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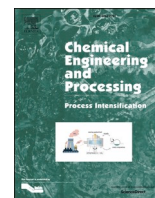
Highly effective emulsion liquid membrane based on Triethylamine for extraction of heavy metals: Investigation of extraction, de-extraction, swelling, and osmotic pressure gradient

Selma Djaber [a,c], Saliha Bouranene [b,c,*], Souheila Bouacherine [a]

[a] Department of Material Sciences, Faculty of Sciences and Technology, University of Mohamed Cherif Messaadia, BP 1553, Souk-Ahras 41000, Algeria
[b] Department of Process Engineering, Faculty of Sciences and Technology, University of Mohamed Cherif Messaadia, BP 1553, Souk-Ahras 41000, Algeria
[c] Laboratory Sciences and Technical Water and Environment LST2E, Mohammed Cherif Messaadia University, BP 1553, Souk-Ahras 41000, Algeria

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ABSTRACT

The aim of this work is to produce a stable W/O primary emulsion which is able to extract a wide variety of heavy metals, namely Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+}. The appropriate conditions through which a better extraction was obtained are: concentration of Span 80 (4 wt%); concentration of TEA (10 wt%); internal phase (HCl 0.5 M); emulsification time (4 min); V_{memb}/V_{int} (2.08); V_{emul}/V_{ext} (0.1); pH of the external solution (4.7) and stirring speed (150 rpm). A second recycling of the emulsion resulted in a drop in extraction about 40 %. The morphological study confirmed a good dispersion of internal globules and a good stability of emulsion for up to 60 days. The extraction of metal cations showed very high extraction ($>$ 90 %) with very fast kinetics. However, it has been shown that the type of anion to which the metal cation is bound, only affects the extraction efficiency above 100 mg/L. Results extraction of heavy metals are in good analogy with evolution of the osmotic pressure difference between the internal and external phases, leading to a significant swelling of emulsion, while de-extraction also appears to be in accord with extraction with a slightly slower rate.

1. Introduction

The toxicity of heavy metals is an important subject in environmental toxicology. Their presence in the environment results from natural causes and human activities such as industry, agriculture and the combustion of fossil fuels [1,2]. Major efforts have been devoted to monitoring and controlling exposure to heavy metals, as they can accumulate in the body over time and cause adverse health effects. Heavy metals are a significant problem for humans, as they affect all aspects of life. The cell is the smallest fundamental biological unit, and heavy metals can lead to its degeneration. Some of them are carcinogenic and can lead to pathologies affecting the physical and mental integrity of human beings. Some have teratogenic effects and others can cause fertility problems. Every fundamental and vital human function is endangered by the presence of heavy metals in the environment [3,4]. It is therefore necessary to completely eliminate the heavy metal ions present in the various industrial effluents or reduce their quantity below the limits defined by the standards [5,6].

For this reason, a large part of the literature has been devoted to the removal of heavy metals from aqueous media by various treatments, such as physical processes like adsorption [7], filtration [8], and flotation [9]; chemical processes as coagulation-flocculation [10], oxidation [11], reduction [12], electrolysis [13], and photochemistry [14]; and biological processes like aerobic and anaerobic degradation [15]. These methods, despite their use, have associated disadvantages such as high operational cost, low efficiency at low metal concentration, the need for a slower processing time and the use of large quantities of chemicals [16].

The extraction process using emulsified liquid membranes (ELM), invented by Li [17] in 1968, is considered one of the most promising separation techniques for the treatment of wastewater loaded with organic and inorganic substances. This process consists of four main steps, which are the emulsification, extraction, decantation and breaking process.

Emulsified liquid membrane extraction is a simple process that offers many advantages such as low chemical and energy consumption, large

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* Corresponding author at: Department of Process Engineering, Faculty of Sciences and Technology, University of Mohamed Cherif Messaadia, BP 1553, Souk-Ahras 41000, Algeria.

E-mail address: saliha.bouranene@univ-soukahras.dz (S. Bouranene).

contact area, high selectivity and efficiency, simultaneous extraction and de-emulsification process and low operating cost [18].

The ELM technique has been widely used in separation and purification processes, for example, the removal of chemical products like phenol from wastewater [19] and nitrophenol as a hydrocarbon from industrial waste [20], the extraction of pharmaceutical products [21], dyes [22], conservatives [23], and pesticides [24] and the recovery of certain heavy metals e.g., copper [25], zinc [26], chromium [27], lead [28], cobalt [29], mercury [30], nickel [31], and uranium [32]. Furthermore, the development of green ELM, an innovative technology based on the replacement of volatile organic solvents in the membrane phase by vegetable oils and the incorporation of ionic liquids in the emulsion to improve the stability of the process [33,34], should not be overlooked.

Most of the work reported in the literature has studied ELM extraction as a function of several parameters related either to the composition of the emulsion itself, i.e. surfactant content, extractant content, nature of the diluent and internal phase, etc., or to the operational conditions, such as emulsification time, volume ratios, and stirring time and speed, etc. On the other hand, few works have examined the stability of W/O/W emulsions and their rheology depending on the evolution of osmotic pressure following the phenomenon of water transfer. In this context, the work reported by Balcaen et al. can be mentioned, in which the authors studied the effect of internal aqueous phase gelation on the sensitivity to shear and osmosis of W/O/W type double emulsions. They found that gelation of the internal aqueous phase significantly limited the maximum rate of osmotic swelling of droplets in the double emulsion. However, this effect is probably due to the coalescence of the drops that occurs when the internal water phase is gelled [35]. Likewise, Beer et al. presented a theoretical model to describe the equilibrium state of osmotic regulation and a new experimental protocol to compare the fractions of the dispersed phase with those predicted theoretically [36].

In order to fight against iron deficiency which is one of the main reasons for anemia in humans, the fortification of foods by microencapsulation is therefore a viable alternative. In this context, the work carried out by Barbosa et al. aimed to encapsulate iron in a double W/O/W emulsion, using whey protein isolate and polyglycerol polyricinoleate as emulsifying agents, tara gum as thickening agent and sucrose as an osmotic active ingredient. Sucrose concentration was used to equalize the osmotic pressures between the inner and outer phases of water in the emulsion, which prevented water transport and subsequent instability of the system [37].

According to Castaño et al., the emulsion can be classified as a colloidal system depending on the scale studied. The authors investigated the influence of temperature, volume fraction and osmotic pressure on the state of the observed system. They found that thermodynamic analysis could predict the change in rheological behaviour of emulsions [38].

DeIuliis et al., studied the agglomeration of ultrafine hydrophobic particles using high internal phase water-in-oil emulsions as a binder, and showed that the difference in salt concentration between the internal emulsion drops and the external water gives rise to an osmotic pressure that involves the transport of water in the drops and the binder [39].

Food grade double W/O/W emulsions were prepared using polyglycerol polyricinoleate (PGPR) as a lipophilic surfactant with various concentrations ranging from 0.5 to 5.0 wt% and at initial osmotic pressure differences of up to 1.1 MPa between the aqueous phases. The aim was to examine the role of the surfactant in water transfer and the physical stability of the emulsion. The emulsions showed very satisfactory physical stability, with encapsulation efficiency near 100 % for surfactant concentrations above 2 %. It was also found that PGPR is implicated in the water transfer between the internal and external aqueous phases with the formation of reverse micelles by PGPR molecules or hydrated PGPR monomers, which allows controlled swelling of the emulsion [40].

Goibier et al. prepared double emulsions without the addition of surfactants by heating the primary W/O emulsion to a temperature above its melting range and cooling the system to trigger fat crystal formation. After that disperse this emulsion in an aqueous protein phase i.e. sodium caseinate to form a multiple W/O/W emulsion that had the property of resisting osmotic stress. This process could be carried out with fats from several sources including coconut, milk, cocoa and palm and can be applied in several fields namely taste masking, encapsulation of hydrophilic drugs and their controlled management, preparation of low fat products, etc. [41].

Iqbal et al. controlled the thermal gelation and osmotic swelling of W/O/W emulsions in order to obtain food grade materials with novel rheological and microstructural properties. They showed that thermal denaturation of globular proteins introduced into the internal aqueous phase can be induced by heating and that dilution of the volume fractions of particles contained in the emulsions causes them to increase, resulting in osmotic swelling. This study was advantageous for the food industry in obtaining products with a new texture with reduced fat content [42].

As indicated in this bibliographic review, most of the work consists of identifying the best membrane matrix for extraction of the targeted solutes and examining the stability of the system without highlighting the relationship between osmotic pressure and membrane extraction capacity. With this in mind, the aim of the present research is to produce an emulsified liquid membrane capable of extracting any type of heavy metal i.e. charged solutes, under the same optimal conditions with very high extraction efficiency and a very fast kinetic. This involves applying the same membrane matrix which makes the process more economical. It should be noted that the extractant employed is triethylamine (TEA), which is almost unused in ELM systems, appears to be a good extractant of heavy metals. The influence of the nature of anions to which the metal cation is bound on the extraction yield was also examined. Moreover, the relationship between osmotic pressure gradient and extraction, de-extraction efficiency as well as the swelling rate of the emulsion has been investigated. To our knowledge, no work in the literature has considered these parameters simultaneously in the extraction of charged solutes by ELM.

2. Experimental part

2.1. Reagents and solutions

All reagents used were of analytical grade and all aqueous solutions were prepared with distilled water.

The surfactant used in the preparation of W/O emulsions is sorbitan monooleate, known as Span 80 and supplied by Sigma Aldrich (S-Louis, Missouri, USA). Sorbitan monooleate is a lipophilic, non-ionic ester surfactant with a hydrophilic/lipophilic balance (HLB) of 4.3 highly recommended for W/O emulsions. It is a yellow oily liquid, its chemical formula is $C_{24}H_{44}O_6$; its molecular weight is 428.61 g/mol and its density is 1 g/cm^3 at 20 °C.

The extractant used is triethylamine (TEA) or N, N-diethylethanamine with the chemical formula $N(CH_2CH_3)_3$, commonly noted Et_3N or NEt_3. It was purchased from Merck (Germany). It is a colourless liquid with a characteristic odour, its molar mass is 101.19 g/mol and its density is 0.728 g/cm^3.

Three analytical grade diluents were used: hexane, heptane and kerosene. The first two were obtained from Merck (Germany) while the third one from Sonatrach (national company for the research, production, transport, transformation and marketing of hydrocarbons, located in Hassi Messaoud, Algeria).

The internal phase reagents are acids: HCl, HNO_3, H_2SO_4 and H_3PO_4 supplied by Sigma Aldrich (Germany), and bases: NaOH and NH_4OH supplied by GPR RECTAPUR (France).

The external phase was prepared from simple solutions of copper sulfate pentahydrate $CuSO_4$ $5H_2O$, copper chloride dihydrate

CuCl$_2$.2H$_2$O, copper nitrate hexahydrate Cu(NO$_3$)$_2$.6H$_2$O, zinc sulfate heptahydrate ZnSO$_4$.7H$_2$O, zinc chloride ZnCl$_2$, zinc nitrate hexahydrate Zn(NO$_3$)$_2$.6H$_2$O, lead sulfate PbSO$_4$, lead chloride PbCl$_2$, lead nitrate et Pb(NO$_3$)$_2$, nickel sulfate heptahydrate NiSO$_4$.7H$_2$O, nickel chloride dihydrate NiCl$_2$.2H$_2$O nickel nitrate hexahydrate Ni(NO$_3$)$_2$.6H$_2$O, mercury sulfate heptahydrate HgSO$_4$.7H$_2$O, mercury chloride HgCl$_2$, mercury nitrate heptahydrate HgSO$_4$.7H$_2$O, cobalt sulfate heptahydrate CoSO$_4$.7H$_2$O, cobalt chloride dihydrate CoCl$_2$.2H$_2$O and cobalt nitrate hexahydrate Co(NO$_3$)$_2$.6H$_2$O; supplied by Sigma Aldrich (Germany). The concentration of metal ions was varied from 100 to 600 mg/L.

Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used to adjust the pH of the external phase.

NaCl was chosen as a test element to study the effect of salt. It was supplied by Sigma Aldrich (Germany).

2.2. Equipment

An analytical balance (Scaltec SBC 31) was used for weighing various required masses. A Bosch high-speed homogeniser was used for the preparation of the primary W/O emulsion. The control of pH and conductivity of the solutions was carried out with a pH-metre (Hanna instruments) and an Ionolab conductivity metre (model Cond 730) respectively. The agitation of the external phase was performed by a Jartest (VELP Scientifica). UV–visible spectra were recorded using a photoLab spectrophotometer, 6600 UV–VIS. An infrared spectrophotometer (IRAffinity-1S Shimadzu) and an optical microscope (OPTIKA) equipped with a camera are also used to analyse our samples.

2.3. Preparation of the primary W/O emulsion

The organic phase (the membrane) chosen is made up of adequate quantities of surfactant (Span 80) and extractant (Triethylamine: TEA); solubilised in a diluent (hexane, heptane or kerosene).

The membrane components were mixed under moderate stirring with a magnetic bar for 5 min to obtain a homogeneous solution. The internal phase solution was then prepared using HNO$_3$, HCl, H$_2$SO$_4$, H$_3$PO$_4$, NaOH or NH$_4$OH dissolved in distilled water. The W/O emulsion was obtained by emulsification a well-defined volume of the organic phase with a certain volume of the internal aqueous phase; using the high-speed homogenizer for a specific emulsification time.

2.4. Extraction of metal ions by ELM

The W/O emulsion was dispersed in a beaker containing the external solution with a predetermined treatment ratio. The mixture is stirred by a test jar propeller. A multiple W/O/W emulsion is thus produced, formed of a large number of globules, and the two extraction and de-extraction operations take place simultaneously. The extraction kinetics was monitored by taking 4 mL samples every 3 min.

When the extraction is completed according to the set stirring time, the contents of the beaker are placed in a separating funnel for 30 min to separate the emulsion from the external aqueous phase by density difference. After separation, the emulsion becomes saturated with solute while the external phase becomes depleted in solute.

To determine the residual concentration of metal ions in the single salt solutions, the samples taken were analysed by UV–Visible spectrophotometry at the maximum wavelength of 242 nm (case of copper cations) after complexation with ethylene diamine tetraacetic acid (EDTA) at pH=10. The same method was followed for the other metal cations.

The extraction yield "R_{ext}" was calculated according to the following equation:

$$R_{ext} \ (\%) = \frac{C_{0 \ ext} \cdot V_{0 \ ext} - C_{f \ ext} \cdot V_{f \ ext}}{C_{0 \ ext} \cdot V_{0 \ ext}} \cdot 100 \tag{1}$$

where $C_{0 \ ext}$ and $C_{f \ ext}$ are the initial and final concentration of the solute in the external phase, respectively, while, $V_{0 \ ext}$ and $V_{f \ ext}$ are the initial and final volume of the external phase respectively.

Likewise, the measurement of the volumes of the emulsions before and after extraction, allowed to calculate the swelling rate "S_w" according to the following equation:

$$S_w \ (\%) = \frac{V_{0 \ E/H} - V_{f \ E/H}}{V_{0 \ E/H}} \cdot 100 \tag{2}$$

with $V_{0 \ E/H}$ and $V_{f \ ext}$ are the initial and final volume of the W/O emulsion.

2.5. Breakage of the emulsion

In order to determine the quantity of solute de-extracted in the internal phase, the emulsion is broken (de-emulsified) by chemical means. 5 mL of octanol is added to the emulsion recovered after extraction, then the whole is stirred until the emulsion is broken, i.e. the separation of the organic phase (membrane) from the internal phase, and decantation is carried out. Once the separation is complete, the internal phase is measured by UV–Visible spectrophotometry after having measured its volume. The de-extraction efficiency "R_{des}" of the solute in the internal phase is calculated by the following equation:

$$R_{des}(\%) = \frac{C_{f \ int} \cdot V_{f \ int}}{\left(C_{0 \ ext} \cdot V_{0 \ ext} - C_{f \ ext} \cdot V_{f \ ext} \right)} \cdot 100 \tag{3}$$

where $C_{f \ int}$ and $V_{f \ int}$ represent the final concentration of metal ions in the inner phase and the final volume of the inner phase respectively.

The dosage of metal ions in the internal phase after the rupture process allowed calculating the variation of the osmotic pressure "ΔΠ" between the two internal and external aqueous phases:

$$\Delta\Pi = n.R.T.\Delta C \tag{4}$$

n represents the number of solute ions, R the perfect gas constant; T the working temperature and ΔC is the difference between the final concentrations of the solute in the inner phase $C_{f \ int}$ and the outer phase $C_{f \ ext}$:

$$\Delta C = C_{f \ int} - C_{f \ ext} \tag{5}$$

It should be noted that UV–Visible and infrared spectroscopic analyses were carried out on both the external and internal phases before and after de-extraction. All experiments have been carried at ambient temperature (18 ± 2 °C).

Optical microscopy was also used to observe the distribution state of the internal phase globules in the organic phase during the emulsification stage.

3. Results and discussion

3.1. Determination of the optimal conditions for the copper ions extraction by ELM

3.1.1. Effect of surfactant concentration

Surfactants are generally amphipathic organic compounds; which means that they contain both hydrophobic groups (their "tail") and hydrophilic groups (their "head"). Thus, they are soluble in both organic solvents and water. Surfactants play a very important role in the formation of emulsions and in the extraction process. It reduces the interfacial tension between oil and water by adsorbing at the liquid-liquid interface [43]. The surfactant concentration was in the range of 3–6 wt %.

According to Fig. 1a, at low concentrations of Span 80 (3 %), the extraction of Cu^{2+} ions is quite low; this is due to the insufficient amount of surfactant to ideally surround the inner phase droplets of the
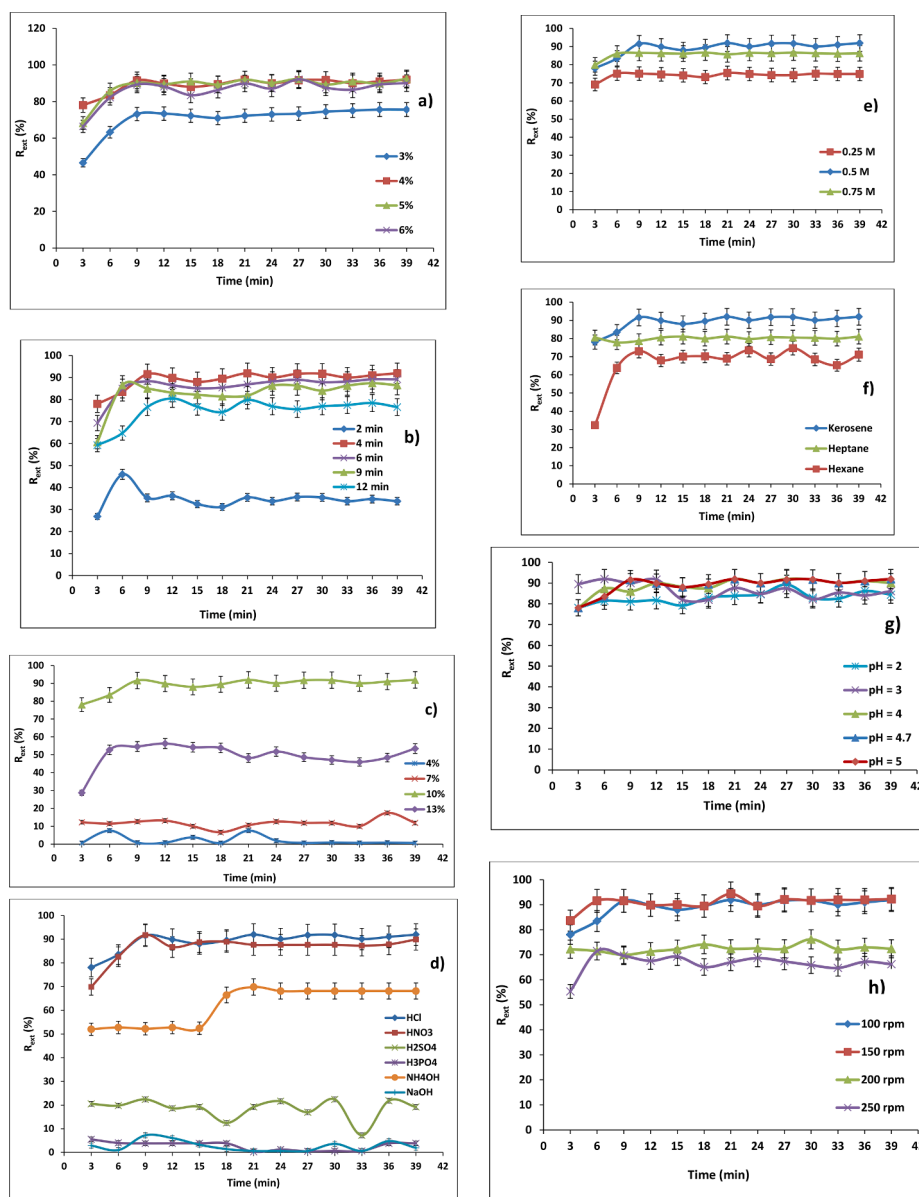
Fig. 1. (a–k): Effect of parameters on the extraction yield of copper ions: (a) surfactant concentration, (b) emulsification time, (c) extractant concentration, (d) nature of the internal phase, (e) internal phase concentration, (f) diluent type, (g) external phase pH, (h) stirring speed, (i) volume ratio of the organic phase to the internal phase (V_{memb}/V_{int}), (j) treatment ratio (V_{emul}/V_{ext}) and (k) external phase concentration. (Optimum conditions: Span 80 concentration: 4 wt%; TEA concentration: 10 wt%; diluent: Kerosene; internal phase: HCl = 0.5 M; [Cu^{2+}]: 500 mg/L; emulsification time: 4 min; V_{memb}/V_{int}: 2.08; V_{emul}/V_{ext}: 0.1; solution pH: 4.7; stirring speed: 150 rpm). All parameters were fixed except when the factor was studied.

membrane, resulting in low emulsion stability and a high breakage rate [44]. On the other hand, when increasing the concentration of surfactant to 4 % and 5 %, the copper extraction is almost the same reaching an optimum (R_{ext} = 91.56 %) for a contact time of 9 min and remains almost stable until 39 min. However, beyond this concentration, the thickness of the liquid film becomes important, which leads to an increase in viscosity as well as the resistance of the membrane interface and a decrease in the mass flow rate of the solute passing through the membrane causing a decrease in extraction efficiency (at a concentration of 6 %, the yield is 89.31 % at 9 min) [45]. Therefore, a concentration of 4 % was chosen as optimal compared to 5 % for economic reasons.

3.1.2. Effect of emulsification time

The emulsion consists of an internal aqueous phase that disperses

into the organic phase (membrane phase) to form the water-in-oil emulsion by homogenisation. The dispersion of the emulsion depends mainly on the homogeniser speed, emulsification time and droplet area, which leads to higher mass transfer rates during the extraction process [46].

