameter.
82 Large droplet diameters result in poor stability and low extraction efficiencies in ELMs [35],
83 because of a low surface/volume ratio and, consequently, reduced interfacial surface area
84 [36]. On contrary, small droplet diameters provide stable emulsions, larger mass transfer area,
85 and hence higher extraction efficiencies. However, if the droplet diameters are too small, the
86 emulsion destabilization step by any mechanical process will be more difficult, once the
87 extraction had been done (fourth step) [35]. Therefore, in order to ensure high ELM extraction
88 and easy W_1/O emulsion destabilization, formulation and preparation method should be
89 optimized [37,38].

90 The use of sunflower oil in the formulation of ELM is a good alternative to conventional
91 organic solvents and their high efficiency on metal extraction has been already tested
92 [5,39,40]. Furthermore, the use of sunflower oil as a extractant solvent presents a clear
93 advantage compared to other frequently used toxic solvents, since it can be heated in safe
94 conditions in order to get the demulsification of the used W_1/O [41].

95 Additionally, the surfactant selection is also a key factor on ELMs formulation in order to
96 have a stable emulsion and high demulsification efficiency. ELMs demulsification did not
97 show high efficiency when common surfactants, such as Span-80, were used to stabilize W₁/O
98 emulsion [24]. On contrary, surfactants with ethoxylates groups, such as Tween 80, can form
99 hydrogen bonds between oxygen atoms in the chain and water. However, this hydrogen
100 bounds can easily be broken at high temperature, being heat treatment a suitable technique for
101 emulsions destabilization where this type of surfactants are present on their formulations [25].
102 Polyglycerol polyricinoleate (PGPR) is a synthetic emulsifier widely used to stabilize food
103 W₁/O emulsions [42] and their use has been recently tested in ELMs stabilization with high
104 extraction efficiency [39, 40]. However, no studies about the demulsification of emulsions
105 with this compound as stabilizer have been reported.

106 In the present work, the extraction and recover of Cr(VI) at different concentrations by ELMs
107 processes was studied. Sunflower oil was used as environmental-friendly solvent and as an
108 alternative to synthetic organic solvents and PGPR and Tween 80 were used as stabilizers.

109 The main goal of this work is to study the feasibility of heat treatment as a demulsification
110 technique of ELMs used for Cr (VI) extraction in a range of temperatures from 30 to 90 °C.
111 ELMs were formulated with sunflower oil as solvent and PGPR and Tween 80 as stabilizers.
112 Moreover, the feasibility of the use of recovered oil for ELMs formulated will be studied.
113 W₁/O and ELMs were characterized in terms of droplet size distribution, stability and Cr(VI)
114 extraction capacity. Recovered oil quality was evaluated by dynamic scanning calorimetry
115 (DSC) and Fourier transform transform infrared (FTIR).

116 **2. Experimental**

117 **2.1. Materials**

118 The liquid membrane solution was formulated using two different stabilizers: Tween[®] 80
119 (polyoxyethylene sorbitan monooleate), a hydrophilic surfactant from Sigma-Aldrich (USA)
120 with hydrophilic-lipophilic balance (HLB) of 15.0, and the lipophilic surfactant PGPR
121 (polyglycerol polyricinoleate), supplied by Brenntag AG (Germany), with HLB of 3.0. The
122 mobile carrier or extractant used was TOPO (tri-n-octylphosphine oxide) supplied by Alfa
123 Aesar, Germany. Food grade commercial sunflower oil was used as solvent (density = 0.689
124 g/cm³, viscosity= 0.044 Pas).

125 Analytical grade hydrochloric acid (HCl), acetone (C₃H₆O), sulphuric acid (H₂SO₄), sodium
126 carbonate (Na₂CO₃. 10 H₂O) and potassium chromate (K₂CrO₄) were supplied from Sigma-
127 Aldrich (USA).

128 **2.2. W₁/O emulsion preparation**

129 In a 100 mL container, 4% (v/v) Tri-n-octylphosphine oxide (TOPO), 4% (v/v) PGPR and 1%
130 (v/v) of Tween 80 (HLB value of the mixture was 5.4) in sunflower oil were dissolved by
131 stirring; the solution formed was used as oily phase. Then a W₁/O emulsion was prepared by
132 dispersing 9 mL of the stripping aqueous solution (Na₂CO₃, 0.5mol/L) into 15 mL of the oily
133 phase (volume ratio W₁/O 0.6) prepared using high shear mixing with Heidolph Silent
134 Crusher M homogenizer with a 6 mm stirrer at 5000 rpm for 20 min at 25 °C. The selection of
135 the stabilizers and other operating parameters was optimized in previous studies [5, 39].

136 **2.3. Extraction experiments**

137 The acidic external phase was prepared by adding HCl to an aqueous solution containing
138 Cr(VI) concentration in the range 0.043-100 ppm. 4 ml of the prepared W₁/O emulsion was
139 mixed under stirring with 20 ml prepared wastewater (W₂) in order to form ELM while
140 Cr(VI) extraction took place (volume ratio W₁O/W₂ 0.2). Once the extraction was done and
141 stirring stopped, the ELM was completely separated by simple decantation in a separator
142 funnel being the external aqueous phase carefully separated in an easy way.

143 Extractions conditions used were 400 rpm for 18 min, following experimental conditions
144 optimized in previous works [40]

145 Samples were taken from the external aqueous phase for determination of Cr(VI)
146 concentration by UV-Vis spectrophotometry (PG Instruments Ltd., UK) using 1,5-diphenyl
147 carbazide as indicator at 542 nm and a multi-selective Inductively Coupled Plasma Mass
148 Spectrometry (ICP-MS, model "Neptune plus" from Thermo Scientific).

149 The metal ions extraction efficiency (EE), removed by ELM, was calculated by equation 1:

$$150 \quad EE(\%) = \frac{[Cr(VI)]_0 - [Cr(VI)]_t}{[Cr(VI)]_0} \times 100 \quad (1)$$

151 Where $[Cr(VI)]_0$ and $[Cr(VI)]_t$ are the concentration of Cr(VI) and at time zero and t in the
152 external aqueous phase respectively.

153

154 **2.4. Determination of demulsification efficiency by heat treatment**

155 The W₁/O after extraction and separation was heated in a constant temperature **shaking** water
156 bath ranging from 30 to 90 °C for 10 hours to destabilize the emulsion and separate water
157 from the sunflower oil phase, **what allows to know destabilization kinetics**. During the
158 destabilization process the stability of each sample was analyzed by measuring backscattering
159 (BS) every hour in a Turbiscan Lab apparatus (Formulation, France).

