Ionic Liquid-Based Process Development for Cobalt Recovery from Aqueous Streams

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ABSTRACT

Using the ionic liquid [P8888][Oleate], liquid-liquid extraction has been studied to recover Co2+ from water. Extraction-regeneration experiments were followed during five consecutive cycles with Na2CO3 (aq) as regeneration solution. Over 99% of Co2+ was extracted and using 0.7-1 M Na2CO3 (aq) the extracted Co2+ was recovered for 99% in the form of CoCO3(s). Co2+ transfer shifted from ion-pair extraction in the first cycle to ion-exchange in the successive cycles. Thus, the measurement of a single extraction–regeneration cycle is not sufficient to perceive conclusive information about the steady-state conditions of the process. In the context of the feasibility of the technology, four key aspects are addressed: extraction efficiency, recovery of the IL, loss of the IL, and the end product.

Keywords: Cobalt (Co2+); Extraction; Hydrophobic ionic liquid; Tetra(octyl)phosphonium oleate [P8888][oleate]

INTRODUCTION

Heavy metal pollution has become a serious environmental threat [1]. Arsenic, cobalt, copper, lead, nickel and zinc are all pollutants that are toxic in nature and can be carcinogenic upon their accumulation in living organisms [2]. Industrial wastewater treatment aims to remove these metals and reduce the level of pollution. Additionally, the process of treatment also allows...
recovering these metals from waste streams. Refining the process of reclaiming metals from waste water plays an important role in establishing a functioning circular economy, especially in the current context of diminishing metal reserves worldwide [3]. As an example, this study focuses on cobalt, a metal involved in many industrial applications, ranging from aircraft engines, rechargeable batteries, paints, coatings and catalysts. The annual growth in cobalt demand is expected to increase by more than 6% in 2020 [3]. Apart from the industrial need for cobalt, from the experimental point of view, the reason to use cobalt in the present study is its distinctive sharp color in both the aqueous and the organic phase. Its distinct color makes it possible to observe the transfer of cobalt from one phase to the other during the extraction and regeneration phase.

Table 1: Overview of publications on metal extraction using ionic liquids.

| Ionic Liquid | Metal Ions | Regeneration Solution | Recovery IL | Loss of IL in Raffinate* | Identified End Product | Extraction Mechanism | Ref |
|--------------|------------|-----------------------|-------------|--------------------------|------------------------|---------------------|-----|
| [Bmim][Cl] | Ce³⁺, Eu³⁺, Y³⁺ | 0.05 M HNO₃, 7.0 g/L acetohydroxamic acid+1.0 M guanidine carbonate, 0.05 M diethylenetriamine pentaacetic acid+1.0 M guanidine carbonate, 0.05 ethylenediamine tetraacetic acid+1.0 M guanidine carbonate, 0.1 M citric acid+0.4 formic acid+0.4 M hydrazine hydrate, 500 mM [Bmim][Cl] | Yes | NDA* | NDA | Cation exchange Mn⁺ ⇔ 3 [Bmim⁺] | [19] |
| Cyphos® IL 101 | Co²⁺, Ni²⁺ | Water | Yes | 40-80 ppm of [P⁺] | NDA | Anion exchange MCl₄⁻ ⇔ 2Cl⁻ | [20] |
| CTMA | Cd²⁺, Cu²⁺, Pb²⁺ | Mixture of acetone and ethyl alcohol | Yes | 2.0 wt.** | NDA | Anion exchange 3M²⁺+2Y²⁻ ⇔ 2[H⁺] | [11] |
| [P₆₆₁₄][Cl]–NaCl–H₂O | Co²⁺, Ni²⁺ | 5 steps stripping: 1 x 6 M HCl, 3 x pure water and, 1 x ammonia | Yes | NDA | <0.2 wt. % | NDA | Anion exchange MCl₂⁻ ⇔ 2[Cl⁻] | [21] |
| [P₆₆₁₄][Cl] | Co²⁺, Ni²⁺ | Nitric and sulfuric acid solution | Yes | 1.40 wt. % | NDA | NDA | Dissolution of metal oxides | [22] |
| [Hbet][Tf₂N] | Co²⁺, Ni²⁺ | Hydrogen bis(trifluoromethylsulfonyl)imide | Yes | NDA | NDA | NDA | [25] |
| [N₄₄₄₄][Cl] | Co²⁺, Ni²⁺ | HNO₃, HCl | Yes | 0.3-1.2 wt.% | NDA | NDA | [24] |
| Alkylquat-336 | Co²⁺, Ni²⁺ | 1 M HCl, 1 M HNO₃, 1 M HClO₄, 1 M Na₂CO₃, 0.05 M thiourea + 0.1 M HCl | Yes | NDA | Yes, solution of metal thiourea | NDA | [27] |
| [C₆mim][DEHP] | Co²⁺, Ni²⁺ | HNO₃ | Yes | NDA | NDA | NDA | Ion exchange Nd³⁺ ⇔ 3[H⁺] | [10] |
| [C₆mpyr][DEHP] | Co²⁺, Ni²⁺ | MilliQ water | Yes | NDA | NDA | NDA | Hydrated anionic complex | [26] |
| [A336][NO₃] | Co²⁺, Ni²⁺ | MilliQ water | Yes | NDA | NDA | NDA | [28] |

