Selective separation and recovery of Cr(VI) in the presence of other metal ions, especially Fe(III), by green emulsion liquid membrane

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ABSTRACT

Nowadays, the green emulsion liquid membrane (GELM) is considered to be an attractive and effective alternative technique for the separation and removal of toxic heavy metals from aqueous wastewater. In the present study, the GELM method is used to separate and remove chromium in the presence of other metal ions especially Fe(III), in a way that contributes to green chemistry. The formulation of the GELMs consists of sunflower oil as vegetable solvent, PGPR, and Tween 80 as surfactants, tri-_n_-octylphosphine oxide (TOPO) as an extractant, and sodium carbonate Na_2CO_3 (0.5 M) as the internal water phase. The influence of several operational parameters are studied, namely: the pH of the external phase, the initial concentration of ions, and the stirring time during the extraction of each metal alone (chromium and iron). The selective extraction of Cr(VI) in presence of other six metals (iron, cobalt, copper, nickel, zinc, and cadmium) is also investigated. The separation of Cr(VI) from the mixture of metal was possible by stirring 5 mL of the green emulsion with 25 mL of the external phase (pH = 1) at a speed of 400 rpm for 20 min. The optimal GELMs formulations with 4% (v/v) tri-_n_-octylphosphine oxide (TOPO), 4% (v/v) PGPR, and 1% (v/v) of Tween 80 in sunflower oil showed very good selectivity for chromium at pH = 1 with an extraction efficiency of 98.8%.

Keywords: Green emulsion liquid membrane; Vegetable solvent; Cr(VI); Fe(III); pH of external phase

1. Introduction

Membrane processes, especially those involving liquid membranes, are gaining importance and are emerging as a viable alternative to conventional separation processes [1–3]. The growing interest in membrane processes can be attributed toward their simplicity, requirement of small quantities of carrier, and low energy consumption. Emulsion liquid membrane (ELM) is one of the most promising methods to recover metal ions such as cadmium [4], tungsten [5], cobalt [6], and dyes [7] from wastewater, and acetic acid from xylose [8].

GELM processes are those involving a selective green liquid membrane phase that are using vegetable solvents for lessening the use of toxic and costly petroleum-based organic solvents [9–15]. Separation is achieved by solute permeation through this green liquid phase from the feed to the receiving phase. The feed and receiving phases are normally miscible while the membrane phase is immiscible in both. A GELM can be considered as a double emulsion consisting of three phases: the external, membrane, and internal

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phases. The receiving phase is emulsified in an immiscible liquid membrane using surfactants and high-speed agitation. Emulsion droplets size ranges from 1 to 3 μm in diameter, thus providing good stability [16]. 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. The use of sunflower oil in the formulation of ELM is a good alternative to conventional organic solvents [17,18]. Furthermore, 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 the applications in food, cosmetic, and pharmaceutical industries [19,20].

The rejection of various carcinogenic metal ions as a mixture into the environment issue to numerous industrial processes generate waste streams which have been viewed as a serious threat to our ecosystem. So, their separation and recovery from wastewater have been considered to be a top priority in the area of wastewater treatment. Cr(VI) receives particular attention because of its high toxicity and numerous industrial applications, for example, electroplating, metal finishing, and corrosion inhibition [21]. Because the Cr(VI) is carcinogenic, mutagenic, and teratogenic in nature, its recovery and concentration from industrial effluents become a necessary task for hydrosphere and environmental safety [22,23]. Many types of wastewater contain Cr(VI) ions mixed with numerous other ions metal and particularly Fe(III) ions. Consequently, several methods have been developed in order to selectively separate Cr and Fe from wastewater [24–27]. The ELM process is known to be one of the most effective methods for separation and concentration of metals. The ELM process can prevent the disadvantages of other extraction techniques by providing a very high interfacial area for the transport of the desired components into the extractant phase. The role of the pH is very important in the ELM process for extraction and separation of metals [28] and so is the role of the selected extractant agents that determine the reactions at the liquid membrane interfaces [29].

