SYNERGISTIC SOLVENT EXTRACTION OF Co(II) AND Li(I) FROM AQUEOUS CHLORIDE SOLUTIONS WITH MIXTURE OF CYANEX 272 AND TBP

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Abstract: In this work, separation of cobalt(II) over lithium(I) ions from aqueous chloride solutions by synergistic solvent extraction (SX) has been studied. A synergistic mixture of commercial extractants such as bis(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and tributyl phosphate (TBP) in kerosene was used as a selective extractant. The investigations were first performed to select optimal conditions for the effective separation including pH of the aqueous phase as well as concentration of synergistic mixture. High selective solvent extraction of cobalt(II) over lithium(I) from chloride solution has been achieved by the mixture of 0.1 M Cyanex 272 and 0.05 M TBP in kerosene while efficient Co(II) stripping has been performed by 0.5 M sulphuric acid.

Keywords: cobalt(II), lithium(I), Cyanex 272, TBP, synergistic extraction

Introduction

Cobalt is a strategic metal, which has many industrial uses. This metal is less available and thus more costly than other transition metals, such as manganese, iron and nickel (Chagnes and Pospiech, 2013). On the other hand, lithium application in batteries has expanded significantly in recent years, because rechargeable lithium-ion batteries (LIBs) have increasingly been used in portable electronic devices, such as: mobile telephones, laptops, video-cameras, etc. They are also used to provide constant electric current for electric automobiles (Pospiech, 2014a). Many investigations have been carried out to recover valuable metals from the waste LIBs by hydrometallurgical technologies, which include the following stages: crushing, physical separation and leaching. The processing of wastes containing metals for their recovery and separation is very important due to the essential two aspects – economic and environmental (Chmielewski et al., 1997; Pospiech 2013; Pospiech 2014a). The solutions after

leaching of LIBs are subjected to separation processes, i.e. precipitation of impurities, solvent extraction, adsorption and ion-exchange to isolate and concentrate the valuable metals. The separation stage is necessary since it enables the next step of the obtaining pure metal or compounds of this metal (Kolodynska et al. 2008; Pospiech 2010; Pospiech 2015).

Solvent extraction processes are very often used for separation of ferrous metals ions from wastewater (Wionczyk 2013; Ochromowicz and Chmielewski 2013) and leach liquors (Chagnes and Pospiech, 2013). This technique requires appropriate extractants whose aim is to provide high selectivity and efficiency of this process. The organophosphorous acids, such as: Cyanex 272, Cyanex 301 and Cynex 302 (Preston, 1982; Gega et al., 2001; Kozlowski et al., 2006) and amines (Marchese et al., 1995) were studied for the extraction of Co(II) from aqueous chloride and sulphate solutions. The specific extraction of cobalt(II) ions with Cyanex 272 have been reported in numerous publications (Rickelton and Boyle, 1988; Gandhi et al. 1993, Swain et al. 2007). However, instead of a single extractant, we can used a mixture of extractants, which may give rise to synergistic effects and better efficiency and selectivity of metal ions extraction from aqueous solutions (Pospiech 2014). In addition, we may observe that the extractive capability of a mixture of extractants is greater than the sum of their individual extractive capabilities (Zhu et al. 2012; Pospiech 2014b, Pospiech and Chagnes, 2015). Synergistic effects have been studied in the extraction of Co(II) and Ni(II) using the sodium salts of D2EHPA, PC88A and Cyanex 272 and their mixtures (Devi et al., 1994; Sarangi et al., 1999) as well as a mixture of D2EHPA and 5-dodecylsalicylaldoxyme (Zhang et al., 2001). The main advantage of mixed extractant systems over developing new reagents is that the reagents are already commercially available (Pospiech and Chagnes, 2015).

The most important aim of this paper was the separation of Co(II) and Li(I) from aqueous chloride solutions using a synergistic mixture of Cyanex 272 and TBP. Up to now, the proposed synergistic mixture was not applied as a selective extractant in solvent extraction of Co(II). The effects of pH, extractant concentrations in the organic phase as well as the concentration of sulphuric acid in the stripping phase on the extraction percent and selectivity with the mixture of Cyanex 272 and TBP have been studied.