160 The demulsification efficiency (DE) (equation 2) is defined as the mass fraction of the
161 separated aqueous phase against the initial internal aqueous phase [28, 30].

$$162 \quad DE (\%) = \frac{\omega_0 - \omega}{\omega_0(1 - \omega)} \times 100 \quad (2)$$

163 Where ω_0 is the initial mass fraction of water in the W₁/O emulsion and ω is the mass
164 fraction of water in the oil phase after demulsification process.

165 Water fractions present in the emulsion and the oil phase were analyzed by volumetric
166 titration using Karl Fischer instrument (DL38 Volumetric KF Titrator, Mettler Toledo). The
167 quality of oil after demulsification was determined by the Differential Scanning Calorimetric
168 analysis (DSC) (Q600-SDT) and the FT-IR spectrophotometer coupled to a microscope with
169 imaging system (Varian 620-IR and Varian 670-IR).

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171 **2.5. ELMs and W₁/O Characterization**

172 Turbiscan LAB apparatus (Formulation, France) provided with an Ageing Station
173 (Formulation, France) was used to analyzed the emulsion stability by measuring
174 backscattering (BS) profiles at different temperatures.

175 The Turbiscan Stability Index (TSI) was also measured. TSI is a parameter that can be used to
176 estimate the stability of dispersions. TSI is a value based on the raw data obtained by the
177 instrument and summarised all processes taking place in the studied probe. An increase in TSI
178 value means that the overall physical stability of the emulsion decreases. It is calculated using
179 the following equation [43]:

$$180 \quad TSI = \sum_j |scan_{ref}(h_j) - scan_i(h_j)| \quad (3)$$

181 where $scan_{ref}$ and $scan_i$ are the initial backscattering (BS) value and the BS value at a given
182 time, respectively, h_j is a given height in the measuring cell and TSI is the sum of all scan
183 differences from the bottom to the top of the cell.

184 Droplet size distributions were measured by laser light scattering technique in a Mastersizer S
185 long bench apparatus (Malvern Instruments, Ltd., UK).

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187 **3. Results and discussion**

188 **3.1. Effect of the temperature on the destabilization kinetics of ELMs**

189 The destabilization kinetics at different temperatures were studied by comparing the TSI
190 values as a function of time. Results are shown in Fig. 2. It can be seen that the heating has a
191 **positive** effect on emulsion destabilization, since the TSI increases with temperature. When
192 the temperature increases from 30 °C to 50 °C, no noticeable destabilization was observed
193 during the 10 hours monitored, but from the 60 °C to 90 °C the TSI increase sharply during
194 the first 2h, indicating a **strong** destabilization in the sample. Highest TSI values were
195 achieved at 80 °C. **The demulsification time of 2 h will be the time selected for further**
196 **experiments, since was the point that sharply destabilization was observed.**

197

FIG.2.

198 **3.2. Demulsification efficiency (DE)**

199 The effect of temperature on DE of W₁/O was also investigated in the range of 30-90 °C and
200 the results are shown in Fig. 3. **As it was aforementioned, the higher the temperature, the**
201 **lower the emulsion stability, resulting in emulsion breakdown.** The water content was
202 analyzed by Karl Fisher volumetric titration and DE value calculated from equation 2, an
203 increased from 4.69 % to 96.02 % was observed when temperature increases from 30 °C to 80
204 °C but no differences were found in DE when samples were treated over 80 °C. Similar
205 results were obtained in other works where demulsification of ELMs was made by heat
206 treatment and temperatures higher than 70 °C were required to achieve high DE values when
207 surfactant OP-4 was used as stabilizer [24].

208

FIG.3.

209 **3.3. Oil quality after demulsification**

210 The best DE value was 96 % meaning that there are still some small water droplets in the oil
211 phase. The water content in destabilized oil phase has been also measured with two different

212 techniques (DSC, FTIR) and the effect of demulsification temperature on the final quality of
213 the oil is depicted in Fig. 4 and 5.

214 Moreover, in order to reuse the oil liquid membrane, it is necessary to confirm that the oil did
215 not suffer significant degradation during extraction and demulsification process. For this
216 reason, the quality of the recovered oil was analyzed using differential scanning calorimetry
217 (DSC) and Fourier transform infrared spectroscopy (FTIR).

218 Thermal analysis of emulsion with W₁/O fresh emulsion and recovered oil after emulsion
219 demulsification at different temperatures (70, 80, 90 °C) during 2hours revealed that the heat
220 treatment does not affect significantly the quality of the oil phase (Fig.4). The DSC profile
221 showed a sharp endothermic peak at 100 °C corresponding to evaporation of water, the
222 difference in the width and height of the peak is due to the difference in water content. It was
223 observed that the amount of water present on the formulated W₁/O emulsions prepared with
224 fresh oil as significantly larger than the amount present on the recovered oils. Being the oil
225 phase that presented nearly any content of water the one recovered at 90 °C followed by the
226 one recovered at 80 °C, presenting both cases a very small peak at 100°C of the DSC profile.

227 Fresh W₁/O emulsion, fresh oil and recovered oil at 70, 80 and 90 °C are analyzed by FTIR
228 (Fig. 5). All samples present similar profiles, indicating that the physical properties of
229 recovered oils at different temperatures remain stable and that are not affected by the high
230 temperature used during treatment. Strong peaks at around 1700 cm⁻¹ and 3000 cm⁻¹ indicates
231 C=O and O-H stretching respectively indicating the presence of PGPR and Tween 80 [44].
232 Comparing all samples analyzed, fresh oil, recovered oils and W/O formulated emulsion
233 slight differences are observed at around 800 and 3400 cm⁻¹, being differences highly
234 appreciated for the W₁/O emulsion and less important in the case of oils recovered at different
235 temperatures. Differences observed around 800 cm⁻¹ can be attributed for differences on
236 aromatic groups degradation which can be either oxidized by the presence of water or even
237 evaporated due to the high temperature used, in the case of differences observed at around
238 3400 cm⁻¹ were typically assigned to the presence of water in oil effluents [45].

239 FIG.4.

240 FIG.5.

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243 **3.4. Characterization of ELMs prepared by recovered oil**

244 Since the best DE values were obtained at temperatures of 70, 80 and 90 °C. ELMs
245 formulated with oil recovered at these temperatures (during 2 hours) were characterized in
246 terms of droplet size distribution, stability and extraction efficiency (EE) of Cr(VI).

247 **3.4.1. Droplet size distributions**

248 In order to define a suitable temperature for demulsification of water in sunflower oil
249 emulsions, measurements of droplet size distributions of the primary W₁/O emulsion and the
250 final ELM formulated with fresh oil and reused oil were performed.