Fig. 1b shows the effect of emulsification time in the range of 2 to 12 min on the extraction efficiency of Cu^{2+} ions by ELM. From the results found, it can be seen that the best yields are obtained for emulsification time equal to 4 min. While for insufficient emulsification time (2 min), the extraction efficiency decreased because the breakup rate increases due to the formation of large droplets, which leads to their coalescence [47]. Similarly, a slow emulsification time (6, 9 and 12 min) can destabilise the emulsion by yielding a high number of droplets from the inner phase and which in turn can easily agglomerate and flush outwards [48].
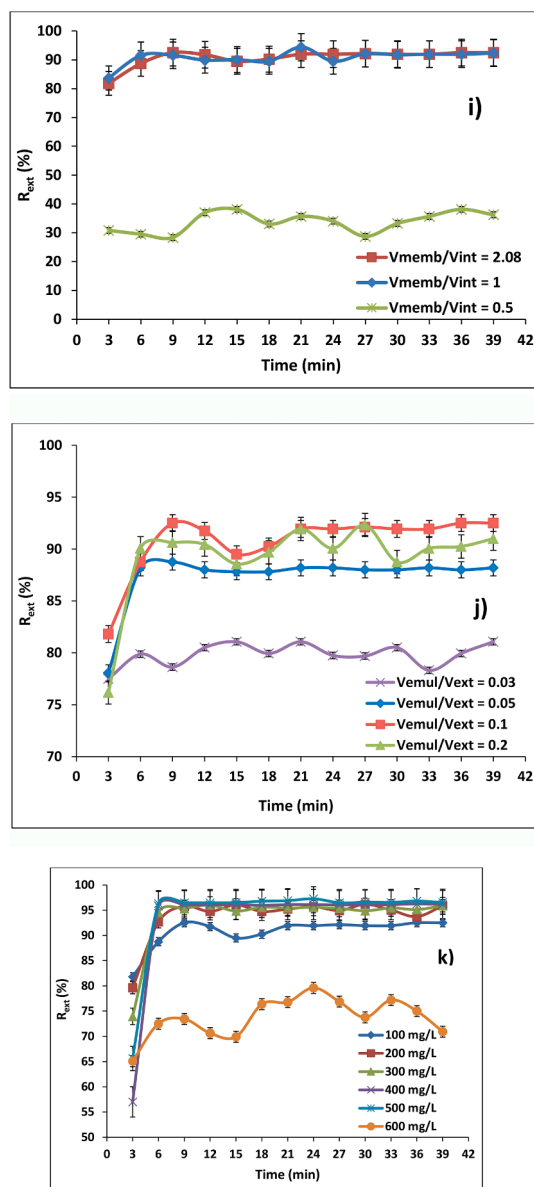
Fig. 1. (*continued*).

Therefore, an emulsification time of 4 min was chosen as optimal for the following experiments.

3.1.3. Effect of extractant concentration

During this series of experiments, the concentration of the carrier (TEA) was varied from 4 % to 13 % by mass (Fig. 1c).

In general, the presence of a carrier agent in the emulsified liquid membrane controls the efficiency of extraction of the target component through the membrane [49]. The increase in Cu^{2+} extraction yield is improved with increasing TEA concentration; this is due to the increase in the number of carrier extractant molecules involved in the extraction process thus improving the extraction performance. The best yield is obtained at a content of 10 % by mass of TEA. However a higher carrier content in the membrane phase (13 % by mass), reduces the extraction performance. This is attributed to the accumulation of extractant molecules in the membrane liquid phase, which leads to an increase in liquid membrane viscosity with formation of larger emulsion globules, affecting the stability of the process [50]. This result is in agreement with the study carried out by Sujatha et al. who observed the adverse effect of high concentration of Cyanex 301 in nickel extraction [51]. In

addition, high concentration of extractant has been reported to trigger interfacial breakdown [52]. This phenomenon can be attributed to the amphiphilic properties of triethylamine which lead to emulsion instability.

3.1.4. Effect of nature of the internal phase

Different solutions were used as internal phases; the results are shown in the Fig. 1d. It can be seen that the extraction yields of copper ions in the presence of acids in the internal phase show this trend: HCl > HNO_3 > H_2SO_4 > H_3PO_4 while in the presence of bases, the yield follows the following sequence: NH_4OH > NaOH. These results may be due to the degree of dissociation of the stripping phase which varies according to the nature of the acid or base and which influences the copper ion trapping reaction at the membrane-internal solution interface.

Hydrochloric acid was selected as the most effective stripping agent.

3.1.5. Effect of internal phase concentration

The concentration of the internal phase in the emulsion is an important parameter for deciding the efficiency of solute transport through emulsified liquid membranes [53]. According to Fig. 1e, at low

internal phase concentration HCl (0.25 M), the extraction yield is at low level (R_{ext} = 75.06 % for a contact time of 9 min). Whereas, when the concentration of HCl increased to 0.5 M, the highest extraction yield was obtained (R_{ext} = 91.56 %). Zhu et al. have found the same phenomenon when they studied the extraction and separation of copper from nickel in ammoniacal solutions by ELM supposing that the stripping of the membrane phase depends on the acid concentration in the internal phase. As the acid concentration increased, the rate of decomposition of the extracted species accelerated at the membrane/internal interface, further promoting the transport of metal ions from the external phase to the internal phase [54]. On the other hand, at higher concentration (0.75 M), the swelling of the emulsion negatively affects the stability of the emulsion and thus reduces the extraction percentage (R_{ext} = 86.5 % for a contact time equal to 9 min). This behaviour can be attributed to the reaction of HCl with Span 80, which leads to a partial loss of its surface active properties [55,56]. Therefore, a concentration of 0.5 M of the internal phase was chosen as optimal.

3.1.6. Effect of diluent type

The viscosity and density of the diluents are essential parameters that guarantee the thickness of the membrane as well as the permeability of solutes through its wall. The experiments were carried out under the same conditions as mentioned above. The extraction of Cu^{2+} ions was studied using different solvents namely; hexane, kerosene and heptane (Fig. 1f).

The extraction efficiency decreased in the following order: Kerosene > Heptane > Hexane, which shows that Kerosene is better than the other diluents. This decrease is consistent with the decrease in viscosity and density of the three diluents. Kerosene was used as an organic diluent in this investigation because of its favourable viscosity and density which allows for greater stability emulsion [57]. According to Admawi et al., kerosene also helps to attenuate interphase tensions with solutions containing metal ions. This is a fundamental property of the organic solvents used in ELM, in addition to their low volatility and insolubility in aqueous solutions [58].

3.1.7. Effect of external phase pH

It is well elucidated that the pH of the external phase in the ELM system affects the interfacial mass transfer as it acts as a driving force between the aqueous phases. The effect of pH on the extraction efficiency of copper ions was examined over a pH range of 2 to 5 (Fig. 1g). At low pH values (2 and 3), the extraction efficiency of copper ions decreased due to inefficient deprotonation of the extractant at the membrane/external phase interface, which reduces the formation of the of metal complexes [58,59]. For higher pH values (4, 4.7 and 5), the extraction of copper becomes greater due to increased formation of metal ion-transporter complex [60]. However if the pH of the feed phase tends towards basic values, the reaction cannot be controlled due to precipitation of metal hydroxide [61]. The best yields are obtained at pH 4.7 (natural pH of the solution).

3.1.8. Effect of stirring speed

The effect of stirring speed was studied in the range of 100 to 250 rpm, as depicted in Fig. 1h. Increasing the stirring speed from 100 to 150 rpm resulted in a slight increase in the extraction efficiency of copper ions due to the increase of the interfacial area of mass transfer between the feed phase and the membrane phase increases which favourite further the ions extraction [62]. On the other hand, an increase in speed to 200 and 250 prm, promotes the transport of large amounts of water to the inner phase, which causes the swelling and breakage of the emulsion by droplet enlargement and consequently decreases the transport rate of copper metal ions [63,64]. The optimal stirring speed is 150 rpm.

3.1.9. Effect of the volume ratio of organic phase to internal phase (V_{memb}/V_{int})

The ratio of the volume of organic phase (membrane) to that of internal phase is another factor controlling the extraction yield of Cu^{2+} ions, as shown in Fig. 1i.

The best yield was obtained for a V_{memb}/V_{int} volume ratio equal to 2.08 (V_{memb} = 12.5 mL and V_{int} = 6 mL), from which an extraction optimum of 92.5 % is reached at a contact time of 9 min. Furthermore, for lower ratios, equal to 1 (V_{memb} = 12.5 mL and V_{int} = 12.5 mL) and 0.5 (V_{memb} = 12.5 mL and V_{int} = 25 mL), the extraction of copper ions dropped giving yields in the order of 91.56 % and 28.38 % respectively. This decrease can be explained by the fact that the volume of the membrane phase is not sufficient to completely enclose the stripping solution resulting in leakage of the internal phase to the feed phase [56]. It should be noted that the volume of the internal phase must be in harmony with that of the membrane phase in order to obtain a stable dispersion of the purification drops (internal phase) in the emulsion [64]. A ratio of 2.08 was therefore chosen as the optimal ratio for the extraction of copper ions.

3.1.10. Effect of treatment ratio (V_{emul}/V_{ext})

To study the influence of the treatment ratio (V_{emul}/V_{ext}) on the extraction efficiency of copper ions, different values of this ratio were used ranging from 0.2 to 0.03 (Fig. 1j).

For very low treatment ratios; V_{emul}/V_{ext} = 0.05 (V_{emul} = 25 mL and V_{ext} = 500 mL) and V_{emul}/V_{ext} = 0.03 (V_{emul} = 25 mL and V_{ext} = 750 mL); the extraction of copper recorded a significant reduction of the order of 88.75 % and 78.63 % respectively and this for a contact time of 9 min. This is because as the volume of the external phase increases relative to that of the emulsion, a small number of emulsion globules are present, thus reducing the surface area available for solute extraction. As a result, the transport flux of copper ions from the external phase into the emulsion is reduced. For higher treatment ratios, i.e. 0.1 (V_{emul} = 25 mL and V_{ext} = 250 mL) and 0.2 (V_{emul} = 25 mL and V_{ext} = 125 mL), the efficiencies mentioned are 92.5 % and 90.63 % respectively. Indeed, the extraction is improved due to the number of globules available which resulted in an increase in the interfacial area per unit volume of the solution, and subsequently the mass transfer is improved from the external phase to the emulsion [65]. The optimal ratio giving the best extraction efficiency is 0.1.

3.1.11. Effect of external phase concentration

The influence of the initial concentration of copper ions on the extraction yield is shown in Fig. 1k. The extraction yield increased with increasing concentration, where the yield rises from 92.5 % for an initial concentration of 100 mg/L to 96.5 % for a concentration of 500 mg/L after 9 min of stirring and remains almost stable until 39 min. This result is due to the increase of the driving force (concentration gradient of copper ions) between the two internal and external phases [63].

At an initial high metal concentration of 600 mg/L, a drop in extraction was reported of about 27 %, this reduction could be due to saturation of the inner phase droplets. The reduction is also due to the swelling of the emulsion as a result of the difference in ionic strength and osmotic pressure between the two aqueous inner and outer phases. A similar trend was obtained by Qudus et al. when studying the removal of lead ions from an aqueous solution by ELM [66,67]. The concentration of 500 mg/L was considered optimal.