Experimental

Inorganic chemicals. Cobalt chloride $CoCl_2 \cdot 6H_2O$, lithium chloride LiCl, sulphuric acid (H_2SO_4), were of analytical grade and were purchased from POCh (Gliwice, Poland). Aqueous solutions were prepared with deionized water (conductivity of 0.1 µS/cm at 25 °C). The aqueous phase containing 0.01 M Co(II) and 0.01 M Li(I) was used for the investigation.

Organic reagents. *Bis*(2,4,4-trimethylpentyl)phosphinic acid (Cyanex 272) and tributyl phosphate (TBP) were of analytical reagent grade (Fluka) and used without further purification.

Solvent extraction. It was carried out as reported in an earlier paper (Pospiech and Chagnes, 2015). Equal volumes of organic and aqueous phases (phase volume ratio O/A=1) were mechanically shaken for 20 minutes at 25±2 °C. Then the aqueous phase was separated from the organic phase. Equilibrium pH of aqueous phases were measured with an Elmetron CX-731 pH-meter equipped with a glass electrode (Hydromet, Poland). Metal ions concentrations in aqueous phases were analyzed with AAS Solaar 939 (Unicam) spectrophotometer (AAS – Atomic Absorption Spectrometry). The concentration of metal ions in aqueous phases was determined before and after solvent extraction for calculating extraction efficiency and after stripping for calculating stripping efficiency. The concentrations of metals in organic phases were deduced by mass balance. Each experiment was carried out in triplicate and the error did not exceed 5%. Distribution ratio (*D*) and extraction percent (% E) were defined as follows:

$$D = \frac{[M]_{org}}{[M]_{aq}} \tag{1}$$

$$\% E = \frac{D}{D+1} \cdot 100\% \tag{2}$$

where $[M]_{org}$ and $[M]_{aq}$ denote metal concentrations in the organic and aqueous phases after solvent extraction, respectively.

Selectivity coefficient ($S_{M1/M2}$) for M_1 over M_2 was calculated as follows:

$$S_{M1/M2} = \frac{D_{M1}}{D_{M2}} \tag{3}$$

ΔD and *SC* were defined as follows to evaluate synergistic effect:

$$\Delta D = D_{mix} - (D_{Cyanex272} + D_{TBP}) \tag{4}$$

$$SC = \frac{D_{mix}}{D_{Cyanex272} + D_{TBP}} \tag{5}$$

where D_{mix} is the distribution ratio by the mixture of Cyanex 272 and TBP, $D_{Cyanex272}$ and D_{TBP} are distribution ratios by Cyanex 272 alone and TBP alone, respectively.

Results and discussion

Effect of equilibrium pH on Co(II) and Li(I) solvent extraction

Although the solvent extraction studies of cobalt(II) by Cyanex 272 have been reported, but report regarding extraction of this metal ions using mixture of Cyanex 272 and TBP by solvent extraction technique has not been showed yet. Cyanex 272, a cationic exchanger, extracts Co(II) from aqueous solution according to the following reaction (Swain et al., 2007):

$$Co_{aq}^{2+} + H_2A_{2,org} \Leftrightarrow CoA_{2,org} + 2H_{aq}^+ \tag{6}$$
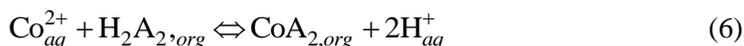
where "aq" and "org" denote aqueous and organic phases, respectively.

On the other hand, TBP is a kind of neutral, solvating extractant which has been used in the separation of many metal ions. This extractant can be also a modifier in the extraction process (Li et al., 2007). The ability of TBP to chemically react with bis(2,4,4-trimethypentyl)phosphinic acid (the active reagent in Cyanex 272) to generate butyl ester species (butyl phosphinate; butyl *bis*(2,4,4-trimethylpentyl) phosphinate) was reported by Barnard et al., 2014). In this work, the presence of neutral donor TBP as synergistic agent was studied and discussed. Solvating agents such as TBP also extract Co(II) from chloride acidic media according to the following reaction:

$$Co_{aq}^{2+} + 2Cl_{aq}^- + 2S_{org} \rightarrow (CoCl_2 \cdot 2S)_{org} \tag{7}$$
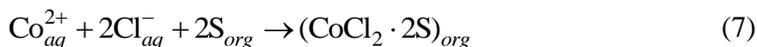
where S is TBP.