The aim of this work is the separation and recovery of chromium ions in the presence of other metal ion (iron, cobalt, copper, nickel, zinc, and cadmium) using the ELM method involving green solvent (sunflower oil) and surfactant (polyglycerol polyricinoleate). Although, Fe(III) is less toxic than Cr(VI), its presence is troublesome during the treatment of effluents. Results obtained indicated that green emulsion liquid membrane (GELMs) are promising systems that allow the selective recovery of metal ions present in wastewater in presence of other metals by controlling the main operation conditions.

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 (extractant) used was TOPO (tri-n-octylphosphine oxide) supplied by Alfa Aesar, Germany. Locally produced market purchased sunflower oil ($P = 100\%$) was used as the green solvent (density = 0.689 g/cm³, viscosity = 0.044 Pa).

Analytical grade hydrochloric acid (HCl), acetone (C_3H_6O), sulfuric acid (H_2SO_4), sodium carbonate ($Na_2CO_3 \cdot 10H_2O$), and potassium chromate (K_2CrO_4) were supplied from Sigma-Aldrich (USA) and were used without purification.

2.2. Methods

2.2.1. GELM 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 in sunflower oil were dissolved by stirring; the solution formed was used as oily phase. Then a water-in-oil emulsion (W_1/O) was prepared by dispersing 9 mL of the stripping aqueous solution (Na_2CO_3, 0.5 mol/L) into 30 mL of the oily phase using high shear mixing in an Ystral X10 mixer (Ystral GmbH, Germany), with a 6 mm stirrer at 5,000 rpm. The selection of the stabilizers was optimized in our previous works [17,18].

2.2.2. Extraction experiments

The acidic external phase was prepared by adding HCl to an aqueous solution containing appropriate amount of metals ions (Cr(VI)/Fe(III)) over an range of 2–50 mg/L. Ten milliliters of the prepared GELM were added to the 50 mL of external phase containing Cr(VI) with others metal ions in acid aqueous solution at different pH. The contents were stirred by means of a magnetic stirrer at a speed of 400 rpm for different time intervals. The stirred solution was allowed to separate by simple decantation in a separator funnel and the external phase was carefully separated. Samples were taken from the external aqueous phase for determination of chromium concentration by UV-vis spectrophotometry (PG Instruments Ltd., UK) using 1,5-diphenylcarbazide as an indicator at 542 nm and the others metals concentration by AAS spectrophotometry (ASC-6000 SHIMADZU U.S.A. Manufacturing, Inc.).

Extraction efficiency (R (%)) was calculated using the following equation:

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

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 analyzed using the 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. 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.

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-weight diameter or Sauter mean d_{32}, were calculated using Eqs. (2) and (3):

$$d_{43} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \tag{2}$$

$$d_{32} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{3}$$

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 10–100× magnification using an UV-vis lamp. Micrographs were used for emulsions visual inspection and to confirm the droplet size obtained by laser light scattering.

3. Results and discussion

3.1. ELMs characterization

Once the extraction conditions, and therefore the formulation, were fixed the GELMs used in this study were characterized in terms of droplet size distribution and visual inspection. It will 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. 1a. The emulsions showed a monomodal distribution of sizes and the d_{32} value was 1.29 ± 0.05 µm for W_1/O emulsions: these results agree with the range suggested by Li et al. [30] who produced a stable W_1/O emulsion at a d_{32} of 0.8–3 µm. For GELM, the d_{43} value 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.

Oil drops containing the inner small aqueous droplets can be clearly identified in an optimal image of the formed GELM (Fig. 1b), the presence of the inner water droplets confirms the formation of double emulsions. Visual inspection of these micrographs indicates that droplet sizes are in good agreement with experimental data given in Fig. 1a.

### 3.2. Effect of the pH of the external phase

The pH of the external phase can affect the degree of ionization as well as the speciation of metallic species and act as an important parameter during the extraction process.