3.2. Emulsion recycling

As can be seen from the results in Fig. 2, the first reuse of the emulsion has no negative effect on the extraction of copper ions, whose yields remained practically constant over the time interval studied. This shows that the carrier is capable of transporting metal cations and concentrating them in a small volume of the internal phase [68]. However, during the second reuse, the extraction efficiency decreased
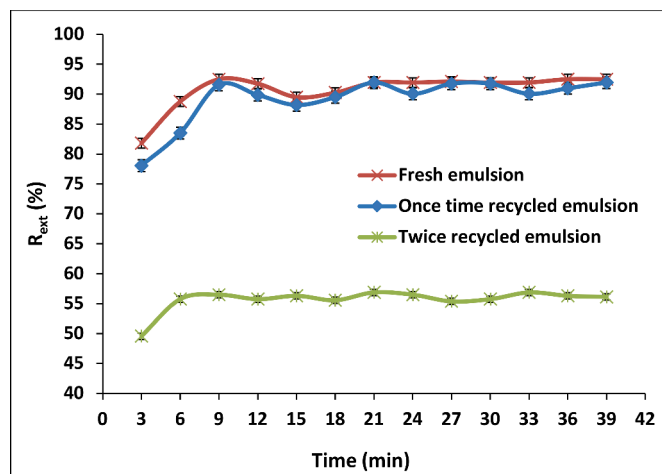
Fig. 2. Effect of emulsion recycling on the extraction yield of copper ions. Span 80 concentration: 4 wt%; TEA concentration: 10 wt%; diluent: Kerosene; internal phase: HCl = 0.5 M; [Cu^{2+}]: 100 mg/L; emulsification time: 4 min; V_{memb}/V_{int}: 2.08; V_{emul}/V_{ext}: 0.1; solution pH: 4.7; stirring speed: 150 rpm.

by about 40 % due to the low availability of the free extractant following the significant accumulation of metal complexes formed in the membrane phase during the ELM process. This may also be due to the swelling of the emulsion as a result of the high metal concentrations in the internal phase, leading to a decrease in extraction [53].

3.3. Morphology of the primary W/O emulsion

3.3.1. Variation of internal globule size with emulsification time

The morphology of the W/O emulsion was examined under the optical microscope (OM) as the emulsification time was varied. As shown in Fig. 3, at $t = 0$ min, large water droplets form without any external stirring energy, this is in agreement with the study reported by Bahtz et al., who explained this phenomenon by the spontaneous emulsification that forms due to the presence of the surfactant [69]. By increasing the emulsification time ($t = 1$ min, $t = 2$ min, $t = 3$ min), the globule size

becomes smaller and smaller. Several researchers have also shown that the internal droplets decreased with increasing emulsification time while keeping the other parameters constant [70,71]. The distribution of internal globules for the emulsion prepared for an emulsification time of 4 min, appeared to be more homogeneous compared to the other emulsions, this time proved to be optimal for the extraction of copper ions. On the other hand, a longer emulsification time ($t > 4$ min) resulted in a larger number of smaller droplets, which is contrary to the stability of the emulsion [72,73].

3.3.2. Analysis of the physical stability of the emulsion at different time intervals

The stability of the primary W/O emulsion prepared under optimal conditions (concentration of Span 80 = 4 wt%; concentration of TEA = 10 wt%; internal phase: HCl = 0.5 M; emulsification time: 4 min; V_{memb}/V_{int}: 2.08) was monitored over time (Fig. 4). After reserving this emulsion, it was found that it can maintain its stability for up to 60 days with clear phase separation observed. This result confirms a long life for the emulsion, and reassures us that the optimal conditions applied for the synthesis of this emulsion are very adequate. The ageing of the emulsion over time obviously leads to its rupture [73,74].

3.4. Extraction of other varieties of heavy metals under the optimal conditions

3.4.1. Extraction kinetics of heavy metals in presence of different anions

The emulsion prepared under optimal conditions was applied to singular solutions containing metal salts based on heavy metals, namely Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+}, from which each metal is bound to three types of anions; sulphates (SO$_4^{2-}$) or chlorides (Cl$^-$) or nitrates (NO$_3^-$).

The extraction kinetics of the various metals contained at an initial concentration equal to 100 mg/L increases rapidly until it reaches a quasi-stable level during the first few minutes (Fig. 5). For a contact time equal to 9 min, the extraction yields of copper ions contained in CuSO$_4$.5H$_2$O, CuCl$_2$.2H$_2$O and Cu(NO$_3$)$_2$.6H$_2$O solutions become almost stable and are equal to 92.5 %, 95 % and 94.43 % respectively (Fig. 5a). The results found in our study prove that the emulsion prepared under
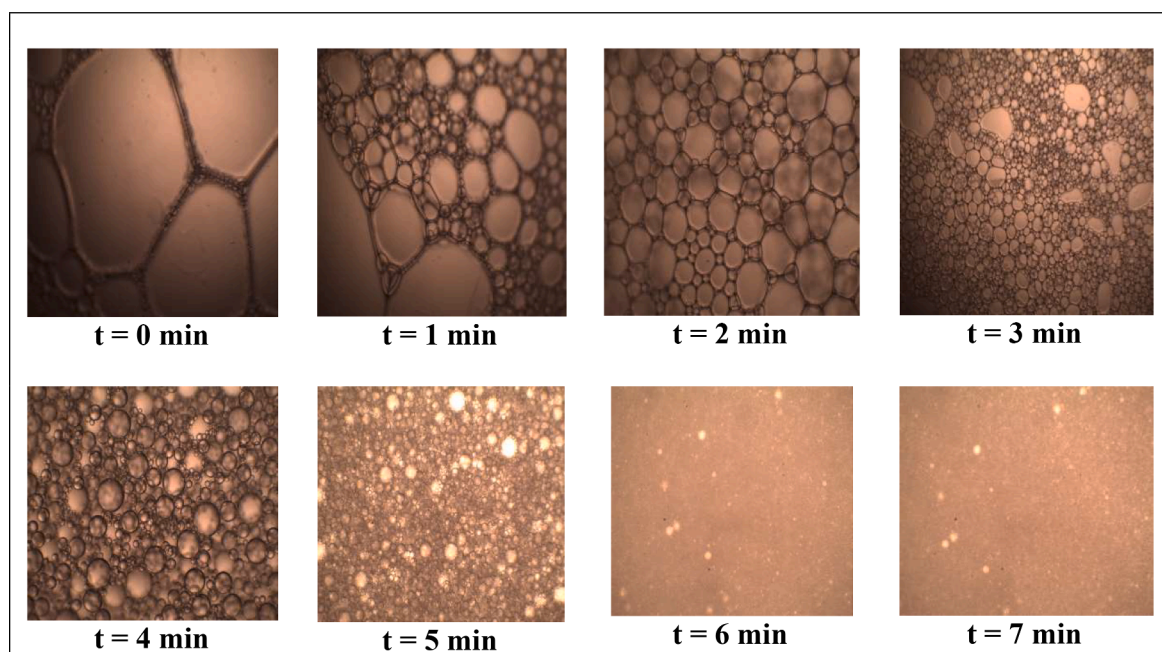

Fig. 3. Optical microscopy images of the primary W/O emulsion for different emulsification times. Span 80 concentration: 4 wt%; TEA concentration: 10 wt%; diluent: Kerosene; internal phase: [HCl] = 0.5 M; V_{memb}/V_{int}: 2.08.
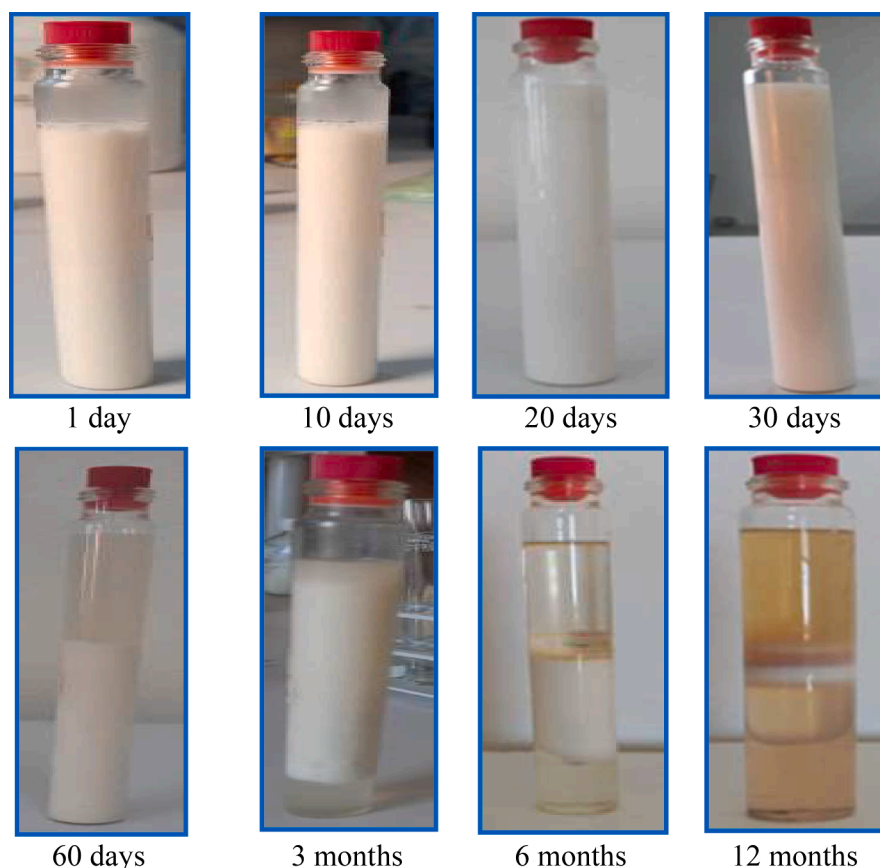
Fig. 4. Photographic images of the primary W/O emulsion at different time intervals. Span 80 concentration: 4 wt%; TEA concentration 10 wt%; diluent: paraffin; internal phase: [HCl] = 0.5 M; V_{memb}/V_{int}: 2.08.

optimal conditions is effective in removing copper ions from aqueous solutions in yields above 90 % and it appears that the type of anions has no significant effect on the extraction efficiency (the difference is estimated at 2.63 %). On the other hand, triethylamine (TEA), which is almost unusable in ELM systems, seems to be a good extractant when compared with other extractants widely used in the literature for the extraction of heavy metals. For example, in the work carried out by Zereshki et al., a green emulsion liquid membrane process based on sunflower oil has been used for the separation of copper ions from aqueous solutions of CuSO₄.5H₂O using the Box-Behnken method. The liquid membrane was prepared with Span 80 as surfactant, D2EHPA as extractant, sunflower oil as solvent and hydrochloric acid as aqueous internal phase. The results showed that more than 94 % of Cu^{2+} ions were successfully extracted in 130 min under the optimal conditions [56]. Similarly, the study by León et al., which describes the removal of Cu^{2+} from acetate-buffered aqueous solutions by emulsified liquid membrane, through a counter-transport mechanism facilitated by benzoylacetone as transporter and HCl as stripping agent. Typical membrane transport parameters, such as flux and permeability, were also determined. Copper ions were removed by 80.3 % in 15 min [75].

For the same contact time (9 min), zinc extraction was 98.57 % for ZnSO₄·7H₂O and ZnCl₂ and 92.14 % for Zn(NO₃)₂·6H₂O (Fig. 5b). This still reflects a negligible difference of about 6.52 %. In this sense the work of Tahmasebizadeh et al. can be reported, who extracted zinc from a sulphide ore, to about 71 % after 20 min, under a speed of 150 rpm, 5 % (v/v) Span 80, 10 % (v/v) D2EHPA, V_{ex}/V_{em} = 5:1 and 1.5 M sulphuric acid as internal phase [76]. On the other hand, Suliman et al., demonstrated that the components used in the ELM system notably in terms of di-(2-l'ethylhexyl) phosphoric acid (D2EHPA) and bis(2,4-trimethylpentyl)thiophosphinic acid (Cyanex 302) as synergistic extractants, palm oil as diluent, sorbitan monooleate (Span 80) and

polyoxyethylene sorbitan monooleate (Tween 80) as surfactants, iron (III) oxide (Fe₂O₃) as a nanoparticle stabiliser and thiourea as a stripping agent in the emulsion manufacture has a high potential to improve the emulsion stability in the liquid membrane zinc extraction process [77].