The effect of equilibrium pH on the competitive solvent extraction of Co(II) and Li(I) from aqueous chloride solutions at pH ranging from 3.5 to 5.8 by 0.1 M Cyanex 272 in kerosene, 0.05 M TBP in kerosene and the mixture of 0.1 M Cyanex 272 and 0.05 M TBP in kerosene is shown in Fig. 1. The increase of the equilibrium pH from 3.5 to 5.8 is responsible for an increase of Co(II) extraction by these extractants. This figure also shows that the use of mixture containing Cyanex 272 and TBP, instead of TBP alone or Cyanex 272 alone, improves the extraction efficiency of Co(II) and at a minor extent of Li(I) from aqueous chloride solution. Conversely, then no significant variation of solvent extraction efficiency of Li(I) vs. pH is observed. Taken account the literature date concerning the participation of a neutral donor molecule (S) in the extracted species of synergistic extraction process (Rafighi et al., 2010), the following corresponding mechanism of Co(II) extraction can be written as:

$$Co_{aq}^{2+} + HA_{org} + S_{org} + Cl^- \Leftrightarrow CoAClS_{org} + H_{aq}^+ \tag{8}$$

Further studies are necessary to confirm the suggested reaction for the studied mixture consisting of cationic extractant (Cyanex 272) and solvating extractant (TBP).
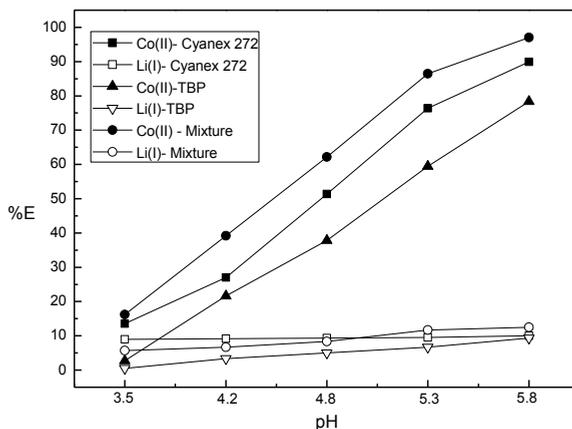
Fig. 1. Extraction percent of Co(II) and Li(I) as a function of equilibrium pH by 0.1 M Cyanex 272
in kerosene, 0.05 M TBP in kerosene and mixture of 0.1 M Cyanex 272 and 0.05 M TBP
in kerosene. Aqueous phase: 0.01 M Co(II) and 0.01 M Li(I)

Table 1 shows that distribution ratios of Co(II) are significantly higher in the range
of pH values between 3.5 and 5.8, while distribution ratio of Li(I) remains low when
Cyanex 272-TBP mixture is used instead of Cyanex 272 or TBP alone. A synergistic
phenomenon occurs during the recovery of Co(II) from chloride solutions with
mixtures of Cyanex 272 and TBP whereas an antagonist effect is observed in the case
of Li(I) solvent extraction throughout the studied pH range (Table 1). The obtained
synergism can be expressed in terms of synergistic coefficient (SC) (Eq. 5). The
formation of adduct species may be responsible for an increase of the extraction
properties of Co(II) when Cyanex 272 and TBP mixture is used. In addition to the
very high distribution ratios of Co(II), the use of mixtures of Cyanex 272 and TBP
appears very interesting because the selectivity coefficients are much more higher with
these mixtures compared to those obtained with Cyanex 272 or TBP alone in kerosene
(Fig. 2). In this present work, the use of mixtures of Cyanex 272 and TBP appears as
very effective method for Co(II) and Li(I) separation. Indeed, the results evidence
the presence of synergistic effect in the competitive solvent extraction of Co(II) from
chloride solutions containing Li(I) ions. The obtained selectivity coefficients of Co(II)
over Li(I) ($S_{Co/Li}$) with this system are significantly higher in comparison with those
obtained with Cyanex 272 or TBP alone. The similar synergistic effect was observed
by Batchu et al. (2014) during solvent extraction of Mn(II) from H_2SO_4 solutions with
Cyanex 301, TBP and their binary mixture. They reported that the observed synergism
may be due to the increased lipophilic nature of extracted complex by the addition of
TBP. Therefore, the addition of TBP has shown synergistic effect. In the earlier work
(Pospiech and Chagnes, 2015) the synergistic effect was described during solvent
extraction of Zn(II) and Cu(II) from chloride solutions with the mixture of Cyanex
272 and Aliquat 336. There it can be observed that the obtained selectivity coefficients

of Zn(II) over Cu(II) ($S_{Zn/Cu}$) from hydrochloric acid and acidic sodium chloride solutions by mixtures of Cyanex 272 and Aliquat 336 are about twice greater than those obtained with Aliquat 336 alone.