251 The results are shown in figure 6. Volume droplet size distributions for W₁/O droplets are
252 given in Fig. 6A. The W₁/O emulsions using the oil recovered after demulsification at 80°C
253 showed monomodal droplet size distributions similar as the ones obtained when fresh oil was
254 used, droplet size distribution results were in the range of the ones reported by Li et al. when
255 they prepared W₁/O emulsions for copper extraction [35] who produced W₁/O emulsion with
256 monomodal droplet size distributions at droplet size of 0.8 to 3 μm. On contrary W₁/O
257 emulsions prepared using recovered oil after demulsification at 70 and 90°C showed wider
258 and bimodal size distributions and significantly different to the one obtained when fresh oil
259 was used.

260 This difference could be attributed to the oil quality used after demulsification because the
261 efficiency of demulsification at 70 °C was a 90 % that means the recovered oil contained a
262 significant quantity of water that can be the responsible of the presence of small aqueous
263 droplets producing a clear wider droplet size distribution.

264 It is important to point out that W₁/O emulsions with lower size distribution has larger
265 interface (i.e., interfacial area between both phases) than those than present large droplet size
266 distribution. It is expected that lower interface will enhance emulsion demulsification since
267 lower stabilizer needs to be removed from the interface and therefore higher droplet
268 sedimentation rate could be expected according to Stoke's law. On the contrary, small
269 droplets could easy diffuse across the oily continuous phase arising easily the heated warm
270 containers walls and hence increasing demulsification rate as it was observed in previous
271 works where O/W emulsions were treated by evaporation [46].

272 Regarding the experimental results obtained higher demulsification efficiency was obtained
273 for samples with high droplet size, indicating that the amount of stabilizer to be removed from
274 the interface and the water droplet sedimentation rate will be the key factor.

275 Fig. 6B show droplet size distributions of ELMs prepared showing polydisperse distribution;
276 a small peak was observed around 0.5 μm , the presence of this small peak was frequently
277 observed in double emulsions characterization and its either attributed to the scattered light
278 produced to the inner aqueous droplets or by the presence of some inverse micelles mainly
279 produced by PGPR [47]. Even the differences observed on W_1/O emulsion characterization
280 when oil recovered at different temperatures was used for reformulation, no significant
281 differences were observed on the resulting ELMs, indicating that the quality of oil do not have
282 a significant effect on the external droplet size, what offers a clear advantage for the
283 extraction process since the transfer area was approximately constant in all cases.

284 FIG.6.

285 3.4.2. Stability of the W_1/O emulsions formulated with fresh and recovered oil

286 Turbiscan Lab equipment has been widely employed to monitor the stability of emulsions,
287 used either as metal working fluids in industry [48] or as food formulations [47,48].
288 Measurements of Backscattering (BS) light flux by Turbiscan provide information of the real
289 condition of the emulsion and the course of destabilization processes.

290 BS profiles in function of sample height were measured after preparation (0 d) and on the
291 following seven days (1 to 7d) to compare the stability of the emulsions prepared with fresh
292 oil and recovered oil.

293 Fig. 7 shows the corresponding BS profiles of the primary W_1/O emulsion formulated with
294 (A) fresh oil, (B) recovered oil at 70 $^{\circ}\text{C}$, (C) recovered oil at 80 $^{\circ}\text{C}$ and (D) recovered oil at 90
295 $^{\circ}\text{C}$.

296 No significant differences were observed. In all cases, a slight clarification process was
297 observed at the bottom part of the cell, resulting in a slight increase in BS at the bottom and a
298 slight decrease at the top, as a result of the sedimentation process of water droplets, *since they*
299 *present higher density than the oily phase. So, despite the different droplet sizes observed*
300 *after the characterization of the different W_1/O emulsion prepared, the emulsions stability was*
301 *not affected, obtaining a good stability during one week in all cases.*

302 FIG.7.

303 **3.4.3. Cr(VI) Extraction Efficiency of the ELMs formulated with fresh and recovered oil**

304 The EE of Cr(VI) by ELMs formulated with fresh oil and with recovered oil obtained after
305 demulsification of the previous ELMs at different temperatures (70,80,90 °C) were measured
306 and their results were compared in Fig. 8.

307 EE values larger than 98 % were observed, for ELMs formulated with fresh oil and recovered
308 oil at 80 °C and 90 °C. However, lower EE values (87.35%) were registered when oil
309 recovered at 70 °C was used. These differences observed by the recovered oils could be due
310 to the fact that DE of emulsions treated at 80 °C and 90 °C was larger, i.e., the phase used as
311 oil phase presents properties similar to the fresh oil and low water content (DE larger than
312 96%). EE values are similar to those obtained in other works where Cr(VI) was extracted by
313 the use of kerosene as solvent and ambertile LA-2 as carrier [49].

314 During the extraction process mass transfer should take place through two interfacial areas
315 (W_1/O and O/W_2). According to droplet size, mass transfer should be more efficient for
316 samples prepared with oil recovered at 70 and 90 °C, since these samples presented lower
317 amount of oil and lower water droplet size, so both mass transfer steps were expected to be
318 favored. However, worse results were registered when oil recovered at 70 °C was used, what
319 is an indication that the presence of water content on the recovered oil was the key factor on
320 the Cr(VI) extraction efficiency since the droplet size obtained was similar to the one obtained
321 by the use of oil recovered at 90 °C.

322 **FIG.8.**

323

324 From the results above of droplet size distribution, stability and extraction efficiency of
325 Cr(VI), it can be concluded that the best demulsification temperature is 80 °C.

326 **3.5. Cr (VI) Extraction Efficiency at different initial concentrations and their recovery** 327 **after demulsification at 80°C**

328 Experiments were carried out formulating ELMs containing different initial Cr(VI)
329 concentrations (ranging from 0.043 to 100 ppm) in W_2 and reused oil after heat treatment at
330 80 °C as oil phase. The resulting EE of Cr(VI) was measured. Results are shown in Fig. 9.

331 It is observed that from 0.043 to 50 ppm of Cr(VI) the EE was higher than 99%, but for larger
332 initial concentrations the EE values decreased significantly from 89.14 % to 42.67 %.

FIG.9.

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As it is known, ELMs provide a potentially powerful technique for enhancing the extraction process, while simultaneously allow the extracted solute to be concentrated in the receiving phase, due to the transfer of solutes from a large volume of external phase (W_2) to small volume of internal phase (W_1). In our process, the volume ratio of the external aqueous phase to internal aqueous phase ($\frac{V_{ext}}{V_{int}}$) was 13.33, therefore, the maximum concentration factor possible was 13.33, what will indicate that Cr(VI) will be not present either in the oil phase and the external aqueous effluent (W_2).