For the extraction of lead ions from PbSO₄, PbCl₂ and Pb(NO₃)₂ solutions, the extraction yields were 96.60 %, 92.98 % and 97.87 % respectively for a stirring time of 9 min, i.e. an insignificant deviation of about 5 % (Fig. 5c). According to the literature, Mesli and Belkhouche were able to extract lead ions from nitrate solutions, at 82.14 % using heptane as a diluent, Aliquat336 as an extractant, nitric acid HNO₃ as an internal phase and TritonX-100 and Tween-20 as surfactants [78]. In addition, Salman and Mohammed studied the impact of α-Fe₂O₃ magnetic particles on the stability of emulsions formed with di-2-ethylhexyl phosphoric acid (D2EHPA) as carrier, Span 80 as surfactant, H₂SO₄ as internal phase and paraffin as diluent. The results confirmed the existence of a co-stabilisation strategy, which leads to emulsion stability and improved extraction efficiency of lead ions contained in lead nitrate solutions, up to 97.2 % after 8 min mixing time under the best operating conditions with a membrane rupture rate of 0.3 % [72]. The screening of operational parameters according to the Plackett Burman design showed that lead ion extraction by ELM is influenced by six parameters which were subsequently optimised by the Box-Behnken design giving a maximum lead extraction from a lead nitrate solution equal to 97, 39 % for a content of 4.6 % (v/v) D2EHPA, 2.14 % (v/v) Span 80, pH of feed solution equal to 4.4, concentration of 2 M sulphuric acid used as internal phase, initial concentration of lead ions of 173 mg/L and a volume ratio of organic phase to aqueous phase equal to 1.3 [66].

The two ions nickel and cobalt showed after 9 min of extraction yields of 94.90 % (Fig. 5d) and 96.96 % (Fig. 5e) respectively for the three types of anions. Ma et al. employed the liquid emulsion membrane technique to remove nickel ions from synthetic aqueous solutions of
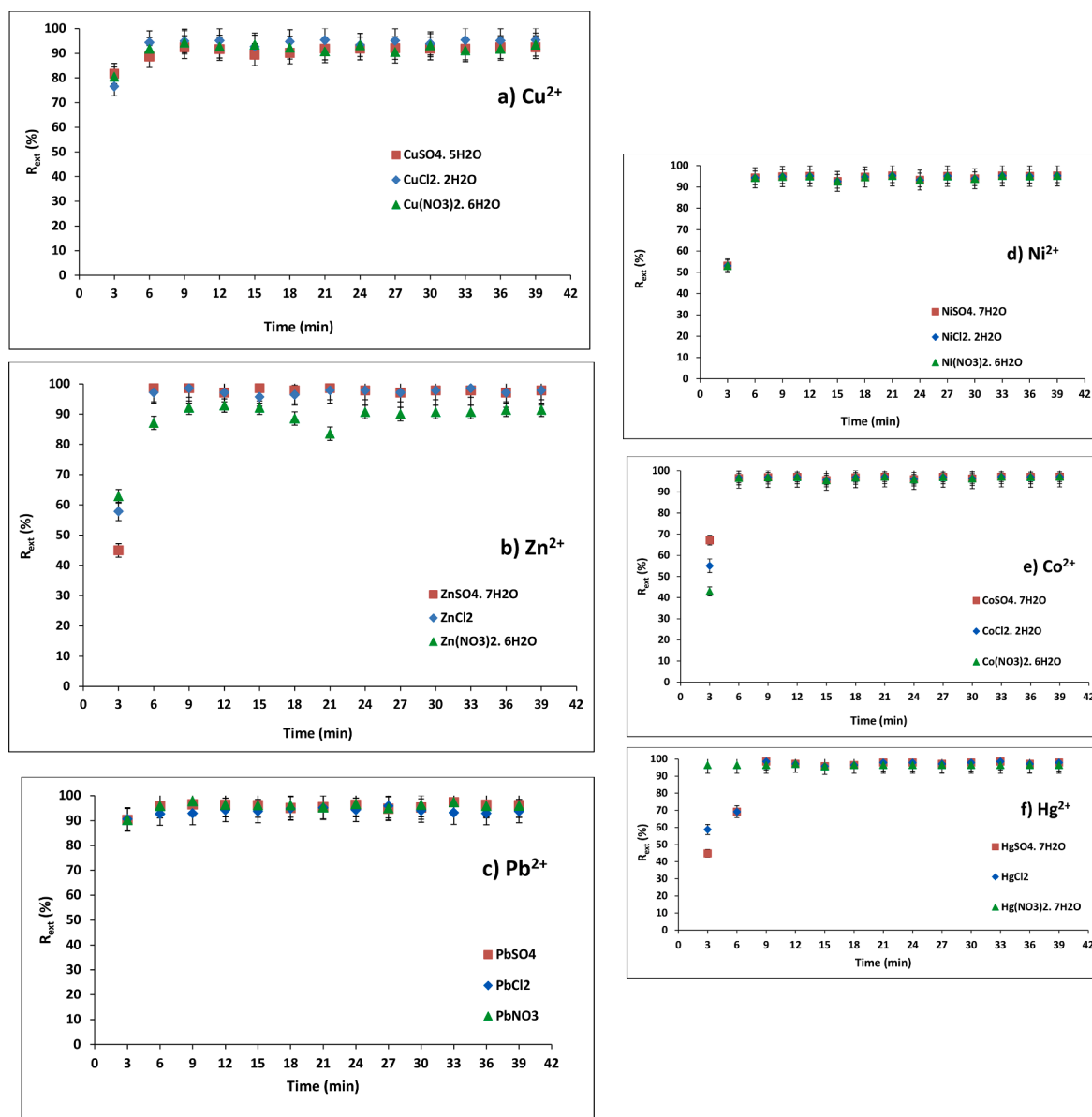
Fig. 5. (a–f): Evolution of the extraction yield of different metallic ions as a function of time in presence of different anions: a) Cu^{2+}, (b) Zn^{2+}, (c) Pb^{2+}, (d) Ni^{2+}, (e) Co^{2+} and (f) Hg^{2+}. Span 80 concentration: 4 wt%; TEA concentration: 10 wt%; diluent: Kerosene; internal phase: HCl = 0.5 M; $[M^{2+}]$: 100 mg/L; emulsification time: 4 min; V_{memb}/V_{int}: 2.08; V_{emul}/V_{ext}: 0.1; solution pH: 4.7; stirring speed: 150 rpm.

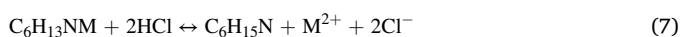nickel sulphates hexahydrate (NiSO$_4$.6H$_2$O) using bis(2,4,4-trimethylpentyl) dithiophosphinic acid (Cyanex 301) as the extractant. Sulphuric acid was chosen as the internal phase. Under the optimal operating conditions, a maximum nickel removal of more than 99 % was achieved [79]. A study carried out on the extraction of nickel from an aqueous solution of nickel sulphates NiSO$_4$ with a green emulsified liquid membrane using waste cooking oil as a diluent and Cyanex 301 as an extractant, showed an excellent nickel extraction potential of 98.7 % during a stirring time of 11 min [51]. Furthermore, the results obtained by Sohan et al., confirmed the possibility of total extraction of cobalt ions from a cobalt chloride solution using the ELM system in the presence of hydrodynamic cavitation. It was also shown that the extraction efficiency of cobalt increases with the concentration of Aliquat 336 used as extractant for different cavitation times [80]. Hachemaoui and Belhamel, obtained almost 99 % extraction of cobalt ions from cobalt chloride solutions (CoCl$_2$.6H$_2$O) using Cyanex 301 as extractant. The effects of extractant and surfactant concentrations, stirring speed, concentration and type of stripping solution, phase ratio, treatment ratio

and nature of diluent on the extraction rate were studied [81].

According to Fig. 5f it is noted that after 9 min of agitation, mercury ions in HgSO4.7H$_2$O and HgCl$_2$ solutions were extracted at 98.60 % and those in Hg(NO$_3$)$_2$.7H$_2$O solution were extracted at 96.51 %, which corresponds to a difference of 2.12 %. Hamzah et al. have performed the extraction of mercury ions from mercury chloride solutions HgCl$_2$ by the emulsified liquid membrane technique using benzoyl acetone as extractant. The extraction yield was 96.8 % under optimal conditions [30]. Another study focused on the removal of mercury ions from HgCl$_2$ mercury chloride solutions by ELM made from 1-phenyl-3-methyl-4--benzoyl-5-pyrazolone (HPMBP) used as a cation carrier. The optimum results show that an optimal extraction of 98.6 % was obtained at a surfactant concentration of 2.5 % with an emulsion to external phase volume ratio of 1:7 and pH equal to 3. Additionally a concentration of HPMBP equal to 0.018 M with an internal phase concentration of nitric acid in the order of 2.0 M [82]. Also the extraction efficiency of mercury ions from mercury chloride solutions by means of a stable W/O emulsion is 92 % on a small scale using D2EHPA as extractant, Span 80 as

surfactant, Glycerol monostearate as co-surfactant, toluene as diluent and sulphuric acid as internal phase. The turbulence created by a larger diameter impeller in a high capacity reactor would increase membrane breakdown, ultimately reducing the overall extraction efficiency to 88 % [70].

The transport process of heavy metals occurs due to concentration gradient between the external and internal phase, where the solute is transported from a region of high concentration to low concentration [66]. The mechanism of solute transfer through liquid membrane starts with reaction (Eq. (6)) which takes place at the first interface, external phase/membrane, and involves the formation of metal complexes between the heavy metal cations (M^{2+}) and the carrier (TEA) with the release of the H^+ protons in the feed solution. The metal complexes then diffuse through the membrane phase and, once they reach the second interface; membrane/internal phase, the decomplexation reaction takes place (Eq. (7)), hence the carrier is recovery and the liberation of metal cations in the stripping phase:

$$C_6H_{15}N + M^{2+} \leftrightarrow C_6H_{13}NM + 2H^+ \tag{6}$$

$$C_6H_{13}NM + 2HCl \leftrightarrow C_6H_{15}N + M^{2+} + 2Cl^- \tag{7}$$

Similar mechanisms have been reported in previous works, e.g. the mechanism mentioned by Khadivi et al. for the extraction of lead ions from aqueous solutions by ELM using Aliquat 336 as a carrier [53] and also for the simultaneous extraction and separation of copper ions from nickel in ammonia solutions by Zhu et al., using M5640 (5-nonyl salicylaldehyde oxime) as an extractant in an emulsified liquid membrane system [54]. These authors describe their mechanisms by the phenomenon of diffusion of the solute from the external solution towards the first membrane interface, then complexation of the solute by the extractant, followed by diffusion of the transporter-metal complex through the membrane phase, finalised by dissociation of the complex by interaction with the internal phase at the second membrane interface, where the solute enters the internal phase and the regenerated extractant diffuses back into the membrane for a new extraction cycle.

