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1. Introduction

Lithium-ion batteries (LIBs) market has known constant growth in the last decade (Choubey et al., 2016). Their unique properties allowed them to become the technology of choice for the empowering of small electronic devices. LIBs are also expected to be used for electric cars and electric power storage, which consequently creates a large increase in the primary materials demand for the manufacture of these batteries (Zhou et al., 2014); (Jaffe, 2017). Several metals are at the basis of these batteries, mainly used for the composition of the cathode, but also for the current collectors as well as for the anode (Nitta et al., 2015). The cathode materials can be made of cobalt-lithium oxide, its high energy content per unit volume being ideal for portable electronic devices. The use of several metals such as aluminum, manganese or nickel for the cathode conception is frequently used to reduce the consumption of cobalt, the metal for which the supply risk is high (Habib et al., 2016). Moreover, lithium nickel cobalt aluminum oxide batteries have a satisfying energy density, allowing these batteries to be used in electric vehicles (Olivetti et al., 2017). Thus, the growing demand for LIBs and the expected increase in consumption due to the emergence of new technologies is a source of concern, knowing the supply risk associated with these metals and the mineral depletion that could be associated with a larger consumption (Bardi et al., 2016).

As an example, lithium consumption is expected to rise by more than 300% in the 15 coming years (Marscheider-Weidemann et al., n.d.). The forecast of manganese, cobalt and nickel consumption is not following the same trend (Simon et al., 2015). The supply risk of nickel and manganese is not elevated due to their abundance in the earth's crust. Cobalt is concerning up to a higher extent due to the numerous applications for which it is needed. Moreover, recent reports have outlined the conditions in which this metal is extracted and have drawn the attention upon severe attempts to the environment and to the health of both workers and people living in the mining zones (Banza Lubaba Nkulu et al., 2018).

In order to overcome these current or coming issues, several options can be considered. The substitution of the most critical metals is one possibility, and for example, sodium batteries have emerged as a potential candidate to replace LIBs (Slater et al., 2013). The use of secondary resources could be an option to recover metals. The recycling of spent LIBs offers the possibility to recover several metals from a vast and already available source, in which the metals' concentration is much higher than in the current ores. Recycling is also clearly beneficial from an environmental point of view, avoiding the release of harmful products (Chagnes and Pospiech, 2013). The economic benefits of recycling could also become relevant but depend on the types of cathode materials recycled. The cobalt-lithium oxide cathodes being the potentially most profitable ones to be recycled (Gratz et al., 2014).

The leaching of the batteries is mainly done using sulfuric acid (Sonoc et al., 2018a). Recovery of metals from leaching solutions was studied using various processes (Sonoc et al., 2018b); (Gratz et al., 2014). Solvent extraction is a useful technique to recover and separate metals due to its high selectivity, knowing that high purity is needed to produce new batteries with recycled metals. Several hydrometallurgical roads based on solvent extraction have been developed to recover metals from spent LIBs from sulfuric acid media (Yao et al., 2018); (Zhang et al., 1998); (Chen et al., 2015a); (Chen et al., 2011). However, in all of these studies, volatile organic compounds like kerosene were used as diluents that cause safety and environmental issues knowing their intrinsic properties (flammability, volatility…). Ionic liquids (ILs) have emerged as a potential alternative to these traditional solvents due to their physicochemical properties (Nakashima et al., 2003); (Domańska and Rękawek, 2009). The use of room-temperature hydrophobic ILs could be progress towards safer solvent extraction processes. The non-volatility of ILs allows to reduce the amount of volatile organic compounds

that need to be managed. However, hydrophobic ILs are still expensive. Moreover, the use of fluorinated atoms is unfavorable in terms of toxicity (Schaeffer et al., 2018). But the use of ILs could be justified by an increase of both the metal extraction efficiency and selectivity of the process as compared to processes based on molecular diluents.

Deep eutectic solvents (DES) are a new class of tailor-made solvents (Abbott et al., 2004). The mixture of two compounds heated up to the eutectic point of the mixture gives a liquid at ambient temperature that shares common properties with conventional ILs and gives the opportunity to tune the physicochemical properties of the liquid obtained by selecting among a large spectrum of molecules. But contrary to the ionic liquids, the synthesis of the deep eutectic solvents is cheap and easy, and there is no need for purification of the obtained product. DESs have already shown promising results recently for the extraction and preconcentration of metals (Ali et al., 2019); (Naeemullah et al., 2013) and other compounds from aqueous media (Tang et al., 2018); (Li and Row, 2019).

The solvent extraction of metals from spent LIBs remains challenging due to the similar chemical behavior of the transition metal ions. Acidic extractants are frequently used for the separation of these metals but both the extraction efficiency and the selectivity are highly dependent on the aqueous phase pH. Moreover, the selectivity is often not high enough and several synergistic systems have been developed to obtain a satisfying selectivity (Joo et al., 2016b); (Joo et al., 2015a).

In this study, we report a hydrometallurgical road to recycle metal value from the mixed cathode of spent LIBs using ILs and DEs. After the removal of impurities (aluminum, iron, etc.) by a chemical pre-treatment, this kind of leach liquor is mainly composed of cobalt, manganese, lithium and nickel (Meshram et al., 2015). We report herein the successive solvent extraction of manganese with N,N,N',N'-tetra(n-octyl) diglycolamide (TODGA) dissolved in imidazolium-based ionic liquids. TODGA extractant has a particular affinity for trivalent metals and particularly for the rare earth elements and actinides (Whittaker et al., 2018) when used in combination with a molecular diluent such as kerosene or toluene. Several studies reported unexpected higher distribution ratio values when using this extracting molecule in combination with ILs (Panja et al., 2012), (Pan and Hussey, 2013), (Turanov et al., 2016), (Zhang et al., 2014), (Shimojo et al., 2008), (Billard, 2013). Moreover, while the

extraction of alkaline earth metals is possible with this extractant in IL media (Turanov et al., 2010), the extraction of transition metal ions has not been detailed.

This preliminary study is focused on the extraction of metals from simulated leach liquors in order to define the parameters that affect the selectivity and the efficiency of solvent extraction. The main objective is to define a relevant hydrometallurgical scheme that can be applied to all kind of leach liquors from spent LIBs. The factors governing the selectivity and efficiency need to be defined in order to obtain the highest recovery rate and purity of the individual metals. Fig. 1 displays the hydrometallurgical scheme that we proposed.