*NDA: No Data available

**Ref [11] shows weight loss percentage of the applied amount of IL’s during extraction while others indicate the weight percentage of IL present in the aqueous phase.
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the LLX process, hydrophobic ionic liquids (HILs) can be used instead since they offer an alternative using non-volatile extractants [9].

HILs are organic salts that consist of an organic cation and an organic/inorganic anion [10-12]. These salts are liquid at temperatures below 100°C, have negligible vapor pressure, high thermal and chemical stability, relatively low water solubility, and are good solvents for many organic and inorganic materials [13,14]. Furthermore, their properties can be fine-tuned through selecting several cations and anions, making it a designer solvent [15].

Despite the high extraction efficiency of many ionic liquids, their high cost hamper if not prevent their implementation in large-scale industrial applications [16,17]. To our opinion, the viability of any potential application of ILs for Co²⁺ recovery (and for that matter the recovery of any other metal as well) should rely on four mandatory criteria:

1) High extraction efficiency
2) The use of a cheap regeneration agent/method that ensures the full regeneration of the IL, also implying
3) No loss of IL
4) Obtaining a commercially interesting Co²⁺ product.

Even though the use of IL’s for metal recovery has been reported previously, to the best of our knowledge the present study is the first one in addressing the combination of all above-mentioned aspects. As illustration, Table 1 lists published studies with some of the aspects categorized. In fact, with almost no identified metal product, Table 1 reflects the common practice that the design of the process starts with the extraction part and the recovery of the IL, instead of defining the regeneration product. We consider the latter approach to be the better option. Therefore, we started out with identifying CoCO₃(s) as valuable product and accordingly designed the process in backward direction. Figure 1 schematically outlines the proposed process. In the extraction step, Co²⁺ is taken up by the IL and in the regeneration (IL recovery) it is back extracted from the IL and simultaneously precipitated as Na₂CO₃(aq). The labeling of the streams in Figure 1 is used throughout the entire paper.

The majority of previous studies show that strong acids and strong bases are able to remove a wide variety of metal ions from a loaded ionic liquid [10,11,18-28]. However, the main drawback of these regeneration solutions is that they do not allow direct re-use of the ionic liquid because strong acids protonate ionic liquids and strong bases form emulsions [18]. In the context of the above mentioned four process criteria, strong acids and bases are often used to merely investigate the extraction process on a lab-scale without considering the consequences for the overall process.

For this study, [P₈₈₈₈][Oleate] was selected for Co²⁺ extraction because it 1) consists of a natural hydrophobic anion and a hydrophobic cation which is assumed to minimize the losses to the aqueous phases, 2) has the ability to selectively extract transition, rare earth, alkaline earth and alkaline metals depending on the pH and composition of the feed [18], and 3) has a relatively low viscosity at room temperature (200 mPa.s) thus eliminating either the need of a hydrophobic solvent to dilute the IL [29,30] and the need for higher temperatures during operation.

In earlier studies, using phosphonium and ammonium-based ionic liquids with the same functionalized anion oleate, sodium oxalate was used as a regeneration solution in both cyclic and continuous experiments. The regeneration efficiency was below 25% in the cyclic experiments (5 cycles) and below 80% in continuous mode (180 minutes) [9,18]. Huang et al. also used sodium oxalate for the regeneration of their acid-base coupling bifunctional ionic liquid, applied for rare earth element separation [31]. Even though the metal regeneration efficiency was higher than in the studies of Parmentier et al., [18] it took at least two days to reach a regeneration efficiency of 90-100% [31]. In the present contribution, Na₂CO₃ has been used instead of sodium oxalate as it is more environmentally friendly, more than ten times cheaper and results directly in the formation of a marketable product (i.e., CoCO₃(s)), which is mainly used as a catalyst and in ceramic pigments. In contrast, cobalt oxalate needs to be calcined to cobalt oxide first before it becomes a commercially attractive product suitable for industrial applications. This calcination process requires high temperatures and produces large amounts of greenhouse gases, notably CO₂. In case cobalt oxide is the desired end product, calcining CoCO₃ produces half the amount of CO₂ compared to oxalate. The aim of this study was to extract and recover cobalt from industrial wastewater. Extraction-regeneration experiments were followed during five consecutive cycles using [P₈₈₈₈][Oleate] for extraction and Na₂CO₃(aq) for regeneration. Further, this study will help understand the extraction mechanism of the recovery process.