Table 1. Variation of the distribution ratio of Co(II) and Li(I) as a function of pH. Organic phase: 0.1 M Cyanex 272, 0.05 M TBP and a mixture of 0.1 M Cyanex 272 and 0.05 M TBP in kerosene; aqueous phase: initially 0.01 M Co(II) and 0.01 M Li(I). $D_{Cyanex272}$ – distribution ratio by Cyanex 272 alone; D_{TBP} – distribution ratio by TBP alone; $D_{mixture}$ – distribution ratio by the mixture of Cyanex 272 and TBP; SC – synergistic coefficient

pH		$D_{Cyanex\ 272}$	D_{TBP}	$D_{mixture}$	ΔD	SC
3.5		0.156	0.028	0.194	0.010	1.054
4.2		0.360	0.253	0.644	0.031	1.051
4.8	Co(II)	1.015	0.571	1.642	0.056	1.035
5.3		3.238	1.466	6.400	1.700	1.361
5.8		8.919	3.625	32.64	20.10	2.602
3.5		0.099	0.005	0.060	-0.044	0.577
4.2		0.101	0.034	0.071	-0.064	0.526
4.8	Li(I)	0.103	0.053	0.091	-0.065	0.583
5.3		0.105	0.071	0.132	-0.044	0.750
5.8		0.111	0.103	0.143	-0.071	0.668
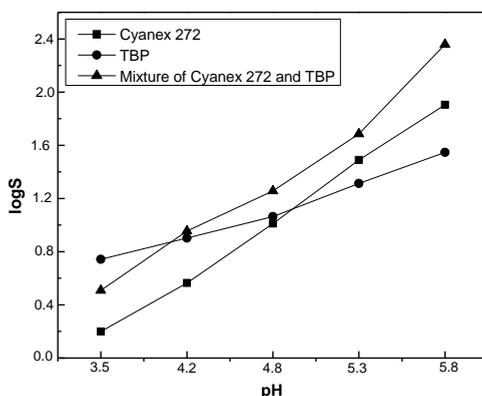
Fig. 2. Logarithm of selectivity coefficient of Co(II) over Li(I) vs. pH under the same experimental conditions as in Fig. 1

Influence of Cyanex 272 and TBP concentrations on Co(II) and Li(I) solvent extraction

Solvent extractions of 0.01 M Co(II) and 0.01 M Li(I) from chloride aqueous solution by Cyanex 272 mixed with TBP in kerosene has been studied as a function of TBP concentration at constant concentration of Cyanex 272. As shown in Fig. 3, the

addition of 0.05 M TBP 336 into 0.1 M Cyanex 272 in kerosene is responsible for an increase of Co(II) extraction percent from 89% to 97% and an increase of Co(II) distribution ratio from 8.9 to 32.6. Conversely, Li(I) distribution ratio and extraction percent remain low in the presence of TBP in 0.1M Cyanex 272 in kerosene. This distribution ratio of Li(I) increases very slightly and reaches 0.14 in the presence of 0.05 M TBP in the mixture contained 0.1 M Cyanex 272 (Table 2). The logarithm of the selectivity coefficient increases from 1.9 to 2.4, when TBP concentration in the mixture varies from 0 to 0.06 M. Above 0.05 M concentration of TBP, distribution ratios of Co(II) and Li(I) are slightly decrease.

Table 2. Selectivity coefficient of Co(II) over Li(I) as a function of TBP concentration.
Organic phase: mixture of 0.1 M Cyanex 272 and various concentrations of TBP in kerosene;
aqueous phase: 0.01 M Co(II) and 0.01 M Li(I). $D_{Co(II)}$ – distribution ratio of cobalt(II);
$D_{Li(I)}$ – distribution ratio of lithium(I); $logS_{Co/Li}$ – logarithm of selectivity coefficient of Co(II) over Li(I)