In this work, the effect of the pH on the extraction of Cr(VI) and Fe(III) with the GELM was studied in the range from 0.5 to 7 for Cr(VI) and from 1 to 8 for Fe(III). HCl and NaOH solutions were used to adjust the pH in each case. The results obtained are given in Fig. 2.

In the aqueous solution, the present species of chromium are $Cr_2O_7^{2-}$, CrO_4^{2-}, $HCrO_4^-$, and H_2CrO_4. In highly acidic conditions (at pH 0.5 and 1), chromium is rapidly protonated by hydronium ions, and a stable chromic acid species H_2CrO_4 is formed [31]. In order to check the presence of different species of Cr(VI) at different pH, Srivastata et al. [32] have showed using the speciation diagram that H_2CrO_4 is present as a major species below pH = 2.0.
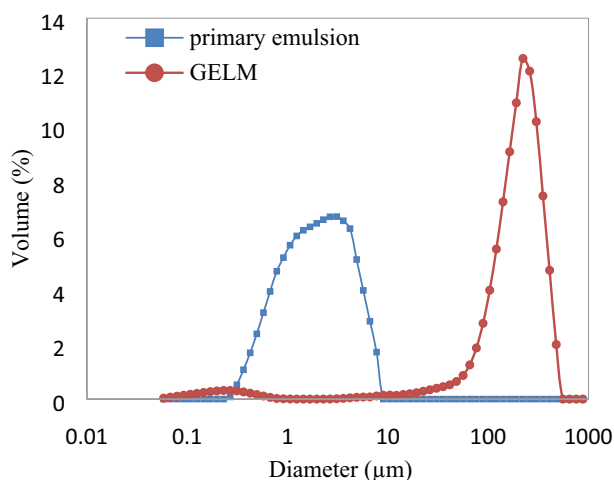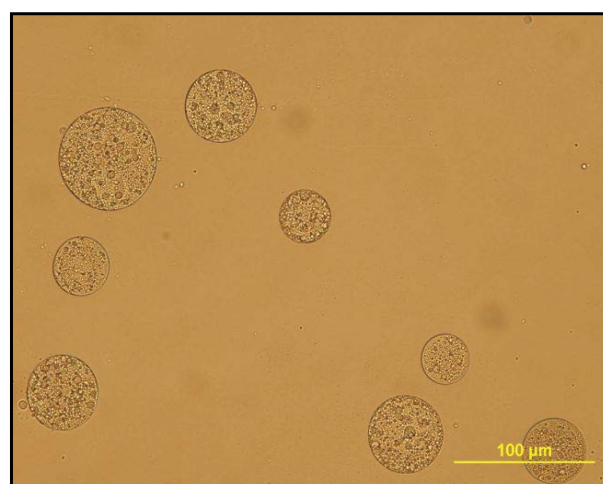
Fig. 1. (a) Droplet size distributions of the primary W_1/O emulsion and the final GELM formulated ($W_1/O/W_2$) with 5% of surfactant (PGPR, Tween 80) in sunflower oil as oily phase, containing Cr(VI) in the external aqueous phase and (b) optical microscopy image of the GELMs.

So, since TOPO (used in this study) is nonionic extractant, the formation of chromic acid species (H_2CrO_4) in the best appropriate state for during the chromium extraction.

In their research work Robila et al. [33] indicated that the transport of the chromium species proceeds through membrane diffusion as a series of steps in which the equilibrium between $HCrO_4^-/Cr_2O_7^{2-}$ in the aqueous phase and between $H_2CrO_4(TOPO)/H_2Cr_2O_7(TOPO)_3$ in the membrane phase took place. At the optimum pH value (pH = 1), we can presume that the transport of Cr(VI) is carried out by a mechanism where an association of H_2CrO_4 (represented as an ion pair H^+, $HCrO_4^-$) with the TOPO. The reaction mechanism is given by the following equation:

$$\left(H^+, HCrO_4^-\right) + TOPO \leftrightarrow H_2CrO_4 TOPO \tag{4}$$

Kumbasar [34] suggested a similar transport mechanism in the case of extraction of the hexavalent chromium by the TOPO using kerosene as solvent.