To the best of our knowledge the aforementioned combination of tetra(octyl)phosphonium oleate and sodium carbonate as a regeneration solution producing solid CoCO₃ has not been reported at present. In order to define the steady-state conditions, the system was investigated by running 5 subsequent extraction - regeneration cycles.

**Figure 1**: Conceptual outline of the process discussed in the present study.
MATERIALS AND METHODS

Chemicals and reagents

All the chemicals utilized in this project were of analytical grade and used as purchased. These chemicals are tetra(octyl)phosphonium bromide (>95%, Iolitec), oleic acid (90%, rest polyunsaturates <7%, unsaponifiable <0.2% and water <0.05%, Alfa Aeser), cobalt(II) chloride hexahydrate (99%, Sigma–Aldrich), sodium hydroxide (≥ 97%, VWR), sodium chloride (100%, VWR), calcium chloride (Across Organics), and sodium carbonate anhydrous (100%, VWR). Throughout the synthesis, extraction and regeneration experiments, Milli-Q water (≥ 18.2 MΩ cm) was used.

Ionic liquid synthesis procedure

Tetraoctylphosphonium oleate was synthesized according to the procedure previously reported, albeit with some modifications [9]. At first, 0.319 mol (12.74 g) of NaOH was dissolved in 800 ml Milli-Q water before adding 0.231 mol (65.24 g) oleic acid. Then the mixture was stirred (650 rpm) at 45°C for 3 hours. After that, 0.177 mol (100 g) of [P8888][Br] was added to the mixture to be stirred for 8 h at 75°C. Following Parmentier et al. [9], an excess of oleic acid was applied to shift the equilibrium towards IL formation. The IL was washed nine times with, in total, 9 L of Milli-Q water using a separatory funnel in order to remove the impurities such as bromide and sodium. Finally, a rotary evaporator (BUNCHI Rotavapor®-R-3) and a vacuum oven at 50°C were used to remove the remaining amount of water.

Analysis of ion and IL concentrations

The concentrations of the metal cations in the aqueous phases (raffinates of extraction and regeneration) and lean IL were determined with Inductively Coupled Plasma (ICP) of Perkin Elmer, equipped with an Optima 5300 DV optical atom emission spectrometer (OES). Anion and sodium concentrations were measured using a Metrohm 761 Compact ion chromatograph (IC). To determine the loss of IL to the aqueous phase the P-content and organic C-content of the raffinate were measured using ICP and Total Organic Carbon Analyzer TOC.

Experimental procedure

Feed solutions were prepared with a concentration of 1 g/L Co²⁺ and 1 g/L Na⁺ from their corresponding Cl salts unless otherwise stated. For the first extraction cycle, 5 ml of this solution was added to 5 ml of water-saturated [P8888][Oleate] (water content around 10 wt.%) and mixed at room temperature for 2 hours using a Heidolph Multi Reax vortex mixer at a speed of 2500 rpm. For the first 3 cycles the volume ratio was unity while for the 4th and 5th cycle the ratio changed because the volume of the ionic liquid decreased to less than 2.5 ml due to sample-taking for analysis. Table S1 shows the volumes of feed (Vf,I), regeneration solutions (VRF,i) and IL (VIL) used in the subsequent cycles. In order to account for the variable volume ratio during consecutive cycles, all ion concentration calculations have been corrected (normalized) by multiplying the measured Co²⁺ concentration in the IL phase by V_IL/V_aq (see SI for details). This is possible since in all cases almost full extraction (>99%) of the Co²⁺ was obtained. Therefore, a lower V_IL/V_aq ratio would not lower the extraction efficiency. Prior to the experiments described here, a separate test applying different contact times revealed that 2 hours are more than sufficient to reach equilibrium (actually, more recent tests showed that even 10 minutes would have been enough). To enhance the phase separation, the mixture was then centrifuged using an Allegra X-12 R Centrifuge (Beckman Coulter) at a speed of 3750 rpm for 20 minutes.

After each extraction the HIL loaded with Co²⁺ was regenerated using different concentrations of Na₂CO₃ (i.e., 0.3, 0.5, 0.7 and 1.0 M), following the same analytical procedures that were applied for the extraction. From that point, the (partly) regenerated IL

![Figure 2: Schematic representation of the synthesis of the ionic liquid [P8888][Oleate].](image-url)
was exposed to fresh feed solution for the next extraction cycles. This procedure was repeated for five complete subsequent cycles of extraction and regeneration.