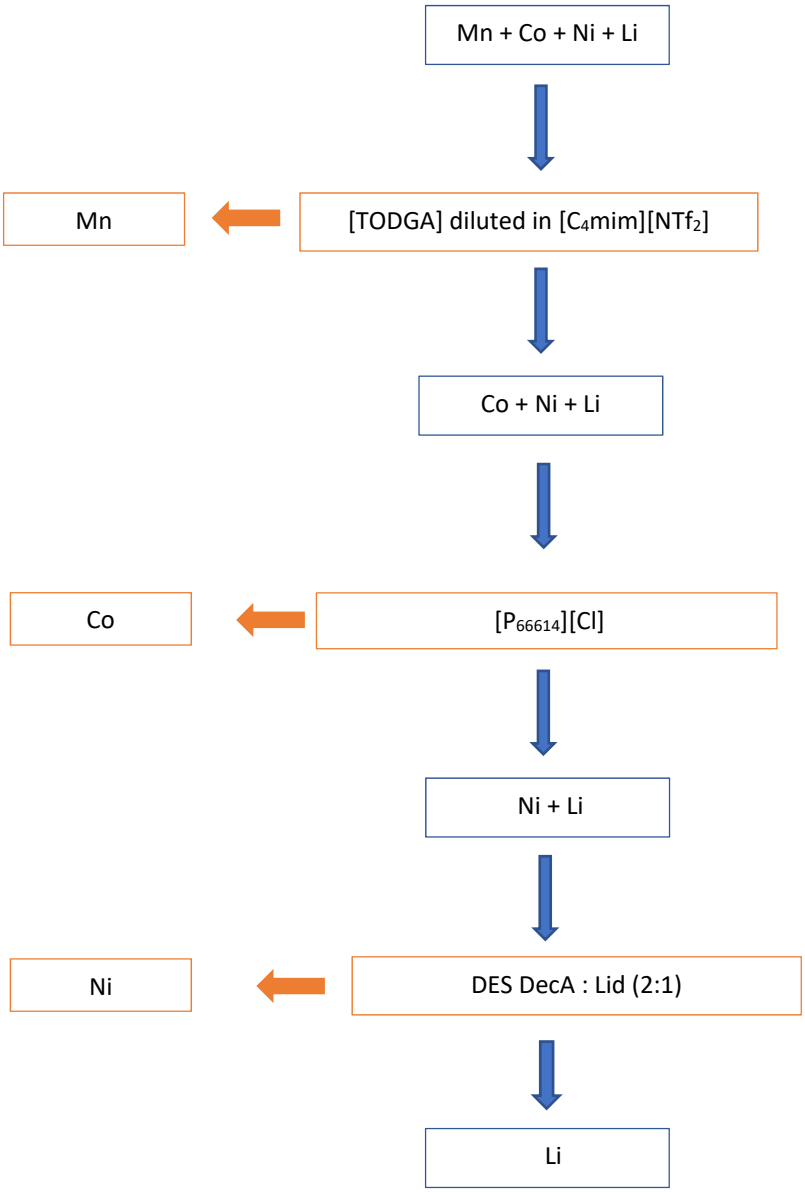

Fig. 1. Hydrometallurgical scheme for the successive recovery of manganese (Mn), cobalt (Co), nickel (Ni) and lithium (Li) from spent mixed cathode of LIBs.

The hydrometallurgical process envisaged allows first to remove manganese from the leach liquor using TODGA extractant diluted in an imidazolium-based IL. Secondly, cobalt can be removed using a phosphonium-based ionic liquid, as evidenced by Onghena *et al.* (Onghena et al., 2017). Nickel in the residual leach liquor is separated from lithium using a DES made of carboxylic acids and lidocaine, as proposed by Van Osch *et al.* (van Osch et al., 2016). Finally, lithium can be recovered using chemical precipitation, for example.

2. Materials and methods

2.1. Reagents

The hydrophobic IL 1-butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide (abbreviated as $[C_4mim][NTf_2]$, 99.5% purity) and tri-hexyl tetradecylphosphonium chloride (abbreviated as $[P_{66614}][Cl]$, >97% purity) were pursued from Solvionic (France), and used without further purification. The *N,N,N',N'*-tetra(*n*-octyl) diglycolamide (TODGA, >95% purity) was purchased from Betulinines (Czech Republic) and used as extractant without further purification. The chemical structures of the ionic liquids and the organic reagents used in this work are shown in the electronic supplementary information (Fig. S1). The sulfate salts of lithium ($Li_2SO_4·H2O$, Fluka, Germany), cobalt ($CoSO_4·7H2O$, Merk, Germany), manganese ($MnSO_4·H2O$, Merk) and nickel ($NiSO_4·6H2O$, Merck) are of the highest purity available and were used as received. For the synthesis of the DES, lauric and decanoic acids (Alfa Aesar, Germany, 99% purity), as well as lidocaine (Acros Organics, Germany, 99 % purity) were used as received. Kerosene (> 95%) was pursued from Fluka.

2.2. Synthesis of the DES

The hydrophobic DESs are synthesized according to the procedure described by Van Osch et al. (van Osch et al., 2016). In brief, decanoic acid and lidocaine (2:1 molar ratio), as well as lauric acid and lidocaine (2:1 molar ratio), are placed in a glass beaker. The mixture is heated

up to 80°C in a water bath for 30 minutes using a hot plate, allowing to obtain a homogeneous and hydrophobic liquid. The mixture is stirred regularly, then allowed to cool down at room temperature for at least one night before use.

2.3. Solvent extraction

The aqueous phases were prepared by dissolving gravimetrically the four metal salts into deionized water. De-ionized water is obtained after percolation through activated carbon and ion exchange resins (type ORC and type R3 resin from Thermo-Fischer Scientific) and used for the preparation of all of the aqueous solutions. The pH of the aqueous solutions was measured using a WTW pH-196 apparatus. The acidity of the aqueous solutions is adjusted by adding small aliquots of sulfuric acid (Thermo-Fischer scientific) or ammonia (Carlo Erba Reagenti, Italy). Different aqueous phases were used (composition displayed in Table 1), in order to simulate the composition of leach liquors from spent lithium-ion batteries. The first solution is a mixture of cobalt(II), manganese(II), nickel(II) and lithium(I) ions in sulfuric acid media which is closed to the proportions encountered in real leach liquors of mixed cathodes from spent lithium-ion batteries (Yang et al., 2017). The composition of the leach liquor is usually varying depending on the type of batteries leached, the chemical pre-treatment applied, *etc.* (Lv et al., 2018). The metal ion concentrations used in our case are lower than the one encountered in the real leach liquor, in order to simplify the experiment (Virolainen et al., 2017).

The second solution is made of cobalt, nickel, and lithium in sulfuric acid media. This solution also aims to simulate the leach solution of mixed cathodes after the removal of manganese. The last solution contains nickel and lithium and aims to simulate a residual leach liquor obtained after the removal of manganese and cobalt.

Table 1. Composition of the aqueous phases used for solvent extraction study.

Aqueous solutions	Mn ($g.L^{-1}$)	Co ($g.L^{-1}$)	Ni ($g.L^{-1}$)	Li ($g.L^{-1}$)
Synthetic leach liquor of mixed cathodes	1.2	1.2	1.2	0.6
Synthetic leach liquor (manganese removed)	–	1.0	1.0	0.6

Synthetic leach liquor (manganese and cobalt removed)	–	–	0.8	0.6

The solvent phase (ionic liquid and extracting molecule) of the desired composition was placed in contact with the aqueous phase (0.6 mL of each phase). The aqueous to organic phase volume ratio was 1 if it is not specified. Both phases were then shaken at 1400 rpm at room temperature (25±2°C) for 30 minutes using a Heidolph multi reax apparatus. Preliminary experiments have shown that a mixing time of 10 minutes or less is sufficient to reach equilibrium (see Table S1). Both phases are then centrifugated at 9500 rpm for 4 minutes using a Sigma 1-16 apparatus. The aqueous and organic phases are then carefully separated, and an aliquot of the aqueous phase is withdrawn to determine the metal content in the aqueous phase. After dilution in an appropriate matrix (H_2SO_4), the metal content in the aqueous phase is evaluated using a Varian 720 ES optical emission spectrometer (ICP-OES). The distribution ratio for metal defines the affinity of the metal for the organic or aqueous phase and was calculated using the following equation:

$$D_M = \frac{[M]_{org}}{[M]_{aq}} = \frac{[M]_{ini,aq} - [M]_{aq}}{[M]_{aq}} \mathrm{x} \frac{V_{aq}}{V_{org}} \quad (1)$$

where $[M]_{ini,aq}$ and $[M]_{aq}$ denote the aqueous metal concentration (mol/L or g/L) before and after extraction, respectively, and V_{aq} and V_{org} refer to the volumes of the aqueous and the solvent phase. V_{aq}/V_{org} is the volume ratio of extraction. In the present study, no significant volume changes due to mutual solubilities of the aqueous and solvent phases, and no phase inversion were observed during the extraction.