The recovery of iron by ELM using TOPO was found to be dependent on the pH of the aqueous phase too. A speciation diagram of iron in aqueous phase shows that $Fe(OH)_3$ is present as a major phase at pH = 6 [35,36].

The equilibrium relation for the ELM extraction is given by:

$$\left(Fe^{3+}, 3\left(OH^-\right)\right) + TOPO \leftrightarrow Fe\left(OH\right)_3 \cdot 2TOPO \tag{5}$$
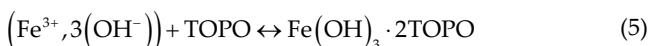
For Fe(III), the extraction efficiency increasing from 5.06% to 85.39% with the increase of pH from 1 to 6 then a decreases with the increase of pH from 6 to 8.

Therefore, optimal Cr(VI) extraction was found at pH 1.0 while Fe(III) extraction was optimal at pH 6.0. These optimum pHs are related to the metal distribution species as a function of pH and the concentration as indicated by other research works [1,37] and also on the nature of the carrier to form the metal-carrier complexes to be transported through the membrane [34].

3.3. Effect of the initial concentration of ions in the external phase

The effect of the initial concentration of ions in the external phase on the chromium and iron removal were studied from 2 to 50 and 5 to 50 mg/L, respectively. The results obtained are given in Fig. 3. It was found that for Cr(VI) no noticeable effect was observed, the extraction efficiency slightly decreases from 98.86% to 90% when moving from the low to high concentration (2–50 mg/L). As for Fe(III), no noticeable change was observed from 5 to 20 mg/L, then beyond 20 until 50 mg/L the extraction efficiency decreased.

These results can be explained by the fact that at low initial concentrations, all the solute diffusing inside the globule of the emulsion rapidly undergoes a stripping by the reagent contained in the droplets of the internal phase. However, for large initial concentrations, the reagent contained in the peripheral region droplets is rapidly depleted by the solute. So, the rest of the solute must penetrate deep inside the globule before its stripping. It means that an increase in the concentration of the solute corresponds to an increase in the length of its diffusion path in the globule. A comparable result was found by Chakraborty and Datta [38] who confirmed that the Te(IV) extraction by liquid surfactant membrane is more effective at low metal concentrations.

3.4. Effect of the extraction time

The extraction time needed to extract the maximum of solute from the external phase is considered to be an important limitation in the ELM process. When the extraction time increases, the movement of water from internal droplets toward the external phase enhances. This fact can lead to the swelling of the membrane phase and subsequently increase the emulsion breakage. Also, adequate extraction time is still required to increase the solute mass transfer rate from the aqueous feed phase to the membrane phase [39].
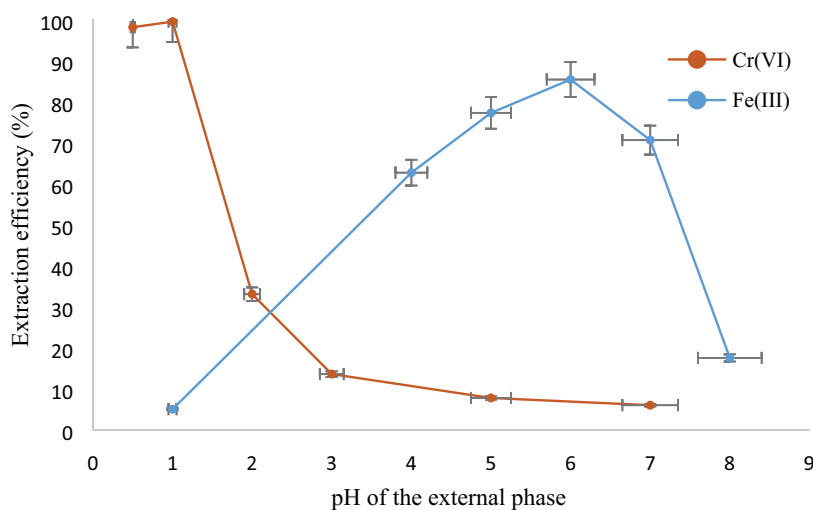

Fig. 2. pH effect of the feed phase on the extraction efficiency of chromium and iron. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); feed solution$_1$: $[Cr(VI)]_0$ = 10 ppm, feed solution$_2$: $[Fe(III)]_0$ = 10 ppm.