Calculation of efficiencies and productivity

The aqueous solutions after extraction and regeneration as well as the lean IL were analyzed for Co\textsuperscript{2+}. The extraction efficiency (\(\eta_E\)) is defined as the percentage of Co\textsuperscript{2+} that is removed from the feed, calculated and expressed for cycle \(i\) as:

\[ \eta_E,i = \left( \frac{C_{i,\text{IL}} - C_{i,\text{R}}}{C_{i,\text{IL}}} \right) \times 100\% \]  

(1)

Where,

- \(C_{i,\text{IL}}\): Co\textsuperscript{2+} concentration in the loaded IL - cycle \(i\), [g/L]
- \(C_{i,\text{R}}\): Co\textsuperscript{2+} concentration in the raffinate - cycle \(i\), [g/L]
- \(V_{\text{RF},i}\): Volume of regeneration feed – cycle \(i\), [L]

Note that this expression assumes equal volumes of feed and raffinate which is realistic since the IL is pre-saturated with water.

The regeneration efficiency (\(\eta_R\)) is defined as the percentage of Co\textsuperscript{2+} that is removed from the IL, calculated and expressed for cycle \(i\) as:

\[ \eta_R,i = \left( \frac{C_{i,\text{IL}} - C_{i-1,\text{IL}}}{C_{i-1,\text{IL}}} \right) \times 100\% \]  

(2)

Where,

- \(C_{i,\text{IL}}\): Co\textsuperscript{2+} concentration in the loaded IL - cycle \(i\), [g/L]
- \(C_{i-1,\text{IL}}\): Co\textsuperscript{2+} concentration in the loaded IL - cycle \(i-1\), [g/L]
- \(V_{\text{IL},i}\): Volume of IL phase – cycle \(i\), [L]

It is to be noted that for \(i=1\), the value of \(C_{\text{IL},0}\) is zero, implying that the experiment starts with a Co\textsuperscript{2+}-free IL.

Additionally, the denominator of the right term of expression 2 is comprised of two contributions, the first representing the freshly extracted Co\textsuperscript{2+} from the feed, and the second representing the Co\textsuperscript{2+} residing in the IL already due to the incomplete regeneration during the previous cycle(s).

The recovery of CoCO\textsubscript{3} (\(R_{\text{CoCO}_3}\)) is defined as the percentage of the Co\textsuperscript{2+} extracted that precipitates in the consecutive regeneration:

\[ R_{\text{CoCO}_3,i} = \left( \frac{V_{\text{IL},i} \cdot (C_{i,\text{IL}} - C_{i,\text{R}})}{V_{\text{RF},i} \cdot (C_{i,\text{IL}} - C_{i-1,\text{IL}})} \right) \times 100\% \]  

(3)

The cumulative recovery (\(R^*_{\text{CoCO}_3}\)), being the amount of Co\textsuperscript{2+} precipitated over the cycles 1 to \(j\) over the amount of Co\textsuperscript{2+} extracted over these cycles, is given by:

\[ R^*_{\text{CoCO}_3} = \sum_{i=1}^{j} R_{\text{CoCO}_3,i} \]  

(4)

\(C_{\text{R},i}\): Co\textsuperscript{2+} concentration in the regeneration raffinate - cycle \(i\), [g/L]

\(V_{\text{RF},i}\): Volume of regeneration feed – cycle \(i\), [L]

RESULTS AND DISCUSSION

Co\textsuperscript{2+} extraction and regeneration efficiency and recovery

Sodium chloride was added to all feed solutions because it enhances Co extraction. Even though the extraction without NaCl in the feed is already as high as 91%, adding NaCl further improves the efficiency to 99% (Figure 3).

Figure 4 shows the normalized Co\textsuperscript{2+} concentration during five consecutive cycles of extraction and regeneration, using a 0.5 (A), 0.7 (B) or 1.0 M (C) Na2CO\textsubscript{3} solution for regeneration. Panel D shows photographs taken after the first regeneration using different Na2CO\textsubscript{3}(aq) concentrations with the Co\textsuperscript{2+}-containing, purple-colored IL phase on top and the solid CoCO\textsubscript{3} precipitate collected at the bottom of the tubes.

The composition of the formed precipitate was evaluated using Energy Dispersive X-ray fluorescence spectrometry (EDX). The main component of each composite was cobalt and oxygen with an atomic ratio of 1 to 3, confirming the hypothesis that the precipitate presents indeed CoCO\textsubscript{3}. The weight percentage (wt %) of Co\textsuperscript{2+} in the solid product is around 45%, whereas impurities (i.e., sodium and phosphorus) make out less than 1%. This weight percentage is in agreement with commercially available CoCO\textsubscript{3} with Co\textsuperscript{2+} wt % ranging from 43-47% [32]. In addition to EDX, Raman spectroscopy identified the precipitate as well as CoCO\textsubscript{3}.