The extraction efficiency (E, %) was calculated as follows:

$$E\ (\%) = \frac{D_M \frac{V_{org}}{V_{aq}}}{1 + D_M \frac{V_{org}}{V_{aq}}} \mathrm{x}\ 100 \quad (2)$$

The selectivity for the target metal (M_1) over another metal (M_2) is defined by the separation factor (SF) and was calculated by the following equation:

$$SF = \frac{D_{M1}}{D_{M2}} \quad (3)$$

2.4. Water content

The water content of the ionic liquid was checked before extraction using a Mettler Toledo Karl Fischer titrator (DL 32 model). The water content in the $[C_4mim][NTf_2]$ ionic liquid is below 100 $mg.L^{-1}$. The ionic liquid $[P_{66614}][Cl]$ and the DESs are highly hygroscopic and able to solubilize a high water content (Wellens et al., 2012), (van Osch et al., 2016). Thus, in order to avoid volume variations, both the phosphonium IL and the DESs are saturated with water prior to use. The saturation is done by shaking vigorously an equal amount of water and the organic phase for one night.

2.5. Fourier transform (FT-IR) spectra

For FT-IR measurements, a Brucker spectrometer is used. The measurements were conducted over a wavenumber range of 500-3500 cm^{-1}.

2.6. UV-visible spectra

UV-visible spectra are recorded with a Shimadzu UV-PC 2401 apparatus. The aqueous samples were analyzed with quartz cells (optical pathway of 1 cm). The absorption band of the imidazolium cations is located at a wavelength of 211 nm (Ropel et al., 2005). The absorption of anionic cobalt chloride complexes can be evidenced between 700 and 800 nm (Onghena et al., 2017).

3. Results and discussion

3.1. Solvent extraction of manganese using TODGA in $[C_4mim][NTf_2]$

First, the solvent extraction of manganese cations (Mn(II)) from synthetic leach liquor of mixed cathodes (Table 1 and Fig. 1) has been studied using TODGA dissolved in the $[C_4mim][NTf_2]$ ionic liquid. The effect of the TODGA concentration in the organic phase on the metal extraction efficiency is shown in Fig. 2.

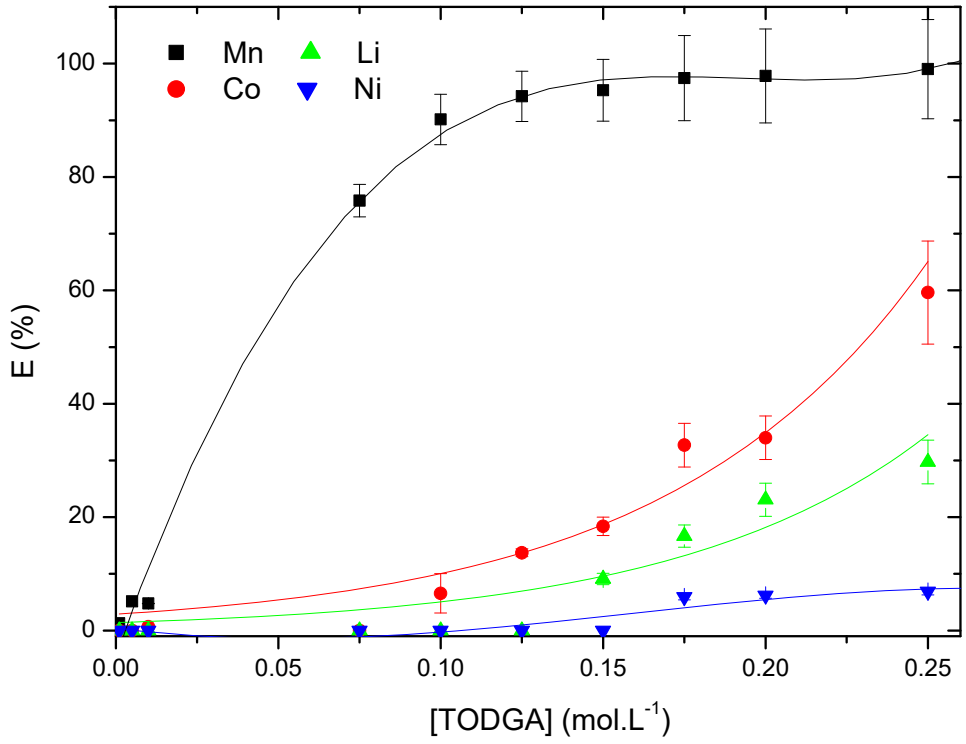

Figure 2. Extraction efficiency (%) for Mn(II), Co(II), Ni(II) and Li(I) as a function of TODGA concentration in [C_4mim][NTf_2]. Aqueous phase: synthetic leach liquor of mixed cathode at an initial pH = 3.3 (see Table 1). Lines are drawn for clarification purposes.

The extraction efficiency for all of the metals was negligible at low TODGA concentrations. While increasing TODGA concentration up to 0.1 mol.L^{-1}, the extraction efficiency for manganese(II) can reach values up to 90% while cobalt(II) is only slightly extracted (<10 %) and no nickel(II) nor lithium(I) is extracted (Fig. 2). With a further increase in TODGA concentration, Co(II) distribution ratio values are increasing while nickel and lithium cations are left in solution. Thus, the sequential extraction of Mn(II) and Co(II) could be considered just by increasing the concentration of TODGA in the organic phase. Taking into account the extraction efficiency and the selectivity for the manganese ions, an initial TODGA concentration of 0.1 mol.L^{-1} is selected for further investigation.

The effect of the initial aqueous phase pH (Fig. 3) on metal extraction efficiency is reported. It can be seen from Figure 3 that the extraction of the Mn(II) is lower when the acidity of the aqueous phase is high. But as long as the pH is higher than one, both the selectivity and the extraction efficiency remain approximately constant. Using acidic extracting molecules, extraction and selectivity for the target metal depend on the aqueous pH, thus requiring strict control of the aqueous phase acidity (Kang et al., 2010). The use of neutral TODGA in ionic liquid media allows to obtain a constant selectivity and extraction efficiency over a wide range

of pH. Moreover, the use of acidic aqueous solutions can be envisaged to strip the loaded metal from the organic phase.