To investigate the effect of the extraction contact time on the extraction of Cr(VI) and Fe(III) at the optimal pH of 1 and 6, respectively, the extraction time was varied from 2 to 50 min for chromium and from 5 to 50 min for iron. The obtained results are shown in Fig. 4. For Cr(VI) removal increases during the first 20 min (56%–99.51%) and after that it increases slightly approaching a limiting value (equilibrium condition), similarly for Fe(III), extraction efficiency increase during the first 20 min (40.37%–65.32%) and after that it slightly increases.

These results showed that the equilibrium is reached after an extraction time of 20 min, so it is a relatively fast kinetic. This equilibrium is due to the absence of emulsion swelling and membrane breakage thanks to the higher stability of the W_1/O formulated emulsions with PGPR and Tween 80 as emulsifier. The opposite behavior was observed by Elsayed et al. [40], in which the extraction efficiency was reduced with the increase in extraction contact time because it affects the stability of the emulsion, formulated with Span 80 surfactant. In the present study, emulsions formulated with PGPR are more stable than those formulated in the mentioned study [18].

Results are consistent with previous works [41] who found that the selection of the surfactant is the key factor to reduce emulsion swelling and membrane breakage resulting more effective metal extraction.

Therefore, 20 min was considered the best and sufficient extraction time to provide a good dispersion of emulsion globules along with high extraction yield in short periods of time.

3.5. Selective separation of Cr(VI)/Fe(III)

The selectivity is a very significant factor for the development and industrial application of any technique for wastewater treatment. To investigate the selectivity of the
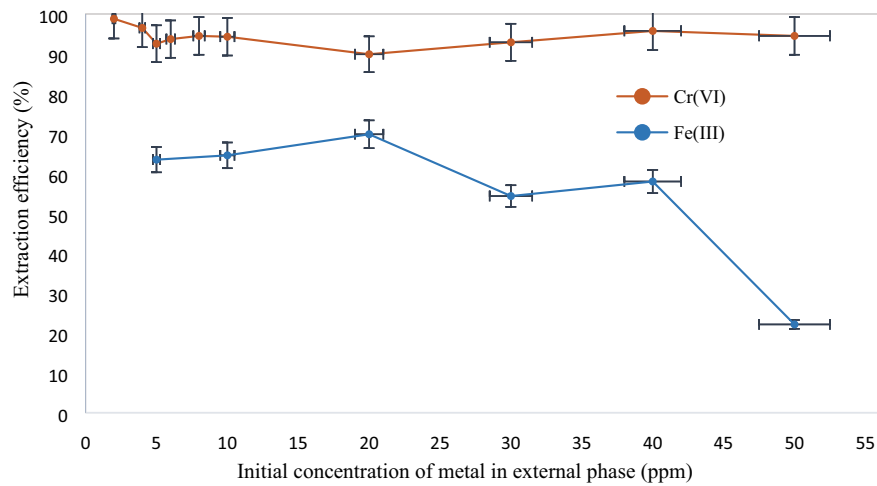