Details on the analysis of the precipitate can be found in S2.

Figures 5 and 6 show the extraction efficiency (5), the regeneration efficiency (6A), the recovery (6B) and the cumulative recovery (6C), respectively, for the different concentrations of Na2CO\textsubscript{3} (and including 0.3 M Na2CO\textsubscript{3}(aq)). Independent of the cycle number and the concentration of Na2CO\textsubscript{3}(aq), the regeneration efficiency and the cumulative recovery did show a dependence on cycle number and/or the concentration of Na2CO\textsubscript{3}(aq) in the regeneration feed (Figure 6). For all Na2CO\textsubscript{3}(aq) concentrations, the regeneration efficiency stabilized in the 5th cycle around 96 ± 3%, whereas the recovery of CoCO\textsubscript{3} stabilized around 99 ± 3%.

The major part of the missing Co\textsuperscript{2+} is present as base load in the lean IL and lost via the IL samples needed for the analysis of the IL phase.

It was observed (Figures 4A-4C) that upon increasing the Na\textsubscript{2}CO\textsubscript{3}(aq) concentration the steady state Co\textsuperscript{2+} content of the lean (regenerated) IL reduced, e.g. from 150 mg/L to 60 mg/L after increasing Na\textsubscript{2}CO\textsubscript{3}(aq) from 0.5 to 1.0 M. The plots of the (normalized) Co\textsuperscript{2+} concentration in the IL show that when using 1
It takes 2 to 4 cycles (depending on the Na\textsubscript{2}CO\textsubscript{3} concentration) to cycle is not sufficient to identify the steady-state of this process as there may slightly differ, the key observation and conclusion remain the same, i.e., a shift from ion pair-like uptake during the 1st cycle towards an ion exchange-like uptake in the 2nd cycle. Also, in this case, charge balances were nearly closed. The extraction efficiency of other ion species (e.g. H\textsuperscript{+} and OH\textsuperscript{-}) to the overall charge balance is only minor. For all cases shown in Figures 7 and S5 the pH of the raffinate increased from 5 to 7.9 during extraction. This is partly due to Co\textsuperscript{2+} extraction next to H\textsuperscript{+} transfer. A dedicated experiment showed that the pH increased from 5 to 6.2 by only Co\textsuperscript{2+} transfer. The rest is due to H\textsuperscript{+} transfer, which is equal to 0.003 μmol H\textsuperscript{+}, an amount that is negligible compared to the total amount of all other ions transferred.

The observed shift in uptake mechanism, in turn, points to an important conclusion as well. One of the key parameters for process design is the mechanism of, in this case, Co\textsuperscript{2+} uptake by the IL during steady state. As Figures 7 and S5 show, conclusive information regarding the nature of the uptake mechanism cannot be established by the analysis of merely a single cycle. This is because as long as the system has not yet reached steady state, the uptake mechanism may change. A conceptual design of the process outlined here is discussed in section 4.

As remarked in the section 2.2, the presence of excess oleate during synthesis resulted in a 20% oleate excess in the finally obtained [P\textsubscript{8888}][Oleate]. To assess the possible role of this excess oleate in terms of the mechanism of Co\textsuperscript{2+} uptake, the experiments of Figure 7A were repeated but with an IL without oleate excess, i.e., containing 1:1 molar amounts of [P\textsubscript{8888}] and [Oleate] and using 0.1 M Na\textsubscript{2}CO\textsubscript{3} (Figure 7B). Even though the absolute numbers may slightly differ, the key observation and conclusion remain the same, i.e., a shift from ion pair-like uptake during the 1st cycle towards an ion exchange-like uptake in the 2nd cycle. Also, in this case, charge balances were nearly closed. The extraction efficiency of this 1:1 IL during the two cycles was above 99%, very similar to...
Cycle - 2

Figure 6: Regeneration efficiency $\eta_{i,j}$ of Co$^{2+}$-loaded [P8888][Oleate] (A), Co$^{2+}$ recovery $R_{\text{CoCO}_3,i}$ (B) and cumulative Co$^{2+}$ recovery $R^*_{\text{CoCO}_3,j}$ (C) using Na$_2$CO$_3$ solutions of various concentrations (0.3 - 1.0 M), during five cycles of operation. Based on error analysis, estimated errors are 3% and 5% for the regeneration efficiency $\eta_{i,j}$ and the (cumulative) recovery $R_{\text{CoCO}_3,i}$ and $R^*_{\text{CoCO}_3,j}$ respectively.

the values obtained with the IL containing excess oleate (Figure 5). These results justify the conclusion that the presence of 20% excess oleate in the IL does not (significantly) alter its behavior.