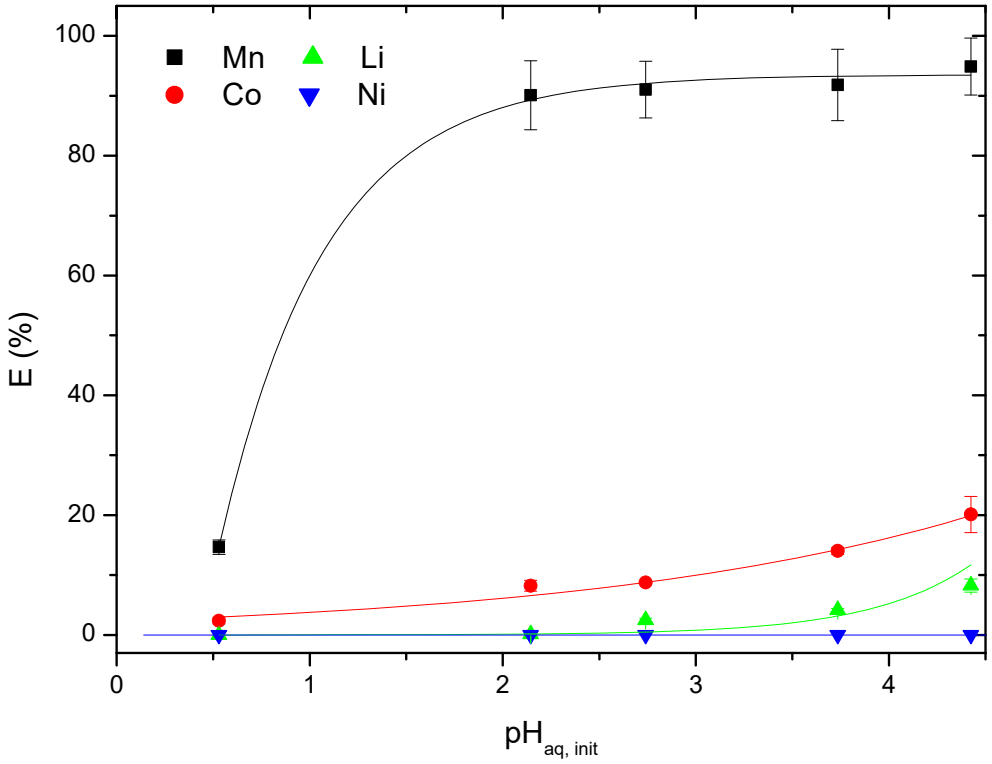

Figure 3. Extraction efficiency (%) for Mn(II), Co(II), Ni(II) and Li(I) as a function of the aqueous phase initial pH. Aqueous phase: synthetic leach liquor of mixed cathode (see Table 1). Organic phase: 0.1 $mol.L^{-1}$ of TODGA in $[C_4mim][NTf_2]$. Lines are drawn for clarification purposes.

Considering the higher extraction efficiency, the initial aqueous pH of 3.3 is retained to investigate the organic to aqueous phase volume ratio (O/A) effect on the extraction efficiency (Fig. 4).

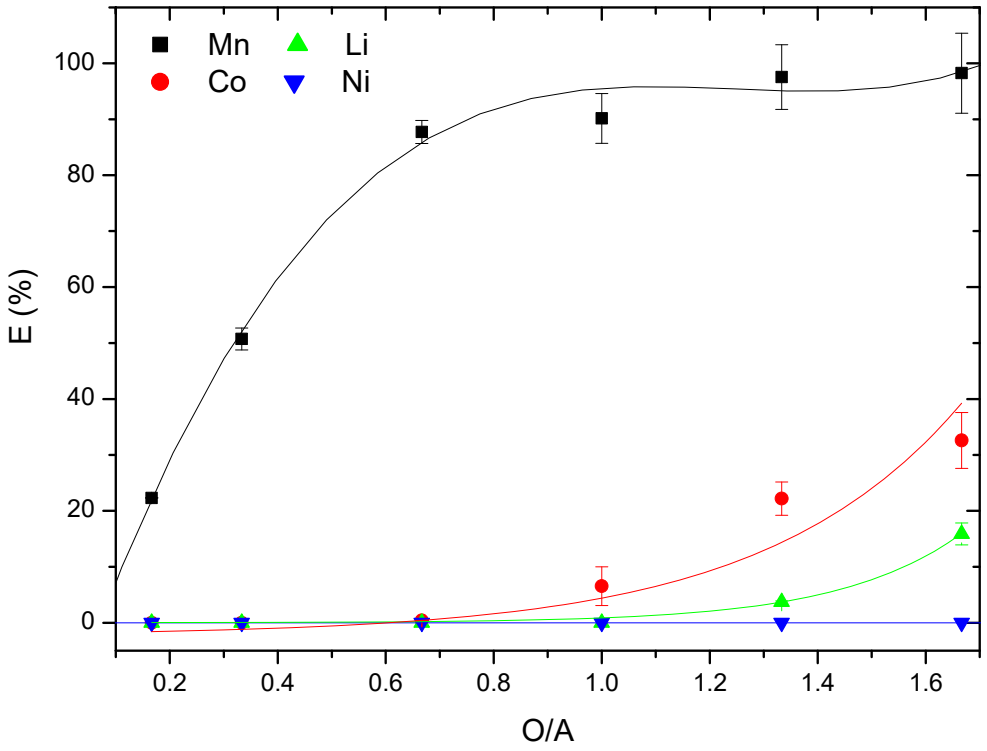

Figure 4. Extraction efficiency (%) for Mn(II), Co(II), Ni(II) and Li(I) as a function of the organic to aqueous phase volume ratio. Aqueous phase: synthetic leach liquor of mixed cathode at an initial pH = 3.3 (see Table 1). Organic phase: 0.1 mol.L^{-1} of TODGA in [C_4mim][NTf_2]. Lines are drawn for clarification purposes.

The extraction efficiency for all of the metals is low when the O/A ratio is low. However, the extraction is gradually increasing with an increase of the O/A ratio due to a higher amount of TODGA available in the organic phase. Considering both the selectivity (high separation factor for manganese) and the economic aspects (high cost of ionic liquid used as diluent), an O/A ratio of 1 (*i.e.* equal volumes of aqueous and organic phases) is suitable for the selective extraction of manganese.

The efficiency and selectivity of the proposed solvent extraction system were compared to the literature data (Table 2).

Table 2. Performances of the solvent extraction system composed of TODGA and IL as compared to the literature data. Names of the solvent extraction reagents can be found in Table S2.

Aqueous phase	Organic phase	Performances	Reference
H_2SO_4 1.2 g/L Mn 1.2 g/L Co 1.2 g/L Ni 0.6 g/L Li	0.1 mol.L^{-1} TODGA in $[C_4mim][NTf_2]$ O/A=1:1	≈99 % Mn extracted at pH=3.3 $SF_{Mn/Co}$ =40-60 $SF_{Mn/Ni}$ =270-370 $SF_{Mn/Li}$=500-700	This work
H_2SO_4 11.7 g/L Mn 11.4 g/L Co 12.2 g/L Ni 5.3 g/L Li	20% (v./v.) PC88-A + 5-20% (volume) Versatic 10 O/A=1:1	D_{Mn}≈65 at pH= 7.5 $SF_{Mn/Co}$ =5-25 $SF_{Mn/Ni}$ =150-300	(Joo et al., 2015b)
H_2SO_4 11.7 g/L Mn 11.4 g/L Co 12.2 g/L Ni 5.3 g/L Li	0.43 mol.L^{-1} DEHPA + 0,7 M Versatic 10 in kerosene O/A=1:1	90 % Mn extracted at pH= 7 $SF_{Mn/Co}$=5-35	(Joo et al., 2016a)
Na_2SO_4 0.004 mol/L Mn 0.004 mol/L Cu 0.004 mol/L Co	0.05 mol.L^{-1} PC88-A + 0,05 Cyanex 272 in n-heptane O/A=1:1	D_{Mn}≈28 at pH 7.5 $SF_{Mn/Cu}$≈5.5 $SF_{Mn/Co}$≈4	(Wang et al., 2012)
H_2SO_4 12.3 g/L Mn 28.5 g/L Co 14.6 g/L Ni 6.5 g/L Li	30% (volume) PC88-A in kerosene O/A=2:1	>90% Mn ; > 90% Co ; ~20 % Ni at pH= 5	(Yang et al., 2020)
H_2SO_4 18.6 g/L Mn 32.7 g/L Co 0.07 g/L Ni 2.3 g/L Li	0.04 mol.L^{-1} saponified Cyanex 272 in kerosene O/A=1:1	92% Mn ; 81% Co ; 6% Ni ; 10% Li at pH= 5	(Nayl et al., 2015)
H_2SO_4 Mn ; Co ; Ni ; Li (no concentration data)	30% (v./v.) P204 in kerosene O/A=1:1	90 % Mn ; 30 % Co at pH = 3.7	(Wang et al., 2019)

The efficiency of the proposed solvent extraction process is similar to the efficiency reported for the solvent extraction of manganese. Moreover, the selectivity for Mn(II) over Co(II) is higher than the selectivity obtained with most of the organophosphorous extracting

molecules. This system is also able to extract cobalt, by increasing the concentration of TODGA in the IL. However, both the extraction efficiency and selectivity for Co(II) is lower than the systems reported in the literature (Fig. S2 and Table S2; names of the solvent extraction reagents can be found in Table S3).