3.4.2. Effect of the initial concentration of metal ions in presence of different anions: evolution of extraction yield, de-extraction yield, swelling rate and osmotic pressure

The effect of the initial concentration was studied for each metal (Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+}) under the optimal conditions
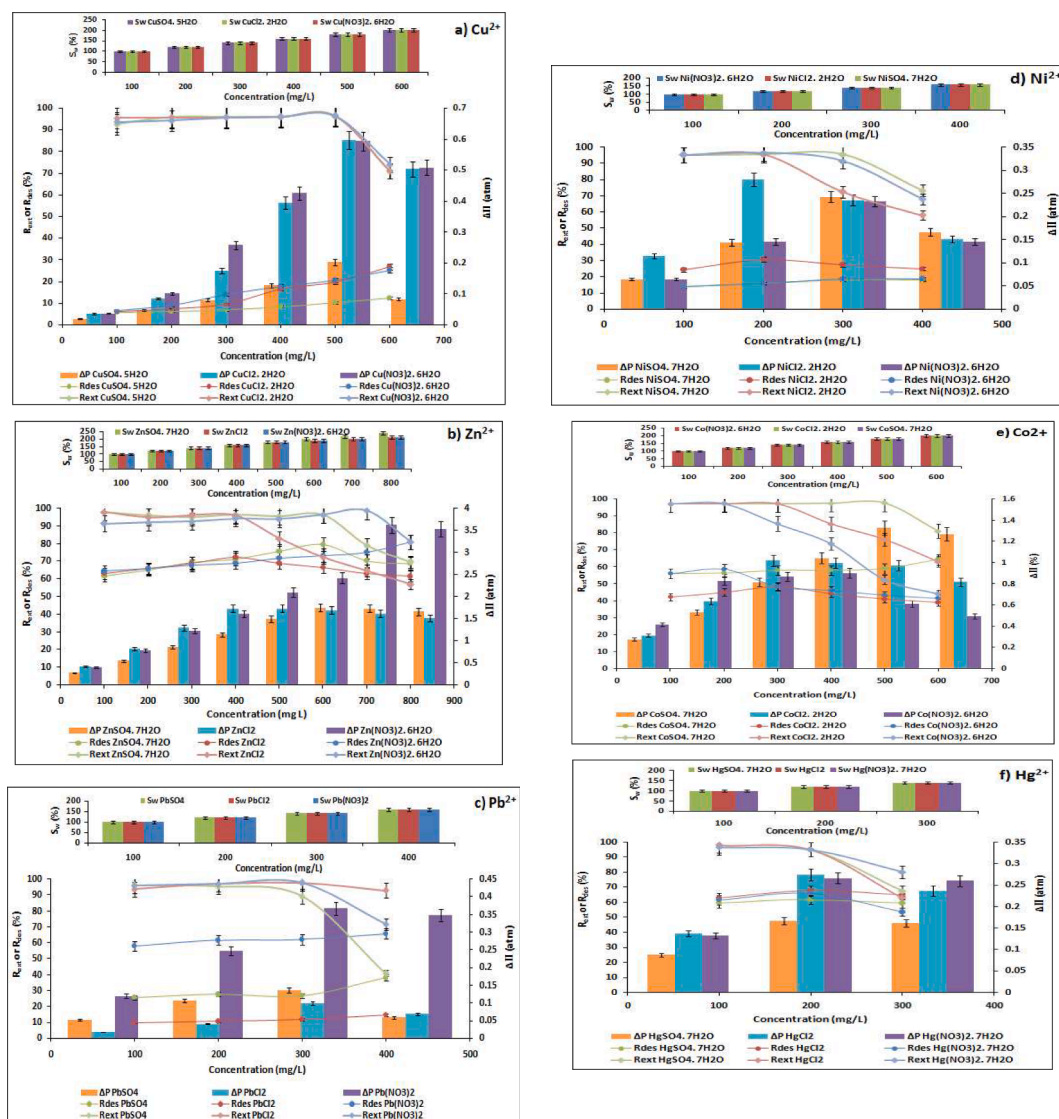

Fig. 6. (a–f): Variation of extraction yield, de-extraction yield, swelling rate and osmotic pressure as a function of initial concentration in the presence of different anions (Sulphates or chlorides or nitrates): (a) Cu^{2+}, (b) Zn^{2+}, (c) Pb^{2+}, d) Ni^{2+}, (e) Co^{2+} and (f) Hg^{2+}. Concentration of Span 80: 4 wt%; concentration of TEA: 10 wt %; diluent: Kerosene; internal phase: HCl = 0.5 M; emulsification time: 4 min; V_{memb}/V_{int}: 2.08; V_{emul}/V_{ext}: 0.1; solution pH: 4.7; stirring speed: 150 rpm; stirring time: 39 min.

by quantifying several parameters, namely extraction and de-extraction yields, swelling rate and osmotic pressure (Fig. 6).

When increasing the concentration of copper ions in solution from 100 to 500 mg/L (Fig. 6a), the extraction yield is kept almost constant (R_{ext} = 96.5 %) for all three types of anions (sulphates, chlorides and nitrates) showing an increase in both osmotic pressure up to 0.2 atm, 0.6 atm and 0.59 atm for copper ions present in the medium of sulphates, chlorides and nitrates respectively and in swelling rate from 100 % up to 180 % caused by the difference in ionic strength between the internal phase and the feed solution [66]. In contrast, for an initial concentration of 600 mg/L, the yield dropped by around 27 % accompanied also by a drop in osmotic pressure, this is due to saturation of the internal droplets of the W/O emulsion, which is reached more rapidly as the metal ion diffuses through the membrane phase to the internal phase [64,83]. This decrease can also be attributed to the constant amount of extractant (10 % TEA by weight) which is considered insufficient for the complexation of copper ions at high concentrations [67]. With regard to the de-extraction quantification, as can be seen, the yields gradually increase with concentration, giving (R_{des} = 12.35 %), (R_{des} = 26.81 %) and (R_{des} = 25.27 %) at 600 mg/L for copper ions contained in sulphate, chloride and nitrate solutions respectively. This pattern can be explained by the fact that at the beginning of the extraction, a large part of the metal ions diffused from the external phase to the internal phase by accumulating in the first interface of the emulsion, especially at high concentrations, which makes the diffusion of copper ions to the internal phase at the second interface of the emulsion (decomplexation process) only increases [84].

In the case of zinc (Fig. 6b), the ELM extraction system was maintained effective in a nitrate medium up to 700 mg/L with a yield of 98.69 % and then a drop of 17.86 % was mentioned for a concentration of 800 mg/L. In a sulphate medium, extraction is efficient up to 600 mg/L with a yield of 96.43 % followed by a successive drop to 27.78 % at 800 mg/L. In the chloride medium, the yields were very high at the first concentrations up to 400 mg/L (R_{ext} = 95.89 %) then the extraction progressively decreased to 56.96 % at 800 mg/L (i.e. a drop of 40.6 %). It should be noted that the shape of the three extraction curves is similar to the histograms describing the evolution of the osmotic pressure. The decrease in extraction can be attributed to the phenomenon of swelling which becomes more important at high concentrations as shown in the same figure and which in turn weakens the membrane walls and leads to the instability of the system and therefore causes a drop in osmotic pressure [85,86]. For de-extraction, it appears to be homologous with extraction over all concentration ranges studied, especially for chloride and sulphate media, which means that the amount of zinc ions caught by the TEA is proportional to the amount released into the internal phase. However, the curve related to the de-extraction of zinc from the nitrate medium shows a continuous increase despite the marked drop on the extraction curve at high concentration (R_{des} = 80.96 % at 800 mg/L), this is probably due to the strong accumulation of zinc ions in the external interface of the emulsion which makes the diffusion process in the internal phase incessant.

For the other metal cations, i.e. Pb^{2+}, extraction is maximum at 300 mg/L, particularly in the presence of nitrates (R_{ext} = 97.84 %) and chlorides (R_{ext} = 97.66 %), above this concentration the extraction efficiency decreases, particularly in the presence of sulphates, from which a drop of 54.15 % is obtained at 400 mg/L (Fig. 6c). For Ni^{2+}, the system proved to be also efficient up to 300 mg/L, particularly in a sulphated environment (R_{ext} = 95.51 %). Above this concentration, the efficiency decreased by about 40 % in the presence of chlorides with a swelling rate of 160 % (Fig. 6d). At higher concentrations, swelling negatively affects the stability of emulsion thereby reducing the percentage extraction. Thus, in both cases of Pb^{2+} and Ni^{2+} ions, the extraction curves have the same trend as the osmotic pressure gradient histograms over the whole concentration range studied, reflecting the strong link between extraction and ionic strength between the inner and outer phase. The excessive transfer of solute from the feed phase to the internal phase further

improves the extraction yield and the osmotic pressure difference between the two phases, this condition allows the penetration of water into the stripping phase which mainly participates in the swelling of the emulsion leading to the destabilisation of the system [87]. By investigating the de-extraction efficiencies for both metals (lead and nickel), it is clear that the evolution of the stripping process as a function of the initial metal ion concentration proceeded at a slower rate than the extraction process, this may be due to the large amount of metal that accumulated in the membrane phase [88]. The highest de-extraction is obtained at 400 mg/L in nitrate medium for Pb^{2+} (R_{des} = 65.79 %) and at 200 mg/L in chloride medium for Ni^{2+} (R_{des} = 30.73 %).

With regard to cobalt ions, the extraction curve for the sulphate medium is almost linear up to 500 mg/L, with a yield of 97.77 %, while that for the chloride medium is constant up to 300 mg/L, with a yield of 97.33 %, and that for the nitrate medium appears to be less effective, remaining stable up to 200 mg/L with a yield of 97.39 %. All the levels obtained were continued by a progressive descent giving a decrease of 16.97 %, 35.11 % and 54.69 % at 600 mg/L in the presence of sulphates, chlorides and nitrates respectively. These falls can be attributed to the swelling phenomenon which becomes more pronounced at high concentrations (Fig. 6e). The general shape of the three extraction curves is almost compatible with the evolution of the osmotic pressure gradient. These findings are similar to those obtained for the previous metals. As for de-extraction, the trend of the curves obtained is generally in line with the extraction curves, which proves that the two operations are carried out simultaneously. The best de-extraction yield is 64.35 %, obtained for cobalt ions contained at 600 mg/L in a sulphate medium.

For mercury ions, the extraction is maintained effective up to 200 mg/L (R_{ext} = 97 %), for all three types of anions showing thereafter a decay that was more significant in a chloride medium at 300 mg/L (Fig. 6f). It should be noted that this decrease is accompanied by an increase in the swelling rate of 140 %. Gupta et al. have shown that there is proportionality between swelling and membrane rupture during mercury extraction by ELM [70]. On the other hand, extraction varies according to the osmotic pressure gradient, which reflects the variation in ionic strength between the two external and internal phases. For de-extraction, the best yields were obtained at 200 mg/L, i.e. 61.67 %, 67.74 % and 65.90 % for mercury contained in sulphate, chloride and nitrate solutions respectively.

4. Conclusion

Emulsion liquid membranes (ELM) have received much attention in the separation of various metal ions from wastewater. Efforts are still needed to achieve the desired level of stability in order to overcome the obstacle to applying ELM technique on an industrial scale. This research has led to the synthesis of a highly stable emulsified liquid membrane capable of extracting a wide variety of heavy metals. The optimal operational conditions defined for a better extraction (R_{ext}= 96.5 %) of copper ions are: Span 80 concentration: 4 wt%; TEA concentration: 10 wt%; internal phase (HC): 0.5 M; emulsification time: 4 min; V_{memb}/V_{int}: 2.08; V_{emul}/V_{ext}: 0.1; pH of the external solution: 4.7 and stirring speed: 150 rpm; initial ion concentrations: 500 mg/L and a contact time: 9 min.

The extraction of metal cations; Cu^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Co^{2+} and Hg^{2+}; contained in simple solutions at a concentration of 100 mg/L and in the presence of sulphate (SO_4^{2-}) or chloride (Cl^-) or nitrate (NO_3^-) ions, showed that extraction kinetics are very rapid for all metals, with very high efficiency (R_{ext} > 90 %).

Increasing the metal concentration made it possible to examine up to what concentration level the ELM process remains effective and revealed that extraction can be influenced by the type of anions present in solution.