Fig. 3. Effect of the initial concentration of ions in the external phase on the extraction efficiency of chromium and iron. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); feed solution$_1$ with Cr(VI), pH = 1; feed solution$_2$ with Fe(III), pH = 6.
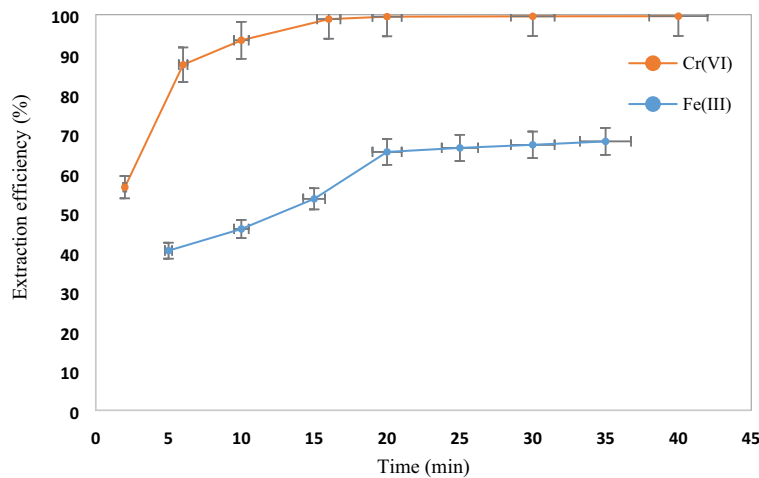

Fig. 4. Effect of the extraction time on the extraction efficiency of chromium and iron. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); feed solution$_1$: $[Cr(VI)]_0$ = 10 ppm, pH = 1; feed solution$_2$: $[Fe(III)]_0$ = 10 ppm, pH = 6.

obtained ELM with respect to the optimum composition, we have started with a study of the extraction of a binary mixture. The selective separation of Cr(VI)/Fe(III) was realized by mixing the two ions at two values of pH (pH = 1 and 6). The ratio concentration of the (Cr(VI)/Fe(III)) mixture was varied as follows: (10/20), (20/20), (50/20), and (20/50). The results obtained are shown in Table 1.

These results clearly show that the extraction of chromium from the mixture (Cr(VI)/Fe(III)) is advantageous over iron at pH = 1, the ELM is in this case selective for the chromium extraction. We can say that at pH = 1 the transport of Cr(VI) is carried out by a mechanism where an association of H_2CrO_4 (represented as an ion pair H^+, $HCrO_4^-$) with the TOPO. In the other hand, at pH = 6, the iron is better recovered than chromium. However, lower value of pH (pH 1 in this work), the formation of the neutral complexes (Fe-TOPO) is disadvantaged and the quantity of these ions recovered in the receiving phase remains negligible compared to the Cr(VI) ions. In their study, Hariharan et al. [42] have indicated that in acidic aqueous solutions, at high pH, containing anions A^-, the solvent extraction of iron(III) with TOPO could be explained may by the formation of anionic complexes of Fe(III) with A^- anions.

Therefore, this technique allows a selective ion separation by pH control whatever the ratio concentration of the (Cr(VI)/Fe(III)) mixture, that means chromium extracted from the mixture (Cr(VI)/Fe(III)) at the optimum conditions of extraction of Cr(VI) alone.

The results published by Kumbasar [43] also showed that it is possible to extract 99% of cobalt using ELM from strong acidic leach solutions, containing cobalt and nickel ions, at the optimum conditions of extraction of cobalt alone.

3.6. Selective separation of Cr(VI) in a mixture containing six other metals

As industrial discharges usually contain a mixture of heavy metals ions, the extraction of Cr(VI) from an aqueous mixture containing six other ions (Fe(III), Co(II), Cu(II), Cd(II), Zn(II), and Ni(II)), at an identical initial concentration of 10 mg/L was investigated at the optimum pH value of the chromium ions extraction (pH 1). The obtained results are shown in Fig. 5. Chromium(VI) was extracted successfully with an extraction efficiency of 98.8%. Thus, this clearly suggests that ELM composed of sunflower oil and TOPO displays a considerable selectivity to Cr(VI) ions. No recovery for Co(II), Cu(II), Cd(II), Zn(II), and Ni(II) was observed and recovery less than 6% was detected for Fe(III). As it is explained in the previous paragraph, at low values of pH, the cationic metal ions formed anionic ions complexes that are not adept to be extracted by the neutral extractant TOPO.