3.2. Synergistic effect in TODGA - [C_4mim][NTf_2] – kerosene on the extraction of manganese and cobalt

When dissolved in a molecular diluent, the TODGA molecules show no affinity for the transition metal ions (Zhu et al., 2004). The distribution ratio values for manganese extraction with TODGA diluted in kerosene and in an ionic liquid are compared in Table 3.

Table 3. Distribution ratios and extraction efficiency of manganese with 0.25 mol.L^{-1} of TODGA diluted in kerosene and in [C_4mim][NTf_2]

Solvent phase	D_{Mn}	E (Mn), %
[TODGA] in kerosene	~0	~0
[TODGA] in [C_4mim][NTf_2]	97.3±7.1	~99

The high extraction efficiency in the ionic liquid media is probably due to the different mechanisms of extraction, which is closely related to the ionic character of the diluent. The TODGA extracting agent is known for its excellent ability to extract trivalent metals ions when diluted in a molecular diluent (Whittaker et al., 2018); (Zhu et al., 2004); (Ansari et al., 2005). The separation of lanthanides from the transition metal ions has been intensively studied using this extractant (Gergoric et al., 2017). However, this molecule has shown an unusual behavior when diluted in an ionic liquid (Panja et al., 2012), thus allowing it to extract the transition metal ions.

It is considered that kerosene is an inert diluent on the contrary of the ionic liquid. Indeed, It is now accepted that it is more likely a reactant, playing an active role in the extraction of the metals (Dietz, 2006). The extraction of these two metals (M^{n+}) can be described by two mechanisms. The first is the cation exchange, according to the following equation:

$$(M^{n+})_{aq} + n(C_4mim^+)_{org} + x(TODGA)_{org} \leftrightarrow (M(TODGA)_x^{n+})_{org} + n(C_4mim^+)_{aq} \quad (4)$$

The subscripts “aq” and “org” referring to the aqueous and organic phases, respectively. The metal is extracted to the organic phase, the ionic liquid cation is exchanged to the aqueous phase in order to maintain the electro-neutrality. The UV-vis spectra (Fig. S3) of the aqueous phase after extraction of manganese shows a clear absorption band at λ=211 nm, which accredits the exchange of the IL cation with the extracted metal.

The solubility of the ionic liquid in water allows a slight amount of ionic liquid to be dissolved in the aqueous phase. The dissolution can be written as follows:

$$(C_4mim^+)_{org} + (NTf_2^-)_{org} \leftrightarrow (C_4mim^+)_{aq} + (NTf_2^-)_{aq} \quad (5)$$

Following its dissolution, the ionic liquid anion in the aqueous phase allows to form ion pairs with the metal that are extracted by TODGA, as written in the following equation:

$$(M^{n+})_{aq} + n(NTf_2^-)_{org} + x(TODGA)_{org} \leftrightarrow (M(NTf_2)_n(TODGA)_x)_{org} \quad (6)$$

In this case, the hydrophobic ionic liquid anion allows to form ion pairs with the metal that are extracted by TODGA. As observed in Fig. 3, the extraction efficiency values are decreasing with increasing acidity of the aqueous phase. This drop in the extraction efficiency could be explained by the progressive protonation of the NTf_2^- anions, thus making impossible to form ion pairs with the metal ions ((Turanov et al., 2008), extraction of the NTf_2^- anion to the organic phase by TODGA is given in Fig. S5). The extraction of bistriflimic acid ($HNTf_2$) to the organic phase is also contributing by decreasing the amount of free TODGA available in the organic phase. Once loaded, the metals in the organic phase can be stripped using aqueous acidic solutions, considering the drop in the extraction efficiency in acidic media.

The method of continuous variations (Renny et al., 2013) was applied to determine the stoichiometry of the complex extracted to the organic phase. To do so, a constant total concentration of TODGA and of ionic liquid was diluted in kerosene. This organic phase was used for the solvent extraction of individual solutions of Co(II) and Mn(II). The initial amount of metal in the solution being low, the amount of ionic liquid exchanged to the aqueous phase is low. Thus, the variation of $\frac{[TODGA]}{[TODGA]+[IL]}$ with the distribution ratio gives an idea of the number of both TODGA and ionic liquid molecules involved for the transfer of one metal ion, kerosene being an inert diluent. This variation is plotted in Fig. 5 for manganese and in Fig. S4 for Co(II).

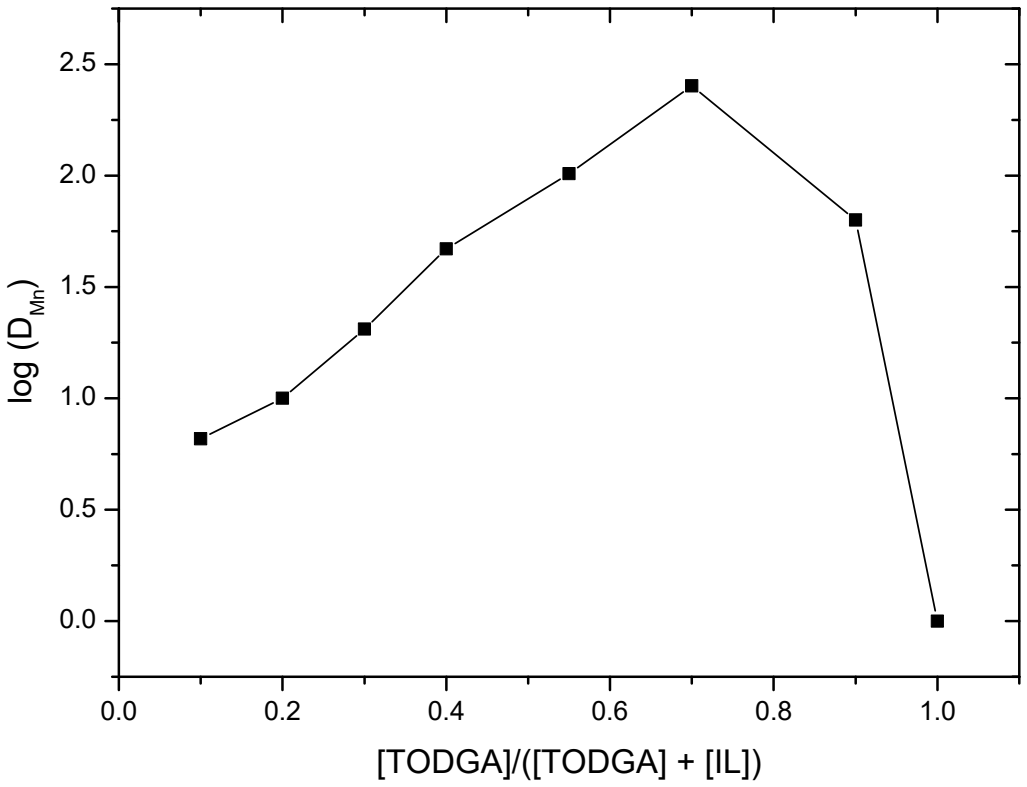

Figure 5. The plot of *logD*$_{Mn}$ as a function of the ratio $\frac{[TODGA]}{[TODGA]+[IL]}$. Aqueous phase: 1 mmol.L^{-1} of manganese(II) at an initial pH = 4. Organic phase: 0.1 mol.L^{-1} of TODGA + [C_4mim][NTf_2] diluted in kerosene. Lines are drawn for clarification purposes.