In the present study, it was wondering to check if the amount of chromium extracted from the external phase has been transferred totally to the internal phase. For this purpose, the theoretical concentration of chromium $[Cr(VI)]_{theoretical}$ in the internal phase (W_1) was calculated using the Equation 4. It was named theoretical because was the concentration expected assuming that all Cr(VI) extracted from W_2 was transferred to W_1 directly without any of them trapped on oil phase.

$$[Cr(VI)]_{theoretical} \text{ in } W_1 = [Cr(VI)]_0 \text{ in } W_2 * \frac{V_{ext}}{V_{int}} * EE \quad \text{Equation 4}$$

The experimental concentration of chromium [Cr(VI)] in the internal phase was determined after it recovery with heat treatment demulsification at 80°C, using multi-selective inductively Coupled Plasma Mass Spectrometry.

Fig. 10 show the comparison between the theoretical (calculated by equation 4) and experimental results in function of the different initial concentration of Cr(VI) from 0.043 ppm to 100 ppm in the external phase.

It was observed that from 0.043 ppm to 50 ppm the experimental results follow the trend predicted by theoretical results. ELM process concentrated the Cr(VI) from 0.043 ppm in W_2 , into 0.355 ppm W_1 and from 50 ppm in W_2 into 593.5 ppm W_1 . The concentration factor range from 8.25 to 11.87 for the initial Cr(VI) concentration in W_2 increased from 0.043 to 50 ppm. Since the EE was less than 100% it was not possible to arise the maximum factor concentration of 13.33. However, the proximity between the calculated theoretical values and the experimental data measured at W_1 indicated that for the initial concentration range from 0.043 to 50 ppm, no Cr(VI) was entrapped on the oily membrane phase, what will make this solvent a suitable phase to be reused in further extraction cycles.

364 Above 50 ppm different behavior was observed, the concentration of Cr(VI) in the internal
365 phase remained constant despite of the increase in the initial concentration of Cr(VI) in the
366 W_2 , which increased from 50 ppm to 100 ppm. This behavior can be explained by a saturation
367 of Cr(VI) in the internal phase (W_1), producing a decrease in the EE. Moreover, larger
368 differences between the calculated Cr(VI) concentration on W_1 and the experimentally value
369 obtained were measured for this range of experiments indicating that some Cr(VI) was
370 entrapped on the oily phase. These differences tended to disappear at very high initial
371 concentration of Cr (VI) in W_2 (larger than 90 ppm).

372 It can be concluded that the studied formulation could be valid up to a Cr(VI) concentration of
373 50 ppm, since at higher concentrations of Cr(VI) in W_1 could favor the retention of the metal
374 ions in the oily phase. However, this is not a limitation since, as it was aforementioned, the
375 main advantage of ELM process is that it can be used from very diluted effluents, since
376 diluted effluents frequently require more expensive and specific technologies.

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FIG.10.

379 **3.6. Reuse of oil phase after demulsification**

380 Moreover, the number of cycles which the recovered oil could be reused without significant
381 decrease in the EE was studied. In this way, oil phase after demulsification by heat treatment
382 at 80 °C was repeatedly reused to extract Cr(VI) in simulated aqueous wastewater with a
383 heavy metal concentration of 50 ppm, maximum concentration that had shown satisfactory
384 results. As shown in Table 1 it was possible to reuse the oil phase until four cycles with an EE
385 value of 98.9%, similar values as obtained when fresh oil was used. Hence, after four cycles
386 of demulsification, more than 530 ppm was recovered.

387 BS profiles in the Fig. 11A show that the ELMs formulated with the oil recovered after each
388 cycle and destabilized at 80 °C. The first fourth cycles indicated that ELMs was easily
389 separated in two phases (W_1/O and W_2) after each extraction by a simple decantation (Fig
390 11B). However, after the fifth cycle the ELMs emulsions prepared with the recovered oil
391 (four times) was really stable and it was not possible to separate the W_2 from the W_1/O
392 emulsion (Fig. 11C). It was likely due to the excess of stabilizers in the interfaces
393 accumulated after each cycle, which produced extremely stable ELMs, making them not
394 suitable for the extraction process. Therefore, it can be concluded that the maximum cycles

395 for the reused sunflower oil at 80 °C will be four. Kerosene was found to be reused up to fifth
396 cycles when it as used for pyridine extraction [24]. Recent works had found that the reuse of
397 n-heptane up to forth cycles was possible for the extraction of methylparabens without the use
398 of any destabilization mechanism [44]. However, is important to point out that sunflower oil
399 is a green solvent compared with the other mentioned, and the absence of any destabilization
400 mechanism can be always possible if the saturation concentration is not arise on the stripping
401 phase.

402 Table 1

403 FIG.11.

404 **4. Conclusions**

405 In this study, the application of a heating demulsification treatment in an ELM process using
406 sunflower oil as vegetable solvent and PGPR and Tween 80 as surfactants was evaluated for
407 the extraction and recover of Cr(VI) at different concentrations from aqueous solution.

408 An extraction efficiency higher than 99 % was observed in the extraction of Cr(VI) from
409 aqueous solutions in heavy metal concentrations ranging from 0.043 ppm to 50 ppm. This so
410 formulated green ELMs were able to concentrate Cr(VI) from the external phase to internal
411 phase achieving concentration factors from 8.25 for the lowest Cr(VI) concentrations up to
412 11.87 for an external phase concentration of 50 ppm. For initial Cr(VI) concentration larger
413 than 50 ppm a maximum saturation concentration on the inner phase was reached, making no
414 possible to obtain high extraction efficiencies at those concentrations.

415 Heat treatment at 80 °C during 2 hours has been shown to be an effective and simple process
416 for breaking W₁/O emulsions with a demulsification efficiency of about 96 % for the solvent
417 recovery in ELMs used in the extraction of Cr(VI). Similar characteristics of W₁/O and ELMs
418 formulated with fresh oil and oil recovered at this temperature were observed. Recovered oil
419 phase by demulsification was reused up to four times to extract Cr(VI) from simulated
420 aqueous wastewater samples with an extraction efficiency up to 98.9 %. The use of larger
421 number of cycles was not possible due to the excessive amount of surfactants which hindered
422 the ELM destabilization once the extraction process had finished