Similar results were reported by Kumbasar [44], who studied the Selective extraction of chromium(VI) from multicomponent acidic solutions by ELMs using tributhylphosphate (TBP) as a carrier.

Table 1
Extraction efficiency (%) of different combination of concentration (Cr(VI)/Fe(III)) at pH 1 and 6

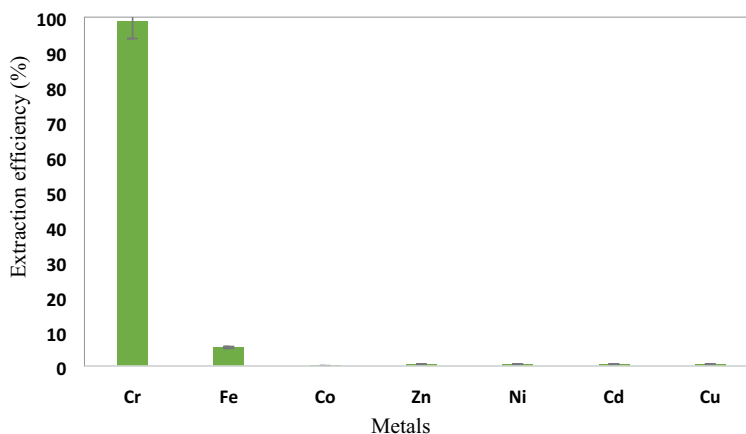| Concentration (ppm) (Cr(VI)/Fe(III))	Extraction efficiency (%) at pH = 1		Extraction efficiency (%) at pH = 6	
	Cr(VI)	Fe(III)	Cr(VI)	Fe(III)
(10/20)	<u>90.53</u>	6	6.74	89.62
(20/20)	<u>94.49</u>	5	5.82	85.77
(50/20)	<u>95.69</u>	5.85	3.08	75.66
(20/50)	<u>94.12</u>	12.4	9.3	**6.15**

Fig. 5. Comparison of the extraction efficiency of metal ions contained as a mixture in the feed solution. Sunflower oil; 5% of surfactant (PGPR, Tween 80); 4% of the carrier (TOPO); stripping solution: Na_2CO_3 (0.5 M); feed solution: $[Cr(VI)]_0 = [Fe(III)]_0 = [Co(II)]_0 = [Zn(II)]_0 = [Ni(II)]_0 = [Cd(II)]_0 = [Cu(II)]_0 = 10$ ppm, pH = 1.

4. Conclusion

Chromium(VI) is successfully extracted from acidic chlorides solutions by a facilitated transport across GELM by means of tri-*n*-octylphosphine oxide (TOPO) as an ion carrier, sunflower as a green solvent, PGPR and Tween 80 as stabilizers, and 0.10 M Na_2CO_3 as the receiving phase. The influence of various parameters on the Cr(VI) extraction has been experienced and the results show that the optimum conditions were established, at pH = 1 of the external phase stirring speed of 400 rpm for 20 min by GELMs formulations with 4% (v/v) tri-*n*-octylphosphine oxide (TOPO), 4% (v/v) PGPR and 1% (v/v) of Tween 80 in sunflower oil.

Using GELMs for the extraction process of ions present in wastewater revealed that is a selective technique that allows to recover the desired ion of the ones present in the wastewater solution. The results obtained in the current study demonstrate that Cr(VI) and Fe(III) can be effectively and selectively separated by GELM by just an accurate control of the pH used. The extraction of the Cr(VI) from the mixture of Cr and Fe is advantageous over Fe extraction at pH = 1, the GELM is in this case selective for the extraction of Cr(VI). However, at pH = 6 the Fe was better separated than Cr(VI).

The optimal pH of the aqueous feed solution for selective separation of Cr(VI) in presence of several metals (Fe, Co, Cu, Cd, Zn, and Ni) was found to be 1 with extraction efficiency of 98.8%.

Therefore, the results presented in this work reveal the excellent selectivity of GELMs-based on sunflower solvent for Cr(VI) recovery, making it a potential technique to be used in wastewater treatment field.

Acknowledgments

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