As can be seen in Fig. 5, $\log D_{Mn}$ reaches a maximum at $\frac{[TODGA]}{[TODGA]+[IL]}$≈0.7. Thus, it can be concluded that three TODGA molecules are involved for two ionic liquid cations and anion.

In the case of cobalt, the maximum value of the distribution ratio is also obtained for a TODGA mole fraction of around 0.7, indicating that an average of three molecules of TODGA and two of the ionic liquid are involved for the extraction of one cobalt ion. Cobalt appears to be extracted under the form of a $(Co(NTf_2)_2(TODGA)_3$ complex in the organic phase. Thus, the mechanism of extraction by cation exchange (Eq. (7)) and by (Eq. (8)) can be written as follows:

$$(M^{2+})_{aq} + 2(C_4mim^+)_{org} + 3(TODGA)_{org} \leftrightarrow (M(TODGA)_3^{2+})_{org} + 2(C_4mim^+)_{aq} \quad (7)$$

$$(M^{2+})_{aq} + 2(NTf_2^-)_{org} + 3(TODGA)_{org} \leftrightarrow (M(NTf_2)_2(TODGA)_3)_{org} \quad (8)$$

This kind of complex is similar to the ones evidenced by Turanov *et al.* for the extraction of alkaline-earth metals using TODGA and [C_4mim][NTf_2] diluted in 1,2-dichloroethane (Turanov et al., 2010). However, the exact form of the metal complex extracted (nature and number of

ligands, structural parameters) can only be confirmed using more precise spectroscopic techniques, such as EXAFS.

Moreover, it can be seen that a large synergistic effect was obtained when diluting TODGA and the IL in kerosene. The distribution ratio values obtained when both the IL and TODGA have diluted in kerosene are higher than those obtained when TODGA was diluted in the ionic liquid. Using a molecular diluent could be a solution to increase the performances of the process while reducing the cost of the organic phase used (less expensive IL is needed). This alternative is currently studied and will be discussed in a further study since it could be a solution to treat highly concentrated real leach liquors.

FT-IR spectra were recorded to further confirm the interaction between TODGA molecules and the metal cations. The characteristic bands of TODGA and the IL are listed in Table 4.

Table 4. Characteristic vibrational bands of the IL cation and anion, and TODGA.

Species	Vibration band	Wavenumber	Reference
C_4mim^+	C-H stretching vibration	3054 cm^{-1} and 3102 cm^{-1}	(Zheng et al., 2009)
NTf_2^-	C-F	1224 cm^{-1} and 1137 cm^{-1}	(Ao et al., 2013), (Nguyen et al., 2015)
TODGA	C=O stretching	1653 cm^{-1}	(Shaibu et al., 2007)

The FT-IR spectra recorded before and after extraction of Mn(II) (Fig. 6) show a clear displacement of the C=O characteristic vibration band of TODGA from 1649 to 1620 cm^{-1} after extraction, thus evidencing the interaction between TODGA and Mn(II). However, no clear change on the vibration bands of the ionic liquid cation and anion was evidenced from the FT-IR spectra (details of the spectra can be found in Fig. S6).

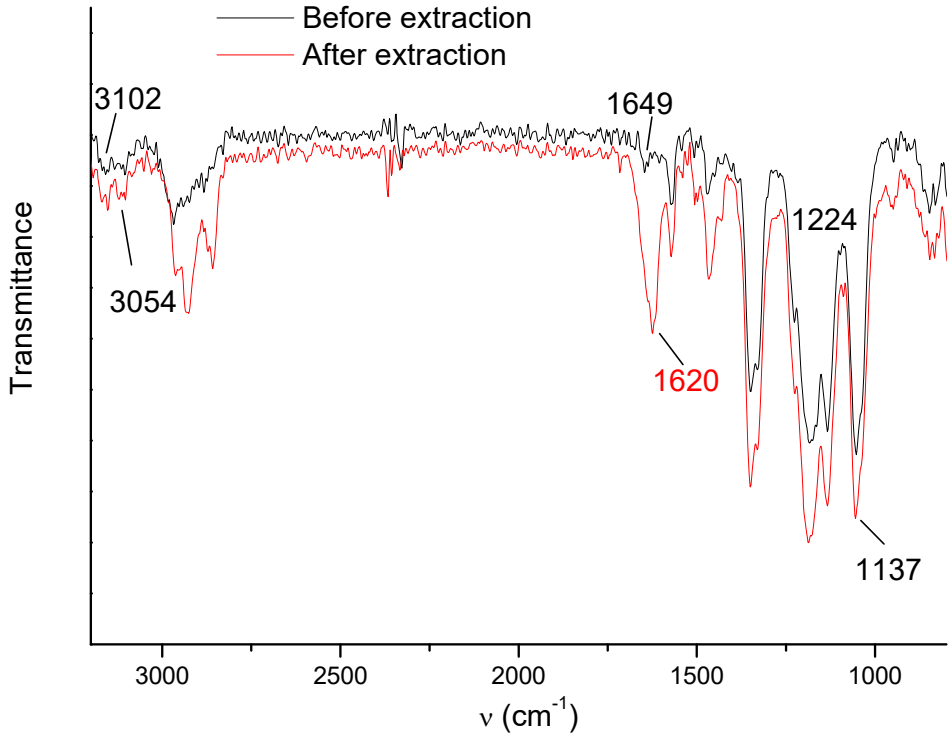

Figure 6. FT-IR spectra of the organic phase before and after extraction of Mn(II).

3.3. Solvent extraction of Co(II) using [P_{66614}][Cl]

After the removal of manganese from synthetic leach liquor, Co(II) needs to be separated from lithium and nickel (Figure 1). Cobalt can be removed using a phosphonium-based ionic liquid ((Onghena et al., 2017), (Wellens et al., 2012)).The distribution ratio values for cobalt(II) obtained in this work are reported in Table 5.

Tableau 5. Composition of the aqueous phase before and after extraction with the [P_{66614}][Cl] IL.

Organic phase	Initial aqueous phase	Aqueuous phase after extraction	D_{Co}	E_{Co} (%)
[P_{66614}][Cl]	Co= 1 $g.L^{-1}$ Ni=1 $g.L^{-1}$ Li= 0.6 $g.L^{-1}$ H_2SO_4= 9 $mol.L^{-1}$	Co≈ 70 $mg.L^{-1}$ Ni=1 $g.L^{-1}$ Li= 0.6 $g.L^{-1}$	13.3±0,3	92.8±1.5

It can be seen from Table 5 that the extraction of cobalt is efficient with no or minor extraction of nickel or lithium. This IL system provides an excellent selectivity for cobalt. The extraction occurs via split anion mechanism and/or anion exchange mechanism (Onghena et al., 2017).