423

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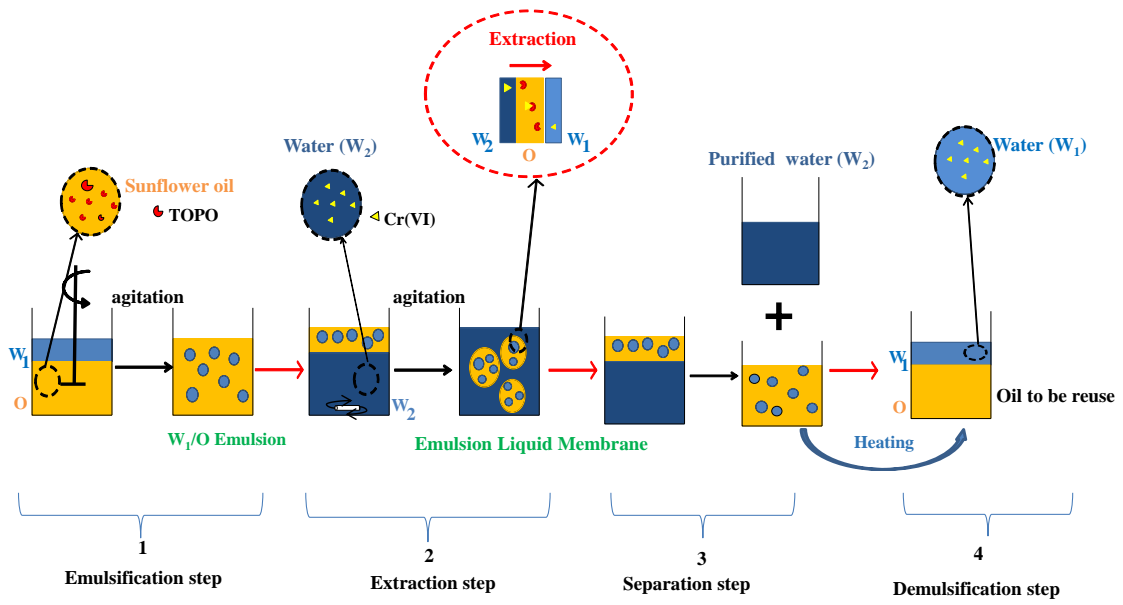


FIG.1. Schematic diagram of the extraction of Cr(VI) using an ELMs process where the oil is recovered by demulsification with heat treatment.

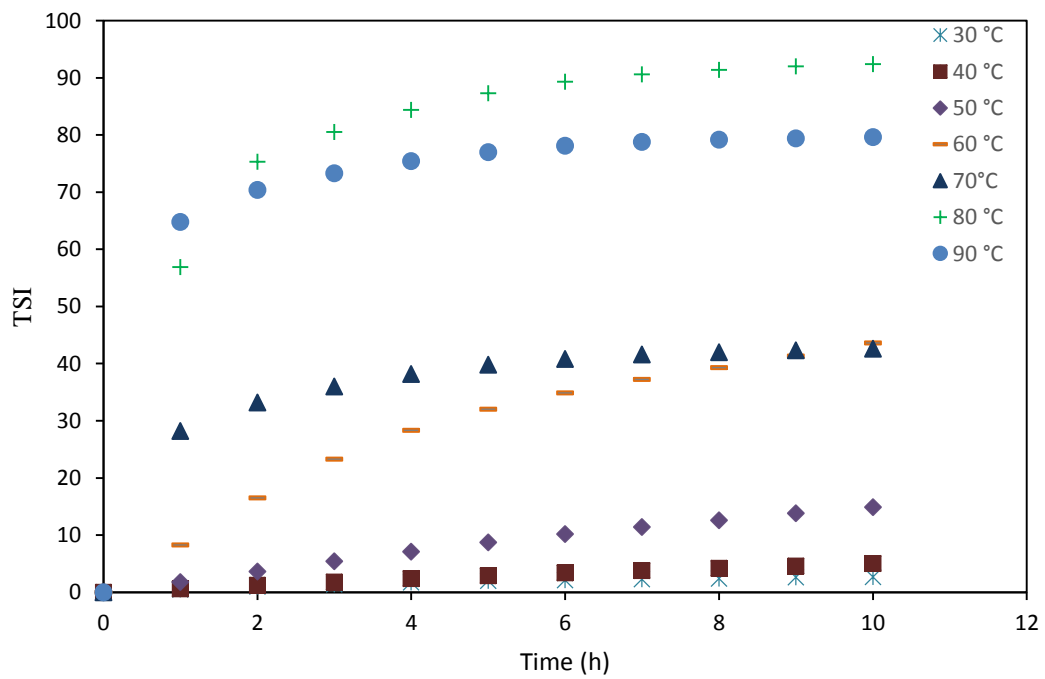


FIG. 2. Effect of the temperature on the destabilization kinetics

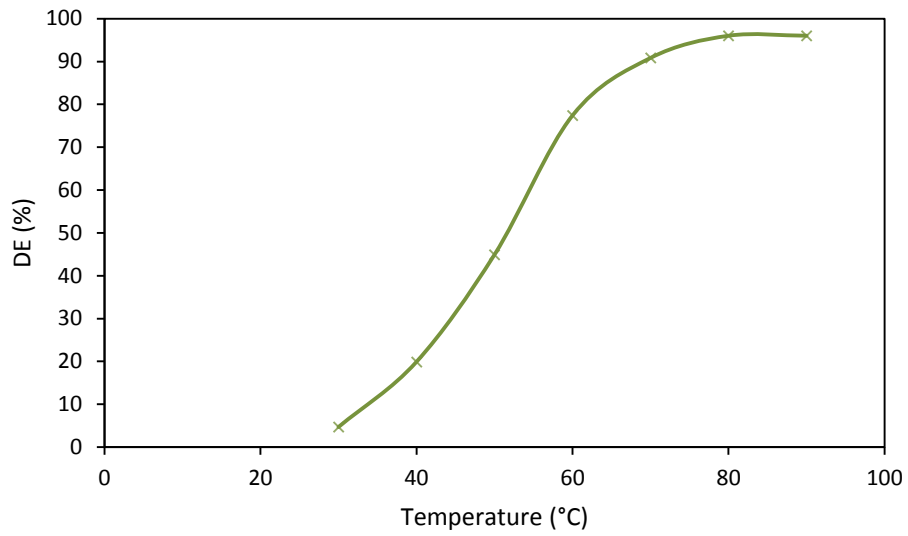


FIG. 3. Effect of temperature on the efficiency of demulsification.