The evolution of extraction was consistent with that of the osmotic pressure difference, reflecting significant mass transfer between the internal and external phases, while de-extraction was generally similar to extraction, but at a slightly slower rate. On the other hand, the swelling

phenomenon resulted in a significant decrease in both extraction and osmotic pressure, as well as a slight decrease in de-extraction.

Finally, an evaluation of the extraction capacity by ELM using the primary W/O emulsion developed in this study for the treatment of industrial effluents loaded with other heavy metals and organic and inorganic pollutants is appropriate and further experimental studies are recommended to better understand the mechanisms involved, in particular, by the anions present in solution. In addition, hybridisation of ELM with other processes such as adsorption, ultrasound, etc., could be more effective; more in-depth morphological characterisation of the emulsion would be useful; a study based on modelling with experimental designs could minimise the number of tests; and integration of this extraction process into a chain of unit operations could play an important role on an industrial scale.

Data availability

All methods and materials used in this study are well exposed in this article.

CRediT authorship contribution statement

Selma Djaber: Validation, Investigation, Resources, Writing – original draft, Visualization. **Saliha Bouranene:** Conceptualization, Methodology, Resources, Validation, Writing – original draft, Writing – review & editing, Visualization, Supervision. **Souheila Bouacherine:** Resources.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgment

References

[1] N. Sedira, S. Bouranene, A.H. Gheid, Ultrasound-assisted adsorption of Pb ions by carbonized/activated date stones from singles/mixed aqueous solutions, J. Indian Chem. Soc. 99 (2) (2022).

[2] S. Bouranene, N. Sedira, L. Zeghadnia, A.K. Guebail, Kinetic Study of the Adsorption of Zinc and Copper Ions on to Activated Carbon Prepared from Date Pits, Int. J. New. Chem. 9 (1) (2021) 21–35.

[3] S.V. Smirnova, D.V. Ilin, I.V. Pletnev, I, V, Extraction and ICP-OES determination of heavy system and oleophilic collector, Talanta 221 (2021), 121485.

[4] M. Arbabi, S. Hemati, M. Amiri, Removal of lead ions from industrial wastewater: a review of removal methods, Int. J. Epidemiol. Res. 2 (2) (2015) 105–109.

[5] S. Björkegren, R. Karimi, A. Martinelli, N. Jayakumar, M. Hashim, A new emulsion liquid membrane based on a palm oil for the extraction of heavy metals, Membranes 5 (2) (2015) 168–179.

[6] A. Hussain, M. Priyadarshi, S. Dubey, Experimental study on accumulation of heavy metals in vegetables irrigated with treated wastewater, Appl. Water Sci. 122 (9) (2019) 1–11.

[7] A.M. Alkherraz, A.K. Ali, K.M. Elsherif, Removal ofPb (II), Zn (II), Cu (II) and Cd (II) from aqueous solutions by adsorption onto olive branches activated carbon: equilibrium and thermodynamic studies, Chem. Int. 6 (1) (2020) 11–20.

[8] F.S. Abdulraheem, Z.S. Al-Khafaji, K.S. Hashim, M. Muradov, P. Kot, A.A. Shubbar, Natural filtration unit for removal of heavy metals from water, IOP Conf. Ser.: Mater. Sci. Eng. 888 (2020), 012034.

[9] D.G. Liu, X.B. Min, Y. Ke, L.Y. Chai, Y.J. Liang, Y.C. Li, Z.B. Wang, Co-treatment of flotation waste, neutralization sludge, and arsenic-containinggypsum sludge from copper smelting: solidification/stabilization of arsenic and heavy metals with minimal cement clinker, Environ. Sci. Pollut. Res. 25 (2018) 7600–7607.

[10] D. Sakhi, Y. Rakhila, A. Elmchaouri, M. Abouri, S. Souabi, A. Jada, M. Ezziyyani, Optimization of coagulation flocculation process for the removal of heavy metals from real textile wastewater. Advanced Intelligent Systems Applied to Environment, Book series, 2019, pp. 257–266.

[11] A.J. Bora, R.K. Dutta, Removal of metals (Pb, Cd, Cu, Cr, Ni, and Co) from drinking water by oxidation-coagulation-absorption at optimized pH, J. Water Process. Eng. 31 (2019), 100839.

[12] P. Wang, L. Yan, Y. Gu, S. Kuboon, H. Li, T. Yan, D. Zhang, Poisoning-resistant NO_x reduction in the presence of alkaline and heavy metals over H-SAPO-34-supported Ce-promoted Cu-basedcatalysts, Environ. Sci. Technol. 54 (10) (2020) 6396–6405.

[13] L.B. Jugnia, D. Manno, M. Hendry, B. Tartakovsky, Removal of heavy metals in a flow-through vertical microbial electrolysis cell, Can. J. Chem. Eng. 97. 10 (2019) 2608–2616.

[14] M. Padervand, G. Lammel, A. Bargahi, H. Mohammad-Shiri, Photochemical degradation of the environmental pollutants on the worm-like Nd_2CuO_4-Nd_2O_3 nanostructures, Nano Struct. Nano Objects 18 (2019), 100258.

[15] N.S. Kislik, Solvent extraction, Classical and Novel Approaches, Elsevier, 2012, pp. 185–314.

[16] S. Sujatha, N. Rajamohan, Y. Vasseghian, M. Rajasimman, Conversion of waste cooking oil into value-added emulsion liquid membrane for enhanced extraction of lead: performance evaluation and optimization, Chemosphere 284 (2021), 131385.

[17] N.N. Li, Separating hydrocarbons with liquid memnranes, 1968. US Patent 3,410,794.

[18] B.A. Masry, M.I. Aly, J.A. Daoud, Selective permeation of Ag^+ ions from pyrosulfite solution through nano-emulsion liquid membrane (NELM) containing CYANEX 925 as carrier, Colloids Surf. A Physicochem. Eng. Asp. 610 (2021), 125713.

[19] M.B. Rosly, N. Jusoh, N. Othman, H.A. Rahman, N.F.M. Noah, R.N.R. Sulaiman, Effect and optimization parameters of phenol removal in emulsion liquid membrane process via fractional-factorial design, Chem. Eng. Res. Des. 145 (2019) 268–278.

[20] Q. Al-Obaidi, M. Alabdulmuhsin, A. Tolstik, J.G. Trautman, M. Al-Dahhan, Removal of hydrocarbons of 4-Nitrophenol by emulsion liquid membrane (ELM) using magnetic Fe_2O_3 nanoparticles and ionic liquid, J. Water. Process. Eng. 39 (2021), 101729.

[21] P. Daraei, A. Shokri, E. Rostami, Extraction of vancomycin antibiotic from water using green emulsion liquid membrane based on sun flower oil, J. Membr. Sci. Res. 8 (2) (2022), 526001.

[22] R. Karmakar, P. Singh, A. Datta, K. Sen, Emulsion liquid membrane in the selective extraction of Dy, Chem. Eng. Res. Des. 187 (2022) 497–506.

[23] R. Shirasangi, H.P. Kohli, S. Gupta, M. Chakraborty, Separation of methylparaben from aqueous source stream by pseudo-emulsion hollow fiber membrane strip dispersion technique: optimization of process parameters using Grey-Taguchi method, Chem. Eng. Process. Process Intensif. 161 (2021), 108302.

[24] R.M. de Souza, D. Seibert, H.B. Quesada, F. de Jesus Bassetti, M.R. Fagundes-Klen, R. Bergamasco, Occurrence, impacts and general aspects of pesticides in surface water: a review, Process Saf. Environ. Prot. 135 (2020) 22–37.

[25] M.D. Asl, I. Salahshoori, A. Seyfaee, A. Hatami, A.A. Golbarari, Experimental results and optimization via design of experiment (DOE) of the copper ion recovery from aqueous solutions using emulsion liquid membrane (ELM) method, Desalin. Water Treat. 204 (2020) 238–256.

[26] M. Rajasimman, N. Rajamohan, S. Sujatha, Recovery of zinc from electroplating waste water using green emulsion liquid membrane, Water Supply 21 (5) (2021) 2008–2018.

[27] N.F.M. Noah, N. Jusoh, N. Othman, R.N.R. Sulaiman, N.A.M.K. Parker, Development of stable green emulsion liquid membrane process via liquid–liquid extraction to treat real chromium from rinse electroplating wastewater, J. Ind. Eng. Chem. 66 (2018) 231–241.

[28] A.A. Mohammed, H.M. Selman, Liquid surfactant membrane for lead separation from aqueous solution: studies on emulsion stability and extraction efficiency, J. Environ. Chem. Eng. 6 (2018) 6923–6930.

[29] R.A. Kumbasar, Selective extraction of cobalt (II) from strong acidic solutions containing cobalt (II) and nickel through emulsion liquid membrane using TIOA as a carrier, J. Ind. Eng. Chem. 18 (2012) 2076–2082.

[30] B. Hamzah, S. Rahmawati, R. Hardani, Application of benzoyl-acetone as a cation carrier in mercury (II) extraction by using liquid membrane emulsion technique, Key Eng. Mater. 811 (2019) 80–85.

[31] N. Rajamohan, M. Rajasimman, F. Al Qasmi, Parametric studies on the removal of nickel using emulsion liquid membrane, Desalin. Water Treat. 141 (2019) 89–94.

[32] P. Zaheri, R. Davarkhah, Rapid removal of uranium from aqueous solution by emulsion liquid membrane containing the noyltrifluoroacetone, J. Environ. Chem. Eng. 5 (4) (2017) 4064–4068.

[33] Purtika, A. Thakur, G.K. Jawa, Comparative study on effect of ionic liquids on static stability of green emulsion liquid membrane, Colloids Surf. A Physicochem. Eng. Asp. 644 (2022), 128776.

[34] Purtika, A. Thakur, G.K. Jawa, Screening of parameters and optimization for green recovery of anionic dye by nanoparticle-ionic liquid-based green emulsion liquid membrane using response surface methodology, Chem. Eng. Process. Process Intensif 181 (2022), 109156.

[35] M. Balcaen, L. Vermeir, A. Declerck, P. Van der Meeren, Influence of internal water phase gelation on the shear-and osmoticsensitivity of W/O/W-type double emulsions, Food Hydrocoll. 58 (2016) 356–363.

[36] S. Beer, D. Dobler, T. Schmidts, M. Keusgen, F. Runkel, On the pressure balance and the resulting phase fraction incompressed multiple emulsions, Colloids Surf. A Physicochem. Eng. Asp. 513 (2017) 196–203.

[37] B.S.T. Barbosa, E.E. Garcia-Rojas, Double emulsions as delivery systems for iron: stability kinetics and improved bioaccessibility in infants and adults, Curr. Res. Food Sci. 5 (2022) 718–725.

[38] E.M. Marín Castaño, R. Paulo. de Souza Mendes, Thermodynamics and rheology of droplet aggregation of water-in-crude oil emulsion systems, Chem. Eng. Sci. 245 (2021), 116955.

[39] G. DeIuliis, G. Sahasrabudhe, R.H. Davis, K.P. Galvin, Water transport by osmosis through a high-internal-phase, water-in-oil, emulsion, Chem. Eng. Sci. 232 (2021), 116348.

[40] V. Eisinaite, P.D. Estrada, K. Schroën, C. Berton-Carabin, D. Leskauskaite, D. Tayloring, W/O/W emulsion composition for effective encapsulation: the role of PGPR in water transfer-induced swelling, Food Res. Int. 106 (2018) 722–728.

[41] L. Goibier, C. Pillement, J. Monteil, C. Faure, C.F. Leal-Calderon, Preparation of multiple water-in-oil-in-water emulsions without any added oil-soluble surfactant, Colloids Surf. A Physicochem. Eng. Asp. 590 (2020), 124492.