In the anion exchange mechanism, the chloride anion of the IL is exchanged with HSO_4^- in the aqueous phase according to the following equation:

$$[P_{66614}][\mathrm{Cl}]_{org} + (HSO_4^-)_{aq} \leftrightarrow [P_{66614}][HSO_4^-]_{org} + (Cl^-)_{aq} \quad (9)$$

Then, cobalt(II) forms anionic complexes with the available chloride anions that can be extracted to the organic phase according to the following equation:

$$2[P_{66614}][HSO_4^-]_{org} + (CoCl_4^{2-})_{aq} \leftrightarrow [P_{66614}]_2[CoCl_4]_{org} + (HSO_4^-)_{aq} \quad (10)$$

In the split anion mechanism, cobalt and HSO_4^- are co-extracted to the organic phase, according to the following equation:

$$4[P_{66614}][\mathrm{Cl}]_{org} + 2(HSO_4^-)_{aq} + (Co^{2+})_{aq} \leftrightarrow [P_{66614}]_2[CoCl_4]_{org} + 2[P_{66614}][HSO_4^-]_{org} \quad (11)$$

In both cases, a tetrachlorocobalt complex is extracted to the organic phase, as evidenced by the UV-vis spectra of the organic phase after extraction, which is similar to the spectra of cobalt in an aqueous chloride media (Fig. 7). The clear blue color of the organic phase after extraction can also evidence the extraction of tetrachlorocobalt species (Fig. S7).

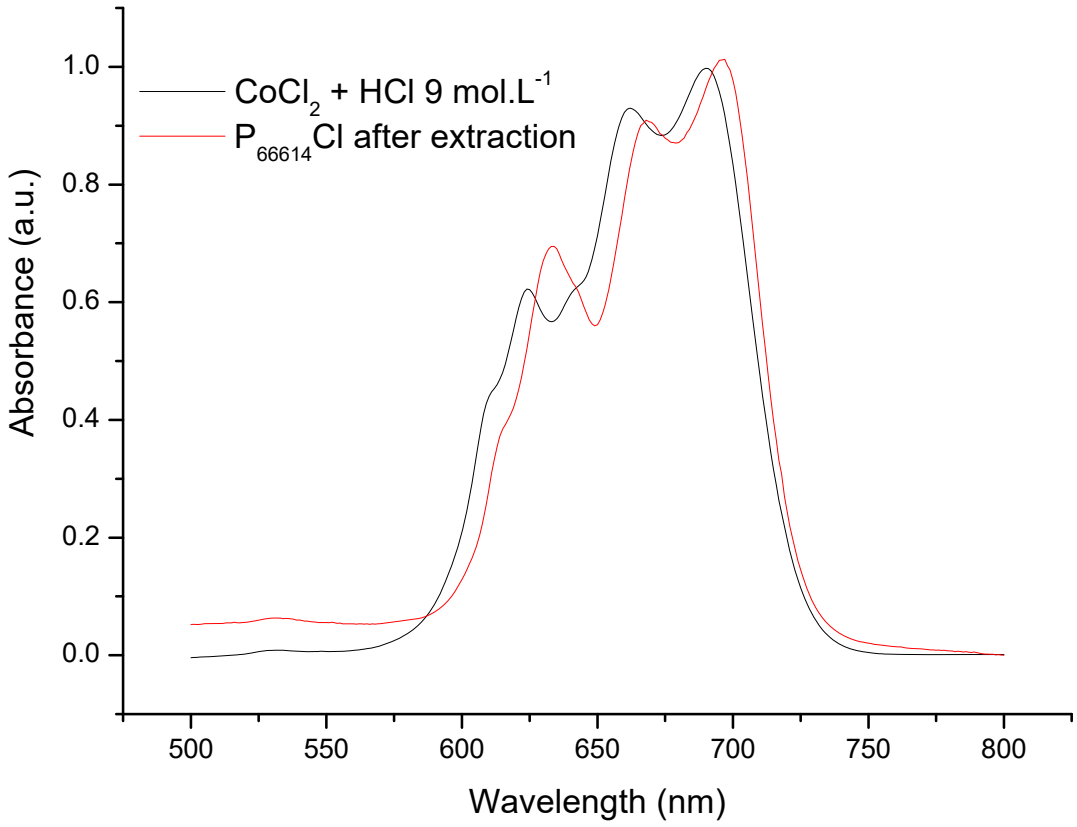

Figure 7. UV-vis spectra of the $[P_{66614}][Cl]$ IL phase after extraction as compared to the spectra of an aqueous phase containing cobalt and 9 mol.L^{-1} HCl

In both mechanisms, a high concentration of HSO_4^- is needed to allow the extraction of cobalt. One could take advantage on the high concentration of sulfuric acid in the leach liquors before application of the pre-treatments. However, as long as the metal is able to form anionic complexes with chloride, it will be extracted to the IL phase, as evidenced for manganese in Table 6. Metals commonly found in the leach liquor of spent lithium-ion batteries such as copper and iron ((Lv et al., 2018)) will be co-extracted (Fig S7), and will surely lower the extraction efficiency of cobalt. Metals that can't form these complexes (Aluminum, nickel, lithium) will remain in the aqueous phase (Wellens et al., 2012). The removal of aluminum, copper and iron is easy and precipitation of their hydroxides ((Lv et al., 2018)) prior to solvent extraction is advantageous in our case.

Table 6. Extraction efficiency of manganese with the IL $[P_{66614}][Cl]$

Organic phase	Initial aqueous phase	D_{Mn}	E_{Mn} (%)
$[P_{66614}][Cl]$	$MnSO_4$ 0.5 g.L^{-1} H_2SO_4= 9 mol.L^{-1}	19.7±0.8	95±2

3.4. Solvent extraction of nickel from the residual synthetic leach liquor using the DES DecA:Lid (2:1)

The remaining solution contains nickel and lithium left in solution after the recovery of cobalt and manganese (Fig. 1). Due to the particular affinity of decanoic acid for the transition metal ions (Ola and Matsumoto, 2019), the extraction of transition metal ions using a DES made of lidocaine and decanoic acid appeared as a very efficient extraction solvent, but this DES has shown a poor ability to extract alkali metals (less than 30 % of lithium chloride extracted from chloride media, (van Osch et al., 2016)). This kind of DES could be suitable for the extraction of nickel and its separation from lithium, which is needed for the treatment of several types of leach liquors [37-38]. Two DESs have been compared based on lidocaine as a HBA and two carboxylic acids as HBDs. The effect of the aqueous phase pH on the extraction efficiency of both metals is reported in Fig. 8.

The strongly hydrophilic lithium cation is slightly extracted whatever the fatty acid. The selectivity is better with decanoic acid and the DES Decanoic acid: Lidocaine (2:1) is retained for further investigations.