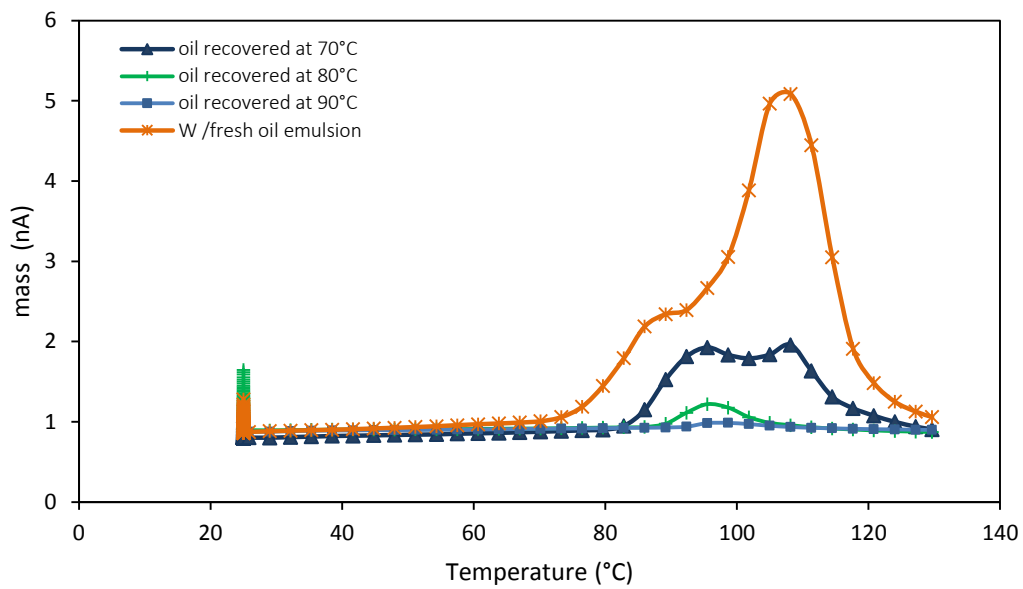


FIG. 4. DSC thermograms of fresh emulsion and recovered oil at different temperatures (70, 80, 90 °C).

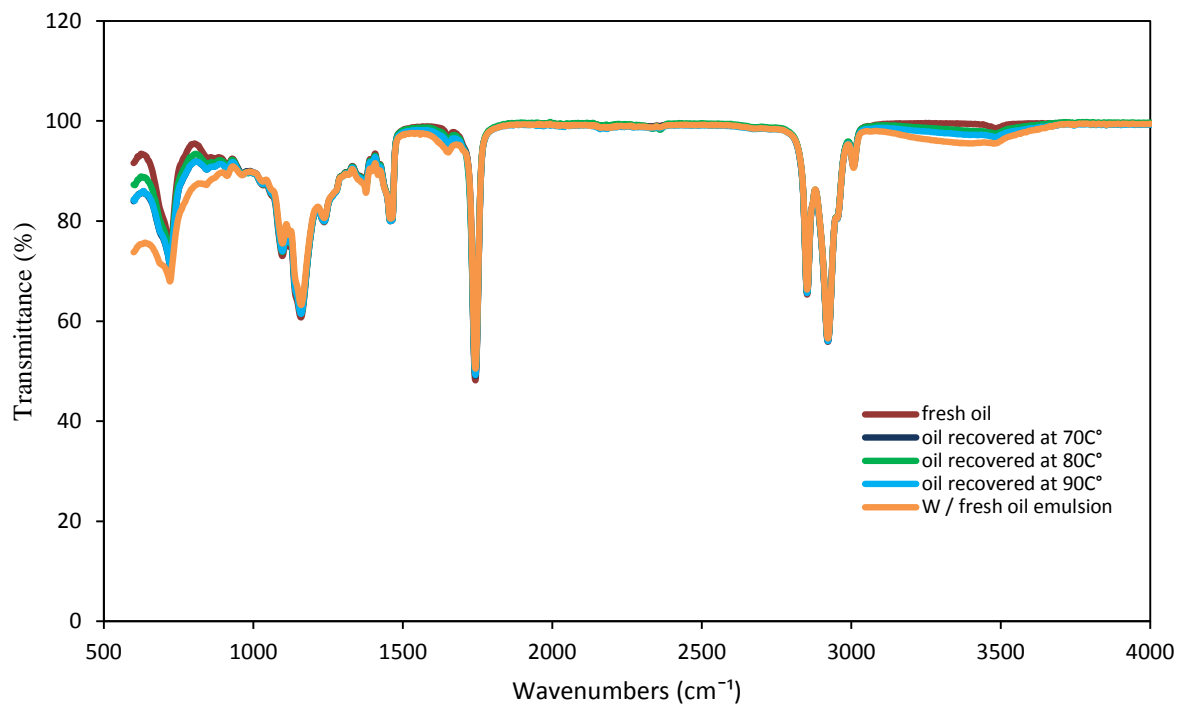
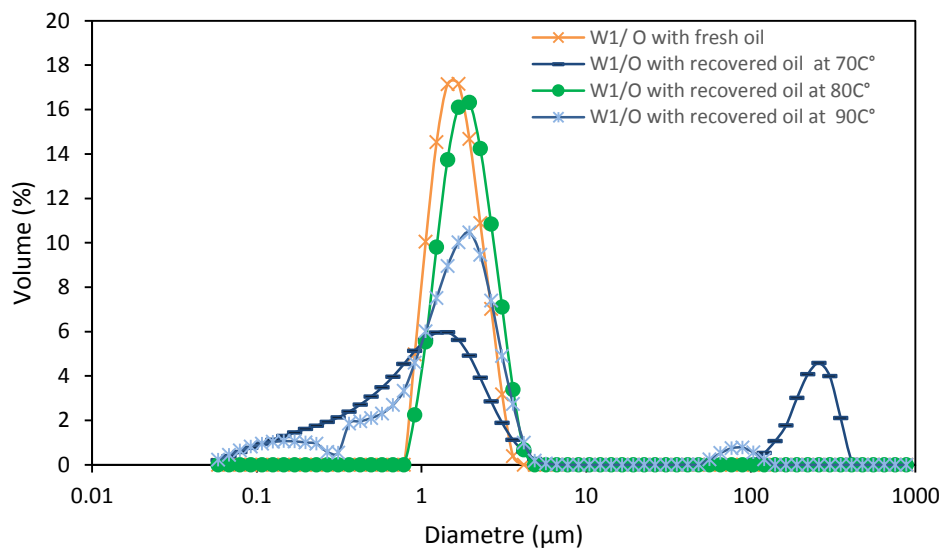
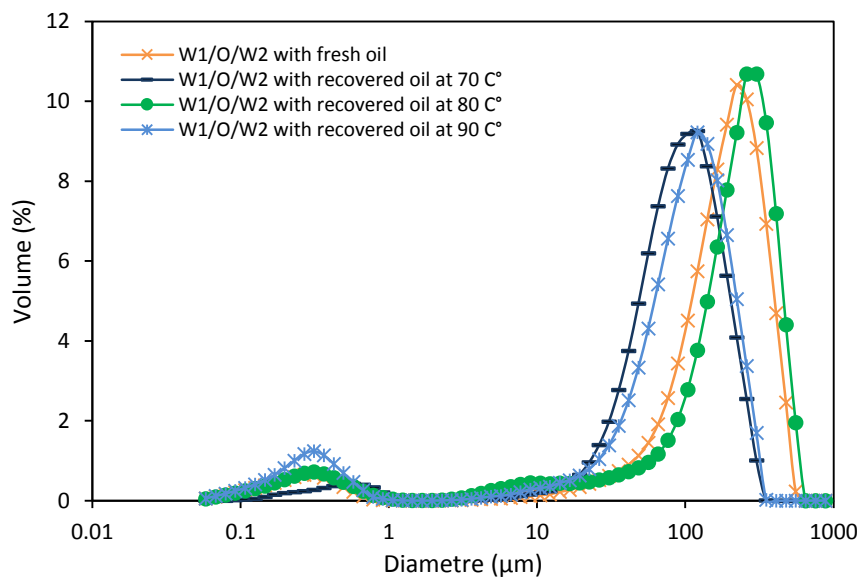


FIG. 5. FTIR-spectra of fresh emulsion, fresh oil and recover oil at different temperatures (70, 80, 90 °C).