[TBP], M	$D_{Co(II)}$	$D_{Li(I)}$	$logS_{Co/Li}$
0.00	8.91	0.11	1.9
0.01	15.3	0.12	2.1
0.02	19.7	0.12	2.2
0.03	24.1	0.13	2.3
0.04	29.8	0.13	2.4
0.05	32.6	0.14	2.4
0.06	31.4	0.12	2.4
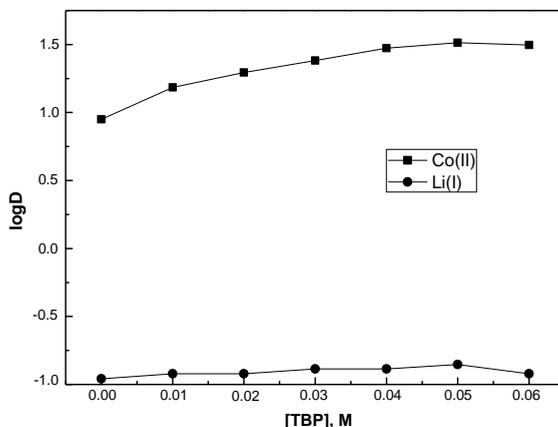
Fig. 3. Logarithm of distribution ratios of Co(II) and Li(I) vs. TBP concentration.
Aqueous phase: 0.01 M Co(II), 0.01 M Li(I); organic phase: 0.1 M Cyanex 272
and different concentration of TBP in kerosene

Banda et al. (2012) reported separation of rare earth elements by Cyanex 272 and its mixture with other extractants (TBP, TOPO, Cyanex 301, Alamine 308). They also

observed synergistic effects with the combination of Cyanex 272 and TBP, which led to complete separation of Pr(III) and Nd(III) over La(III).

The next series of investigations was carried out with the mixture containing 0.05 M TBP and different concentrations of Cyanex 272. The concentration of Cyanex 272 in the mixture of TBP was changed from 0.01 to 0.2 M. Table 3 shows the variation in the distribution ratios (D) of Co(II) and Li(I) from aqueous solutions as a function of Cyanex 272 concentration in the mixture of 0.05 M TBP.

Table 3. Selectivity coefficient of Co(II) over Li(I) as a function of Cyanex 272 concentration. Organic phase: mixture of 0.05 M TBP and various concentrations of Cyanex 272 in kerosene; aqueous phase: 0.01 M Co(II) and 0.01 M Li(I). $D_{Co(II)}$ – distribution ratio of cobalt(II); $D_{Li(I)}$ – distribution ratio of lithium(I); $log S_{Co/Li}$ – logarithm of selectivity coefficient of Co(II) over Li(I)

[Cyanex 272], M	$D_{Co(II)}$	$D_{Li(I)}$	Log $S_{Co/Li}$
0.00	3.63	0.10	1.5
0.01	4.86	0.12	1.6
0.05	15.1	0.12	2.1
0.08	26.4	0.13	2.3
0.10	32.6	0.14	2.4
0.20	32.0	0.14	2.4

As can be seen from Table 3, distribution ratios of Co(II) and Li(I) reach 3.63 and 0.10, respectively by 0.05 M TBP single in kerosene (Table 3). The distribution ratio of Co(II) increases significantly from 3.63 to 32.6 with increasing Cyanex 272 concentration up to 0.1 M. We can also see that, the addition of Cyanex 272 in 0.05 M TBP cause increase in the logarithm of the separation coefficient of Co(II) towards Li(I) ($S_{Co/Li}$) from 1.5 to 2.4.
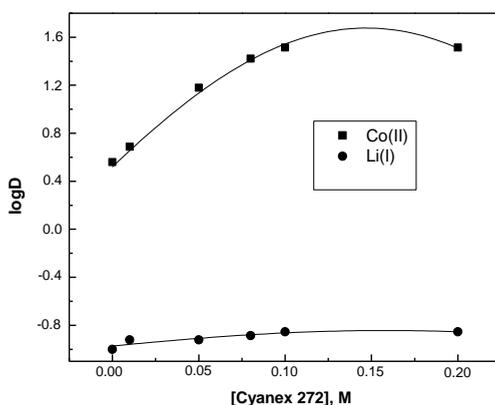
Fig. 4. Logarithm of distribution ratios of Co(II) and Li(I) vs. Cyanex 272 concentration. Aqueous phase: 0.01 M Co(II), 0.01 M Li(I); organic phase: 0.05 M TBP and different concentration of Cyanex 272 in kerosene

Figure 4 shows the logarithm of distribution ratios of Co(II) and Li(I) vs Cyanex 272 concentration. It indicates that logD of Co(II) increases with increase of this extractant concentration. Above 0.1 M concentration of Cyanex 272 further increase in distribution ratio of Co(II) is not observed. On the other hand the extraction of Li(I) was low and only slightly changed with Cyanex 272 concentration increase in mixture with TBP. The highest extraction selectivity was obtained using 0.1 M Cyanex 272 and 0.05 M TBP in kerosene.