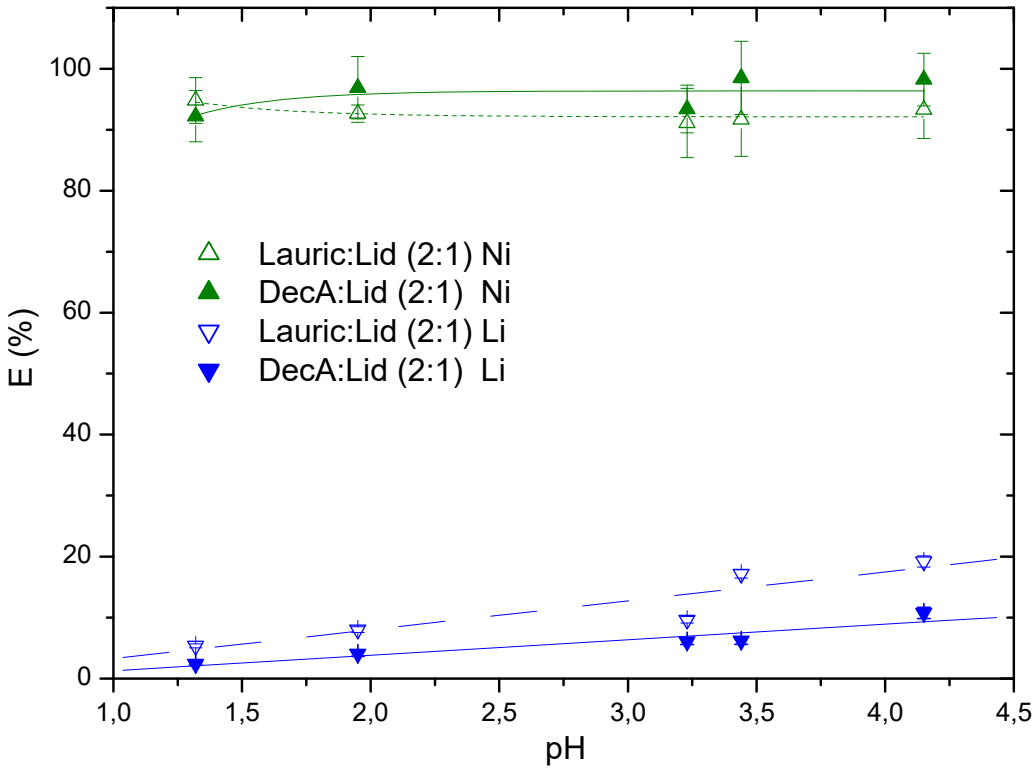

Figure 8. Extraction efficiency (%) for Ni(II) and Li(I) as a function of the aqueous phase initial pH. Aqueous phase: synthetic leach liquor of mixed cathode after the removal of manganese and cobalt (see Table 1). Organic phase: DES DecA:Lid (2:1). Lines are drawn for clarification purpose.

The extraction efficiency value of a nickel is increasing slightly with an increase in the pH. This effect can be related to the mechanism of extraction of the metal into the DES phase. A cation exchange mechanism has been reported, involving two steps (van Osch et al., 2016). The first step is an exchange of protons between the HBD and the HBA, leading to deprotonated lauric acid and protonated lidocaine (Eq. 7).

$$Lauric - H + Lid \leftrightarrow Lauric^{-} + Lid - H^{+} \quad (3)$$

The positively charged form of lidocaine being highly soluble in water, it can be exchanged with the metal ion, according to the following equation:

$$n(Lid - H^{+})_{org} + n(Lauric^{-})_{org} + (M^{n+})_{aq} \leftrightarrow (M(Lauric)_{n})_{org} + (Lid - H^{+})_{aq} \quad (4)$$

The cation exchange is more likely to occur when lauric acid is deprotonated, which could explain the higher extraction efficiency at higher pH. Moreover, the pKa of fatty acid is known

to increase with an increase of the alkyl chain length (Sado Kamdem et al., 2008), leading to higher extraction rates with the decanoic acid-based DES, as compared to the lauric acid-based DES. But the extraction efficiency is sufficient and an initial aqueous pH of 4 is retained to study the effect of the aqueous to organic volume ratio (Fig. 9).

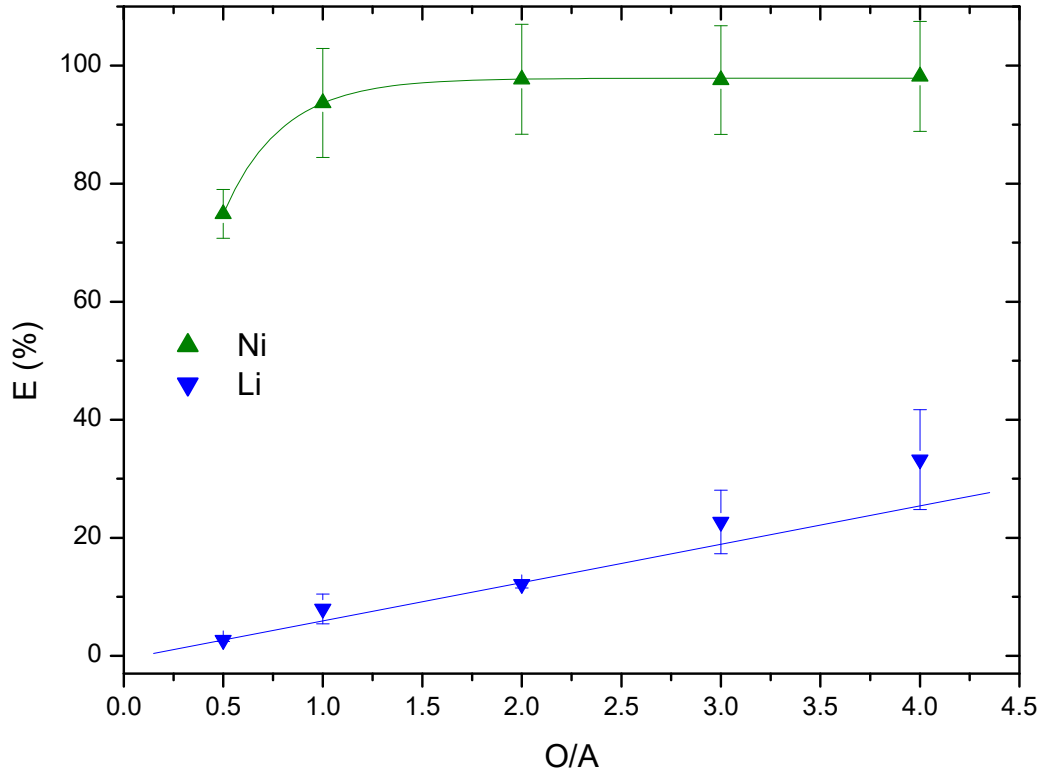

Figure 9. Extraction efficiency (%) for Ni(II) and Li(I) as a function of the organic to aqueous phase volume ratio. Aqueous phase: synthetic leach liquor of mixed cathode after the removal of manganese and cobalt at an initial pH of 4.1 (see Table 1). Organic phase: DES DecA:Lid (2:1). Lines are drawn for clarification purposes.

The extraction efficiency increases with an increase of the organic to aqueous phase ratio. A non-negligible extraction of lithium is observed when the O/A ratio is higher than 1. However, an organic to an aqueous ratio of one is suitable (knowing the efficiency at this ratio), and economically favorable.

Conclusions

In this work, several solvent extraction processes were applied for the successive recovery of metals from simulated leach liquor of spent lithium-ion batteries. A new solvent extraction process was proposed for the extraction of manganese and cobalt using TODGA extracting agent diluted in a room-temperature ionic liquid. The hydrometallurgical process presented here (Fig. 1), allows first to remove manganese very selectively from the leach liquor using

TODGA extractant diluted in an ionic liquid. Secondly, cobalt can be removed using a phosphonium IL with very high selectivity over nickel and lithium.

Then, the remaining mixture of nickel and lithium can be further separated by extracting nickel using a DES, lithium being left in solution. Lithium can then be recovered using chemical precipitation for example.

The distribution ratio being low in acidic media, cobalt and manganese could be stripped from the loaded ionic liquid phase using aqueous acidic solutions, while the loaded DES phase can be stripped using sodium oxalate (van Osch et al., 2016). But both the ionic liquids and the deep eutectic solvents can be used in a large electrochemical window. The recovery of metals from the loaded organic phase can also be investigated using electrochemistry, in order to save water resources as well as to avoid managing highly acidic solutions.

The opportunity of using these reagents has been outlined in this work. However, some aspects have to be considered: the design of a process based on ILS and DESs has to be entirely detailed and all of the aspects considered. It is now recognized that replacing molecular diluents by ionic liquids does not lead inevitably to greener processes. In order to improve the efficiency of the current processes by using the unique properties of the ILs and DESs, these reagents should be used in more compact systems, for which the amount of reagents needed is lower.

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