A



B

FIG. 6. Droplet size distributions of the primary W₁/O emulsions (A) and the corresponding ELMs (B) formulated with fresh and reused oil recovered at several temperatures

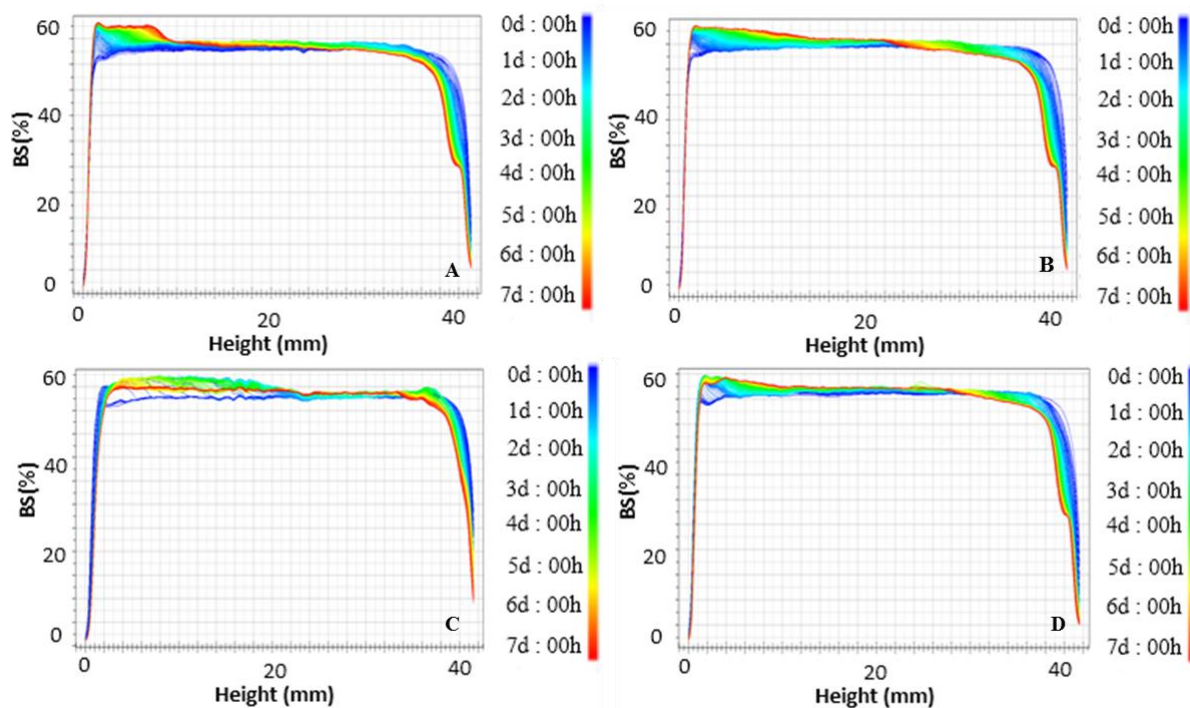


FIG. 7. Backscattering (BS) profiles of W₁/O emulsions formulated with (A) fresh oil, (B) recovered oil at 70 °C, (C) recovered oil at 80 °C and (D) recovered oil at 90 °C.

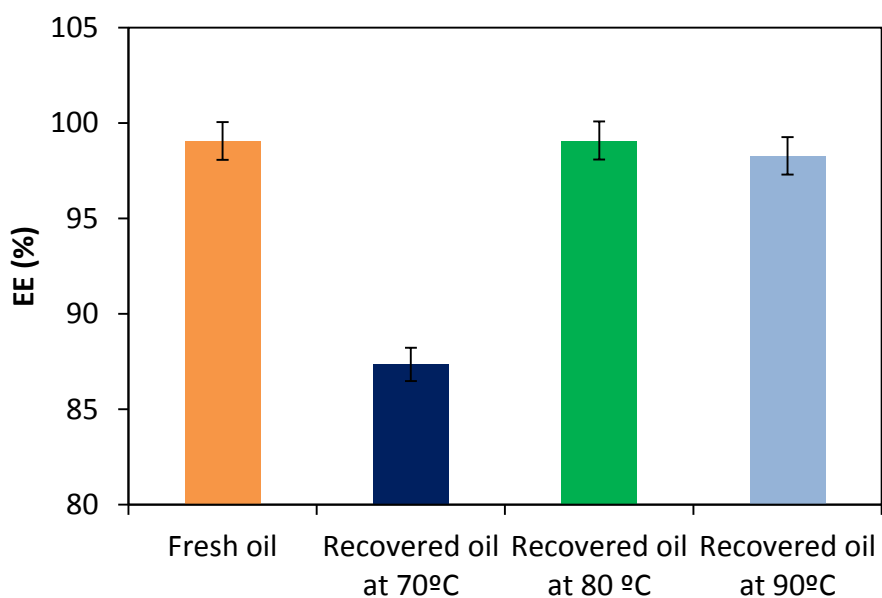


FIG. 8. Extraction efficiency of Cr(VI) with ELMs formulated with fresh oil and recovered oil at different destabilization temperatures (70, 80 and 90°C).