[42] S. Iqbal, M.K. Baloch, G. Hameed, D.J. McClements, Controlling W/O/W multiple emulsion microstructure by osmotic swelling and internal protein gelation, Food Res. Int. 54 (2013) 1613–1620.

[43] M. Chakraborty, C. Bhattacharya, S. Datta, Emulsion liquid membranes: definitions and classification, theories, module design, applications, new directions and perspectives, Liq. Membr. (2010) 141–199.

[44] A. Shokri, P. Daraei, S. Zereshki, Water decolorization using waste cooking oil: an optimized green emulsion liquid membrane by RSM, J. Water Process. Eng. 33 (2020), 101021.

[45] M.B. Rosly, N. Jusoh, O. Norasikin, A.B. Hilmi, F.M.N. Norul, R. Norimie Raja Sulaiman, Synergism of Aliquat336-D2EHPA as carrier on the selectivity of organic compound dyes extraction via emulsion liquid membrane process, Sep. Purif. Technol. 239 (2020), 116527.

[46] M.A. Hussein, A.A. Mohammed, M.A. Atiya, Application of emulsion and pickering emulsion liquid membrane technique for wastewater treatment: an overview, Environ. Sci. Pollut. Res. 26 (2019) 36184–36204.

[47] S. Zereshki, P. Daraei, A. Shokri, Application of edible paraffin oil for cationic dyeremoval from water using emulsion liquid membrane, J. Hazard. Mater. 356 (2018) 1–8.

[48] A.L. Ahmad, M.M.H. Shah Buddin, B.S. Ooi, A. Kusumastuti, Utilization of environmentally benign emulsion liquid membrane (ELM) for cadmium extraction from aqueous solution, J. Water Process. Eng. 15 (2017) 26–30.

[49] I. Salahshoori, A. Hatami, A. Seyfaee, Investigation of experimental results and D-optimal design of hafnium ion extraction from aqueous system using emulsion liquid membrane technique, J. Iran. Chem. Soc. 18 (2021) 87–107.

[50] N. Jusoh, M.B. Rosly, N. Othman, H.A. Rahman, N.F.M. Noah, R.N.R. Sulaiman, Selective extraction and recovery of polyphenols from palm oil mill sterilization condensate using emulsion liquid membrane process, Environ. Sci. Pollut. Res. 27 (2020) 23246–23257.

[51] S. Sujatha, N. Rajamohan, S. Anbazhagan, M. Vanithasri, M. Rajasimman, Extraction of nickel using a green emulsion liquid membrane–Process intensification, parameter optimization and artificial neural network modeling, Chem. Eng. Process. 165 (2021), 108444.

[52] A. Ahmad, N.D. Zaulkiflee, A. Kusumastuti, M.S. Buddin, Removal of acetaminophen from aqueous solution by emulsion liquid membrane: emulsion stability study, Ind. Eng. Chem. Res. 58 (2) (2018) 713–719.

[53] M. Khadivi, V. Javanbakht, Emulsion ionic liquid membrane using edible paraffin oil for lead removal from aqueous solutions, J. Mol. Liq. 319 (2021), 114137.

[54] G. Zhu, Y. Wang, Q. Huang, R. Zhang, D. Chen, S. Wang, X. Yang, Emulsion liquid membrane for simultaneous extraction and separation of copper from nickel in ammoniacal solutions, Miner. Eng. 188 (2022), 107849.

[55] A.A. Mohammed, M. Atiya, A.A. Hussein, Simultaneous studies of emulsion stability and extraction capacity for the removal of tetracycline from aqueous solution by liquid surfactant membrane, Chem. Eng. Res. Des. 159 (2020) 225–235.

[56] S. Zereshki, A. Shokri, A. Karimi, Application of a green emulsion liquid membrane for removing copper from contaminated aqueous solution: extraction, stability, and breakage study using response surface methodology, J. Mol. Liq. 325 (2021), 115251.

[57] S. Laguel, M.H. Samar, Removal of Europium (III) from water by emulsion liquid membrane using Cyanex 302 as a carrier, Desalination Water Treat. 165 (2019) 269–280.

[58] H.K. Admawi, A.A. Mohammed, A comprehensive review of emulsion liquid membrane for toxic contaminants removal: an overview on emulsion stability and extraction efficiency, J. Environ. Chem. Eng. 11 (2023), 109936.

[59] A.A. Al-Hemiri, H.E. Mahmoud, Minimization of toxic ions in waste water using emulsion liquid membrane technique, IJCPE 11 (1) (2010) 11–19.

[60] A. Kumar, A. Thakur, P.S. Panesar, Extraction of hexavalent chromium by environmentally benign green emulsion liquid membrane using tridodecyamine as an extractant, J. Ind. Eng. Chem. 70 (2019) 394–401.

[61] S. Bouranene, M.E.H. Samar, A. Abbaci, Extraction of cobalt and lead from waste water using a liquid surfactant membrane emulsion, Acta Chim. Slov. 50 (2003) 663–675.

[62] P.S. Kankekar, S.J. Wagh, V.V. Mahajani, Process intensification in extraction by liquid emulsion membrane (LEM) process: a case study; enrichment of ruthenium from lean aqueous solution, Chem. Eng. Process. 494 (2010) 441–448.

[63] M. Mesli, N.D. Belkhouche, Extraction and pre-concentration of lead from copper by emulsion liquid membrane technique using an ionic liquid, Euro Mediterr. J. Environ. Integr. 3 (2018) 1–10.

[64] A. Benderrag, B. Haddou, M. Daaou, H. Benkhedja, B. Bounaceur, M. Kameche, Experimental and modeling studies on Cd (II) ions extraction by emulsion liquid membrane using Triton X-100 as biodegradable surfactant, J. Environ. Chem. Eng. 7 (3) (2019), 103166.

[65] N. Othman, N.F.M. Noah, L.Y. Shu, Z.Y. Ooi, N. Jusoh, M. Idroas, Easy removing of phenol from wastewater using vegetable oil-based organic solvent in emulsion liquid membrane process, Chin. J. Chem. Eng. 25 (1) (2017) 45–52.

[66] N. Jusoh, N.F. Noah, N. Othman, Extraction and recovery optimization of succinic acid using green emulsion liquid membrane containing palm oil as the diluent, Environ. Prog. Sustain. Energy 38 (3) (2019) 1–9.

[67] N. Qudus, A. Kusumastuti, S. Anis, A.L. Ahmad, Emulsion liquid membrane for lead removal: intensified low shear extraction, Int. J. Innov. Learn. 25 (3) (2019) 285–295.

[68] F.B. De Souza, A.A.U. De Souza, J.V. Oliveira, S.M.A.G.U. De Souza, Green extraction based on emulsion liquid membranes: removal of Cr (III) from synthetic effluents, Environ. Nanotechnol. Monit. Manag. 16 (2021), 100579.

[69] J. Bahtz, D.Z. Gunes, A. Syrbe, N. Mosca, P. Fischer, E.J. Windhab, Quantification of spontaneous W/O emulsification and its impact on the swelling kinetics of multiple W/O/W emulsions, Langmuir 32 (23) (2016) 5787–5795.

[70] S. Gupta, M. Chakraborty, Z.V.P. Murthy, Removal of mercury by emulsion liquid membranes: studies on emulsion stability and scale up, J. Dispers. Sci. Technol. 34 (12) (2013) 1733–1741.

[71] M. Chakraborty, H.J. Bart, Emulsion liquid membranes: role of internal droplet size distribution on toluene/n-heptane separation, Colloids Surf. A Physicochem. Eng. Asp. 272 (2) (2006) 15–21, 1.

[72] H.M. Salman, A.A. Mohammed, Extraction of lead ions from aqueous solution by co-stabilization mechanisms of magnetic Fe_2O_3 particles and nonionic surfactants in emulsion liquid membrane, Colloids Surf. A Physicochem. Eng. Asp. 568 (2019) 301–310.

[73] S. Laki, A. Kargari, Extraction of silver ions from aqueous solutions by emulsion liquid membrane, J. Membr. Sci. Res. 2 (2016) 33–40.

[74] A.R. Raval, H.P. Kohli, O.K. Mahadwad, Application of emulsion liquid membrane for removal of malachite green dye from aqueous solution: extraction and stability studies, Chem. Eng. J. Adv. 12 (2022), 100398.

[75] L. León, G. León, J. Senent, C. Pérez-Sirvent, Optimization of copper removal from aqueous solutions using emulsion liquid membranes with benzoylacetone as a carrier, Metals 7 (1) (2017) 19 (Basel).

[76] P. Tahmasebizadeh, S. Javanshir, A. Ahmadi, Zinc extraction from a bioleaching solution by emulsion liquid membrane technique, Sep. Purif. Technol. 276 (2021), 119394.

[77] S.S. Suliman, N. Othman, N.F.M. Noah, K. Johari, Stability of primary emulsion assisted with nanoparticle in emulsion liquid membrane process for zinc extraction, Mater. Today Proc. 65 (2022) 3081–3092.

[78] M. Mesli, N.E. Belkhouche, Emulsion ionic liquid membrane for recovery process of lead. Comparative study of experimental and response surface design, Chem. Eng. Res. Des. 129 (2018) 160–169.

[79] H. Ma, O. Kökkılıç, C.M. Marion, R.S. Multani, K.E. Waters, The extraction of nickel by emulsion liquid membranes using Cyanex 301 as extractant, Can. J. Chem. Eng. 96 (7) (2018) 1585–1596.

[80] S.A. Parbat, B.A. Bhanvase, S.H. Sonawane, Investigation on liquid emulsion membrane (LEM) prepared with hydrodynamic cavitation process for cobalt (II) extraction from wastewater, Sep. Purif. Technol. 237 (2020), 116385.

[81] A. Hachemaoui, K. Belhamel, Simultaneous extraction and separation of cobalt and nickel from chloride solution through emulsion liquid membrane using Cyanex 301 as extractant, Int. J. Miner. Process. 161 (2017) 7–12.

[82] B. Hamzah, S. Rahmawati, R. Hardani, M. Nurdin, Mercury(II) extraction from solution with W/O type of liquid membrane emulsion using surfactant combination (span-80 + span-20) and 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone as carrier of cation, Int. J. Eng. Technol. 7 (4) (2018) 4278–4281.

[83] M. Alaguraj, K. Palanivelu, M. Velan, Removal of Cu (II) using emulsion liquid membrane, Int. J. Chem. Tech. Res. 1 (3) (2009) 722–726.

[84] R.A. Kumbasar, Selective separation of chromium (VI) from acidic solutions containing various metal ions through emulsion liquid membrane using trioctylamine as extractant, Sep. Purif. Technol. 64 (1) (2008) 56–62.

[85] G. Muschiolik, E. Dickinson, Double emulsions relevant to food systems: preparation, stability, and applications, Compr. Rev. Food Sci. Food Saf. 16 (3) (2017) 532–555.

[86] I. Salahshoori, A. Seyfaee, A. Babapoor, I. Cacciotti, Recovery of manganese ions from aqueous solutions with Cyanex 272 using Emulsion Liquid membrane technique: a design of experiment study, J. Sustain. Metall. 7 (2021) 1074–1090.

[87] A.L. Ahmad, M.M.H. Shah Buddin, B.S. Ooi, Adhi Kusumastuti, Cadmium removal from aqueous solution by emulsion liquid membrane (ELM): influence of emulsion formulation on cadmium removal and emulsion swelling, Desalin. Water Treat. 57 (58) (2016) 28274–28283.

[88] S.H. Chang, T.T. Teng, A. Ismail, Soybean oil-based bulk liquid membrane for simultaneous extraction and stripping of Cu (II) from aqueous solutions, Int. J. Environ. Sci. Dev. 2 (5) (2011) 389.