Figure 7 also shows another key feature of the system studied here, especially the properties of [P8888][Oleate]. In the 1st and 2nd cycle the amount of [P8888][Oleate] passing to the raffinate was always below 0.3 μmol (~26 mg/L). Compared to the amount of transferred Co$^{2+}$ (approximately 80 μmol) this is just a very small amount. This observation is in line with TOC analysis, showing a concentration of organics (IL and/or oleate) in the raffinate in the range of 10-50 mg/L.

Conceptual process development

Conceptually, the process consists of an extraction step in which Co$^{2+}$ is taken up by the HIL and a regeneration step in which it is back extracted from the HIL and simultaneously precipitated by, in this case, Na$_2$CO$_3$(aq). The proposed process does not make much sense for a feed just containing a Co$^{2+}$-salt, because mixing the feed with solid Na$_2$CO$_3$(s) would have the same result without the need of using the HIL, nor extraction and regeneration devices. The only advantage of extraction - regeneration for this feed would be concentrating the Co$^{2+}$ which may simplify its precipitation. The proposed process concept seems most applicable for:

- Extraction of a mixture of metals by a non-selective IL and the subsequent precipitation of each metal in a stepwise approach by using different regeneration salts. The advantage is the treatment of IL with the regeneration salt without mixing it with the water feed and avoiding the presence of the salt anions in the extraction raffinate (feed cleaned from Co$^{2+}$).
- Selective recovery of metals. The HIL used demonstrated selectivity between transition and (earth) alkali metals, though under extreme pH conditions and rather narrow pH windows [20]. Further research is needed to develop more selective HILs that operate under more neutral pH conditions.

Figure 7: Absolute amount of ion species exchanged (in μmol) between aqueous (CoCl$_2$+NaCl) and organic IL phase during extraction, calculated for the first and second cycle. The intermediate regeneration step was performed with 0.1 M Na$_2$CO$_3$ (aq). Panels a) and b) refer to an IL with (A) and without 20% excess oleate (B).
Figure 8 schematically presents the conceptual flowsheet of a Co$^{2+}$ extraction/regeneration process combined with a stream table. The extraction column is fed at the top with wastewater containing cobalt chloride and sodium chloride. The recirculated ionic liquid enters at the bottom of the column and moves as small droplets to the top, while extracting the Co$^{2+}$ out of solution. It should be stated that this is only one of the operation modes possible, alternatives are the Karr column, Kuhni column or Rotating Disk Column (RDC). It is important for the mixing to not be vigorous to avoid emulsifying the two liquids. This last requirement makes the Karr column an interesting alternative. The Co$^{2+}$-loaded ionic liquid, due to phase separation collected at the top of the column, is transferred to the regeneration column. Here the IL is contacted (again as small droplets moving up the column) with an aqueous sodium carbonate solution in order to perform the back-extraction of Co$^{2+}$ and the regeneration of the IL. The Co$^{2+}$-lean ionic liquid collected at the top of the column is recycled to the extraction column. More recent analysis of the batch extraction experiments showed that a contact time of 5-10 minutes is sufficient to reach equilibrium. By adjusting the droplet size and the operation mode of the extractor, the rise velocity of the droplet can be controlled. In combination with the column height the residence (contact) time can be adjusted. As mentioned above, the LLX column should enable a contact time of at least 10 minutes. The solid CoCO$_3$ will settle at the bottom and leave the column with the water stream. The two-phase separator next in line to the regenerator serves to separate out the solid cobalt carbonate (end-product). In more detail, the methodology applied depends on the properties of the solid (e.g., density, particle size) and can range from a relatively simple gravity separator to a filtration unit or a centrifugal separator. Preliminary experiments showed that the solids settle easily. An effective regeneration process does not require per se the full, 100%, removal of the solids from the regeneration fluid before recycling. The separated sodium carbonate solution is pumped back to the regeneration column. In case of excess water, a purging process is carried out, after which fresh sodium carbonate is added. It is important to note that the IL will also be loaded with some NaCl.

The data presented in the stream table are calculated based on the mol/mass balance for the different components, the distribution coefficient for Co$^{2+}$ (assumed to be minimal 5, which was confirmed with equilibrium experiments) as well as analysis data for the different ions in the system. Furthermore it is assumed that steady-state is obtained (Co$^{2+}$ exchanged for 2 Na$^+$), no IL is lost to the water phase (which means no fresh IL needs to be added to the system) and all the water added to the regeneration cycle through the fresh soda leaves during the purge. Charge balance calculations (not added) for the IL phase revealed that not all ions present in the IL were analyzed. The mass balance calculation shows that operating with a Feed to Solvent ratio of 5 (mass based) in the extraction and the regeneration column is possible. This will reduce the flow in each recycle by a factor of 5 (see total of stream S-1, S-4 and S-6 in the stream table) and consequently the equipment size is reduced as well. Regeneration with 1 M Na$_2$CO$_3$ results in a concentration drop to 0.6 M, which is still acceptable for the regeneration efficiency.