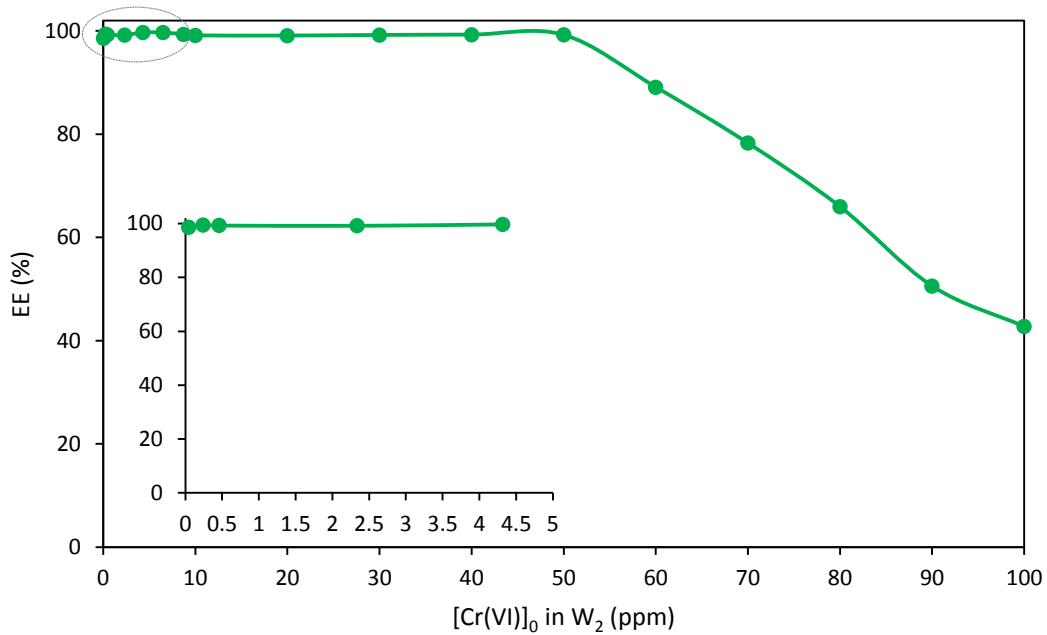


FIG. 9. Effect of initial concentration of Cr(VI) in the external phase on the extraction efficiency.

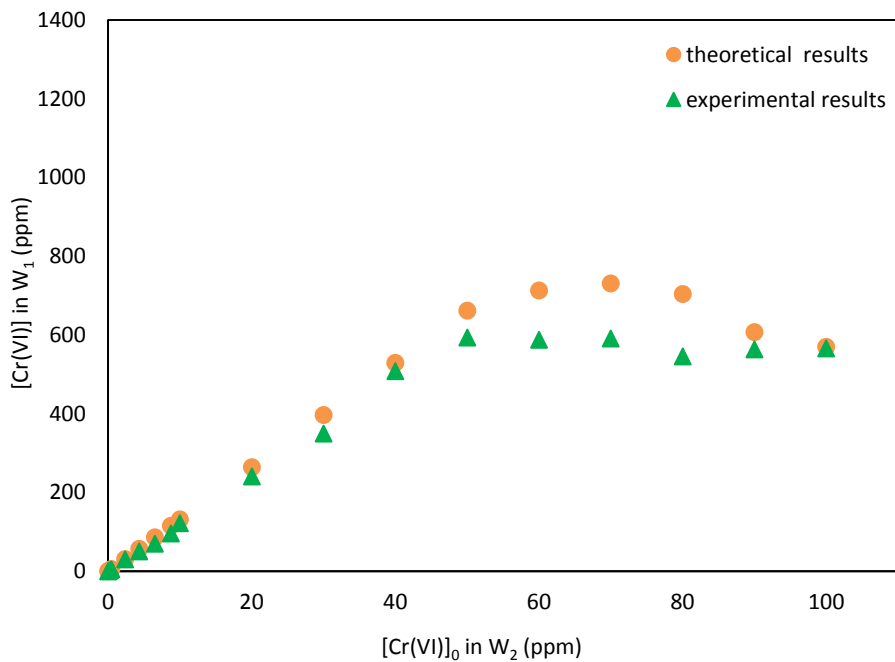


FIG. 10. Experimental and theoretical concentrations of Cr(VI) in the internal phase on function of the initial concentration of Cr(VI) in the external phase.

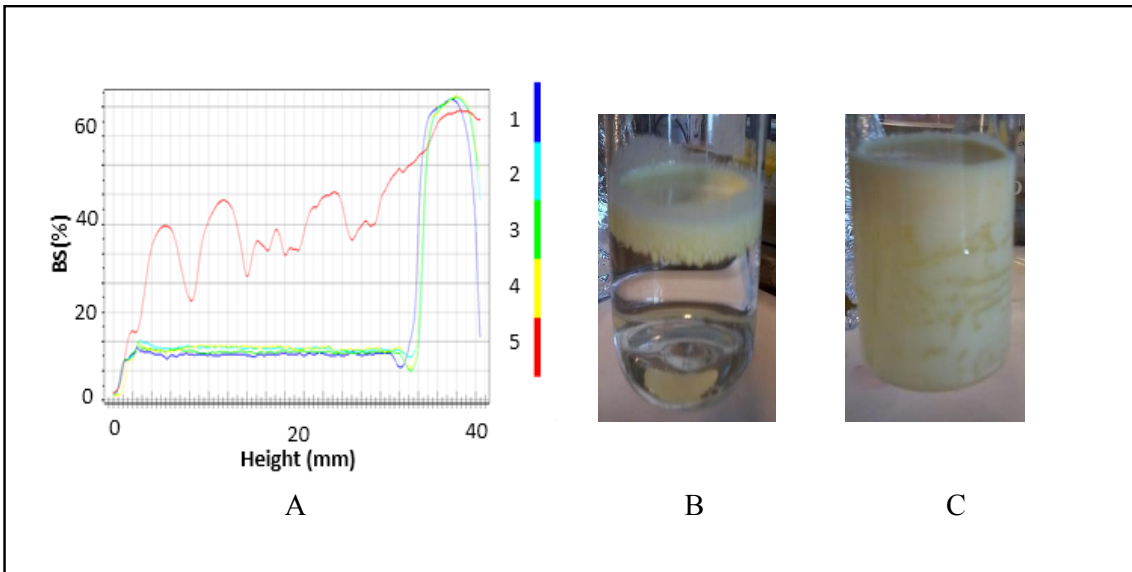


FIG. 11. (A) Backscattering (BS) profiles of ELMs after each cycle of the extraction with reuse of oil five times, (B) photograph of ELMs after extraction and decantation in fourth cycle four, (C) photograph of ELMs after extraction and decantation in fifth cycle



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Table
table 1.docx



Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Author Contributions

Katia Anarakdim: Investigation, Data curation, Writing- Original draft preparation, Funding acquisition
María Matos: Data curation, Conceptualization, Supervision, Funding acquisition.
Ángel Cambiella: Conceptualization, Visualization, Writing - Review & Editing, **Ounissa Senhadji-Kebiche:** Conceptualization, Supervision, **Gemma Gutiérrez:** Data curation, Supervision, Writing - Review & Editing, Funding acquisition ,Project administration.