Stripping investigation

The stripping investigations were carried out in order to determine the appropriate concentration of H_2SO_4 required for stripping Co(II) from the loaded organic phase. A range of 0-1M acid concentration was investigated. Stripping investigations were carried out on the organic solution consisting of the mixture of 0.1 M Cyanex 272 and 0.05 M TBP in kerosene containing Co(II) and Li(I) after extraction from aqueous solution. In order to evaluate the stripping percent by sulphuric acid, extraction solvent was first contacted with an aqueous solution containing 0.01 M Co(II) and 0.01 M Li(II) by mixture of 0.1 M Cyanex 272 and 0.05 M TBP at phase volume ratio O:A=1. After settlement, the organic phase was separated from aqueous phase. Organic phase was then contacted with the stripping solution (deionized water and sulphuric acid solutions) at phase volume ratio O:A=1 at 25±2 °C. After shaking, organic and aqueous phases were separated and metal concentrations in aqueous phases were determined by AAS in order to calculate stripping percent.
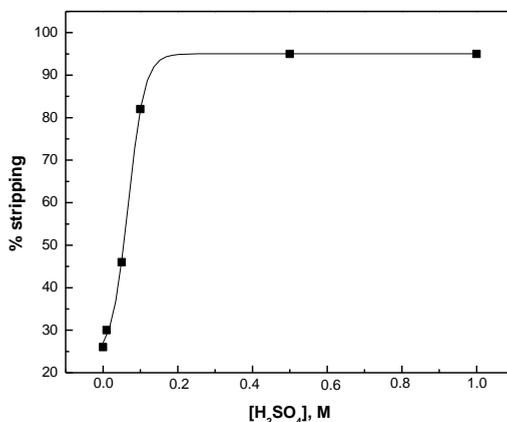
Fig. 5. Co(II) stripping percent by water and sulfuric acid from 0.1 M Cyanex 272 and 0.05 M TBP mixtures in kerosene previously loaded by contacting the extraction solvent with an aqueous phase containing 0.01 M Co(II) and 0.01 M Li(I).

The results are presented in Fig. 5. As can be observed the stripping was highly selective since no Li(I) was found in the stripping solution. Figure 5 shows that maximum stripping of Co(II) was obtained with 0.5 M H_2SO_4. This solution can be

considered as a promising stripping agent since it leads to good stripping of Co(II) (95%). Further increase of this acid concentration has no significant effect on cobalt(II) stripping.

Conclusions

The extraction system Cyanex 272-TBP can be recommended for the separation of Co(II) and Li(I) from chloride solutions with regard to the high values of separation coefficients. Co(II) ions were successfully separated from Li(I) in a synergistic solvent extraction process using the mixture of 0.1 M Cyanex 272 and 0.05 M TBP. The obtained selectivity coefficient of Co(II) over Li(I) ($S_{Co/Li}$) by this mixture is significantly greater than those obtained with Cyanex 272 or TBP alone. This mixture exhibits no synergistic effects for Li(I) which provides possibilities for Co(II) and Li(I) separations at a proper ratio of extractants. Sulfuric acid at 0.5 M concentration, appears as the good stripping agent with a stripping efficiency of about 95% at room temperature. Finally, the separation system presented in this paper can be useful for the separation of Co(II) and Li(I) from aqueous chloride solutions. These metal ions are present in the leach liquor from hydrometallurgical recycling of spent lithium-ion batteries (LIBs). This type of batteries is considered as an attractive secondary resource of valuable metals such as cobalt and lithium (Sun and Qiu, 2011, Zeng et al., 2014; Wang et al., 2014). Their effective recovery is possible only after separation process of metal ions from solution after leaching of the spent batteries in hydrometallurgical technology (Xu and al., 2008). In this work, the proposed novel synergistic mixture offers an efficient way to separate metal ions. Therefore this separation process by synergistic solvent extraction can be very important for the recycling of LIBs by hydrometallurgical method.

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