| Kg/h | S-1 | S-2 | S-3 | S-4 | S-5 | S-6 | S-7 | S-8 | S-9 | Purge | Fresh Soda | CoCO$_3$ Solid |
|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------|-------------|----------------|
| H$_2$O | 995.00 | 995.00 | 18.00 | 18.00 | 18.00 | 40.00 | 40.00 | 40.00 | 36.40 | 3.60 | 3.47 |
| IL | 0.00 | 0.00 | 180.00 | 180.00 | 180.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Co$^{2+}$ | 1.00 | 0.01 | 0.01 | 1.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Na$^+$ | 1.00 | 1.78 | 1.70 | 0.92 | 1.70 | 1.80 | 1.02 | 1.02 | 0.93 | 0.09 | 0.89 |
| Cl | 2.75 | 2.75 | 0.11 | 0.11 | 0.11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CO$_3$$^{2-}$ | 2.40 | 1.39 | 1.39 | 1.27 | 0.13 | 1.16 |
| CoCO$_3$ | 2.00 | | | | | | | | | |
| NaCO$_3$·10 H$_2$O | 5.52 |
| Total | 999.75 | 999.54 | 199.82 | 200.03 | 199.82 | 44.20 | 44.41 | 42.41 | 38.60 | 3.82 | 5.52 | 5.52 | 2.00 |

Figure 8: Conceptual flow-sheet for Co$^{2+}$ recovery from water using the ionic liquid [P$_{oleate}$]$^{oleate}$ for extraction and a 1 M Na$_2$CO$_3$ solution for regeneration.
CONCLUSION

Using the hydrophobic ionic liquid [P_{8888}][Oleate], the proof-of-principle of a new process for metal ions removal from water has been demonstrated. The extraction efficiency of Co^{2+} was above 99% and by using Na$_2$CO$_3$(aq) as regeneration solution up to 98% of the initially present Co$^{2+}$ in the feed was recovered as CoCO$_3$(s), being a marketable product. The proposed process is most interesting for the selective recovery of metals and can accommodate any HIL that shows selectivity, can be regenerated, and has a low loss rate to the aqueous phases. [P_{8888}][Oleate] already shows selectivity, though under extreme pH conditions. Furthermore, it has a low loss rate to the aqueous phases. By performing five extraction-regeneration cycles it became evident that the measurement of a single extraction – regeneration cycle is not sufficient to perceive conclusive information about the steady state conditions of the process with respect to efficiencies, recoveries, and ion transfer mechanism. The case discussed in this paper shows the need for multiple subsequent extractions – regeneration cycles as a sound basis for process development.

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REFERENCES

1. Stojanovic A, Keppler BK. Ionic liquids as extracting agents for heavy metals. Sep Sci Technol. 2012;47(2):189-203.
2. Jadhav U, Hocheng H. A review of recovery of metals from industrial waste. JAME. 2012;54(2):159-167.
3. European Commission, Report on Critical Raw Materials for the EU. 2014.
4. Barakat M. New trends in removing heavy metals from industrial wastewater. Arabian J Chem. 2011;4(4):361-377.
5. Fu F, Wang Q. Removal of heavy metal ions from wastewaters: A review. J Environ Manage. 2011;92(3):407-418.
6. Dietz ML. Ionic liquids as extraction solvents: Where do we stand? Sep Sci Technol. 2006;41(10):2047-2063.
7. Schweitzer PA. Handbook of separation techniques for chemical engineers.1988;McGraw-Hill New York.
8. Visser AE, Swatloski RP, Griffin ST, Hartman DH, Rogers RD. Liquid/liquid extraction of metal ions in room temperature ionic liquids. Sep Sci Technol. 2001;36(5-6):785-804.
9. Parmentier D, Paradis S, Metz SJ, Wiedmer SK, Kroon MC. Continuous process for selective metal extraction with an ionic liquid. Chem Eng Res Des. 2016;109:553-560.
10. Rout A, Kotlarska J, Dehaen W, Binnemans K. Liquid-liquid extraction of neodymium (iii) by dialkylphosphate ionic liquids from acidic medium: The importance of the ionic liquid cation. Physical Chemistry Chemical Physics. 2013;15(39):16533-16541.
11. Vergara MV, Lijanova I, Likhanova N, Xometli OO, Vigueras DJ, Morales Ramirez AJ. Recycling and recovery of ammonium-based ionic liquids after extraction of metal cations from aqueous solutions. Separation and Purification Technology. 2015;155:110-117.
12. Rout A, Wellens S, Binnemans K. Separation of rare earths and nickel by solvent extraction with two mutually immiscible ionic liquids. RSC Adv. 2014;4(11):5753-5758.
13. Welton T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. Chem Rev. 1999;99(8):2071-2084.
14. Berthod A, Carda-Broch S. Uses of ionic liquids in analytical chemistry. Reactions. 2004;1:6.
15. Newington I, Perez-Arlandis JM, Welton T. Ionic liquids as designer solvents for nucleophilic aromatic substitutions. Org Lett. 2007;9(25):5247-5250.
16. Shamsuri AA, Abdullah DK. Ionic liquids: Preparations and limitations. Makara Sains. 2010;14(2):101-106.
17. Mai NL, Ahn K, Koo YM. Methods for recovery of ionic liquids—a review. Proc Biochem. 2014;49(5):872-881.
18. Parmentier D, Valia YA, Metz SJ, Burhme OS, Kroon MC. Regeneration of the ionic liquid tetracoctlammonium oleate after metal extraction. Hydrometallurgy. 2015;158:56-60.
19. Nakashima K, Kubota F, Maruyama T, Goto M. Feasibility of ionic liquids as alternative separation media for industrial solvent extraction processes. Ind Eng Chem Res. 2005;44(12):4368-4372.
20. Wellens S, Govaerts R, Møller C, Luyten J, Thijs B, Binnemans K. A continuous ionic liquid extraction process for the separation of cobalt from nickel. Green Chem. 2013;15(11):3160-3164.
21. Ongena B, Opsomer T, Binnemans K. Separation of cobalt and nickel using a thermomorphic ionic-liquid-based aqueous biphasic system. Chem Communications. 2015;51(88):15932-15935.
22. Wellens S, Vander Hoogerstraete T, Möller C, Thijs B, Luyten J, Binnemans K. Dissolution of metal oxides in an acid-saturated ionic liquid solution and investigation of the back-extraction behaviour to the aqueous phase. Hydrometallurgy. 2014;144:27-33.
23. Yang F, Kubota F, Baba Y, Kiniya N, Goto M. Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system. J Hazard Mater. 2013;254:79-88.
24. Platter S, Kar M, Leyma R, Chib S, Roller A, Jirs J, et al. Task-specific thioglycolate ionic liquids for heavy metal extraction: Synthesis, extraction efficacies and recycling properties. J Hazard Mater. 2017;324:241-249.
25. Vander Hoogerstraete T, Ongena B, Binnemans K. Homogeneous liquid–liquid extraction of metal ions with a functionalized ionic liquid. J Phys Chem Lett. 2013;4(10):1659-1663.
26. Rout A, Binnemans K. Separation of rare earths from transition metals by liquid–liquid extraction from a molten salt hydrate to an ionic liquid phase. Dalton Transactions. 2014;43(38):3186-3195.
27. Wei W, Cho CW, Kim S, Song MH, Bediako JK, Yeoung-Sang L. Selective recovery of Au (iii), Pt (iv), and Pd (ii) from aqueous solutions by liquid-liquid extraction using ionic liquid alquat-336. Journal of Molecular Liquids. 2016;216:18-24.
28. Rout A, Venkatesan K, Srinivasan T, Rao PV. Liquid-liquid extraction of p-u (iv) and am (iii) using malonamide in room temperature ionic liquid as detergent. J Hazard Mater. 2012;221:62-67.
29. Parmentier D, Vander Hoogerstraete T, Metz SJ, Binnemans K, Kroon MC. Selective extraction of metals from chloride solutions with the tetracoctlammonium oleate ionic liquid. Ind Eng Chem Res. 2015;54(18):5149-5158.
30. Parmentier D, Metz SJ, Kroon MC. Tetraoctylammonium oleate and...
linoleate based ionic liquids: Promising extractants for metal salts. Green Chem. 2013;15(1):205-209.

31. Huang C, Huang B, Dong Y, Chen J, Wang Y, Sun X. Efficient and sustainable regeneration of bifunctional ionic liquid for rare earth separation. ACS Sustain Chem Eng. 2017;5(4):3471-3477.

32. Digne M, Marchand K, Bourges P. Monitoring hydrotreating catalysts synthesis and deactivation using raman spectrometry. OGST. 2007;62(1):91-99.

33. Dietz ML, Dziela JA. Ion-exchange as a mode of cation transfer into room-temperature ionic liquids containing crown ethers: Implications for the 'greenness' of ionic liquids as diluents in liquid-liquid extraction. Chem Commun. 2001;(20):2124-2125.

34. Jensen MP, Dziela JA, Rickert P, Dietz ML. EXAFS investigations of the mechanism of facilitated ion transfer into a room-temperature ionic liquid. J Am Chem Soc. 2002;124(36):10664-10665.