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# Continuous process for selective metal extraction with an ionic liquid



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#### ABSTRACT

This work describes for the first time a continuous process for selective metal extraction with an ionic liquid (IL) at room temperature. The hydrophobic fatty acid based IL tetraoctylphosphonium oleate ([P<sub>8888</sub>][oleate]) was specifically chosen for its low viscosity and high selectivity towards transition metals. Applying [P<sub>8888</sub>][oleate] for continuous metal ion extraction with 0.1 M sodium oxalate for regeneration resulted in a process with good and stable extraction efficiencies over time. The selectivity of the IL resulted in a process in which cobalt was selectively removed from two mixed salt solutions (Co/Na, Ca/Co/K) to obtain a pure cobalt stream after stripping the IL. The performed experiments showed that the contact time of the IL for extraction and stripping strongly influenced the achieved efficiencies. The stability of the IL was tested and it was shown that the fatty acid based IL was stable for the duration of the experiment. Liposome tests showed that the IL is very hydrophobic, which limits its leakage towards the water phase, but also results in a higher toxicity towards cell membranes. Economic analysis shows that the IL based process is not (yet) economical compared to ion-exchange resins, in case demineralised water is the only product. However, if the recovery of valuable metals is also taken into account and/or if brine disposal is an issue, then continuous IL metal extraction systems must be regarded as promising alternatives.

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#### 1. Introduction

Since the late 1990, research about ionic liquids (ILs) came into the attention of a broader scientific community (Plechkova and Seddon, 2008). These liquids are ionic salts which are liquids at room temperature, and are also referred to as "molten salts" (Rogers and Voth, 2007). The ions in these ILs are large and are held together by electrostatic attractions, which result in different physical and chemical properties compared to conventional solvents. They are liquid over a wide range of temperatures, have a negligible vapour pressure, have a low flammability, but they also have a specific structure and coordination ability (Huddleston and Rogers, 1998; Zhao et al., 2005; Wilkes, 2002). Selecting specific anions and/or cations leads to ILs which are applicable for gas separation (Althuluth et al., 2014; Romanos et al., 2013; Galán

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Sánchez et al., 2007) and purification (Abai et al., 2015; Zarca et al., 2014), dissolution of cellulose (Swatloski et al., 2002; Zhao et al., 2009), selective extraction of organics from other media (Blanchard et al., 1999; Nasir Shah et al., 2015; Lebedeva et al., 2015; Królikowska and Karpińska, 2015), dissolving metal oxides (Nockemann et al., 2006; Vander Hoogerstraete and Binnemans, 2014), and extraction of metals from the aqueous phase (Belova et al., 2009; Fischer et al., 2011; Vander Hoogerstraete et al., 2013, 2014; Rout et al., 2013; Sato et al., 2005; Tsaoulidis et al., 2013).

All of the above mentioned literatures on the applications of ILs for metal extraction are performing its research in batch modes. However, to be industrially applicable, these processes should be performed in a continuous mode. In literature, there is to the authors' knowledge at this moment only one article that describes a continuous metal extraction process based on ILs in a continuous mode (Wellens et al., 2013). In this work, cobalt is selectively extracted from a cobalt/nickel stream by applying the ionic liquid, trihexyl(tetradecyl)phosphonium chloride, commercially known as Cyphos<sup>®</sup> IL 101. However, the disadvantage of this process is that the five mixer-settlers that were applied have to be heated to 50 °C in order to keep the viscosity of the IL sufficiently low to obtain fast extraction/stripping kinetics. This makes the process high energy demanding.

To overcome this limitation, a newly synthesized fatty acid based ionic liquid (IL), tetraoctylphosphonium oleate ([P<sub>8888</sub>][oleate]), was selected, which shows promising characteristics as an extractant for a sustainable process on selective metal recovery (Parmentier et al., 2013). This IL has the advantage of having a very low viscosity (10.8 wt% H<sub>2</sub>O results in a viscosity of 183 mPas at 20 °C) after water saturation (Parmentier et al., 2015a). This results in a fast extraction/stripping kinetics which allows this process to be operated in a continuous mode at room temperature. Regeneration is also easily achievable by applying an aqueous 0.1 M sodium oxalate solution as stripping agent to recover the metals (Parmentier et al., 2015b).

In this work, a system was developed and operated for the first time at room temperature in order to obtain continuous metal extraction based on the IL  $[P_{8888}]$ [oleate]. In this system, selective metal extraction of an aqueous waste stream was done in one compartment, while in a second compartment the IL loaded with the metal was stripped so that the IL could be recirculated to be reused for metal extraction. Also in this study, the long-term stability, degradation and harmfulness of the IL are evaluated, as well as the cost effectiveness of the continuous process.

#### 2. Experimental

#### 2.1. Materials

Tetraoctylphosphonium bromide (>95%) was supplied by lolitec (Heilbronn, Germany). Oleic acid (90%) and sodium oxalate dihydrate (98%) were delivered by Alfa Aeser (Karlsruhe, Germany). Cobalt(II) chloride hexahydrate (99%) and monobasic hydrogen sodium phosphate ( $\geq$ 99.0%) were delivered by Sigma–Aldrich (Zwijndrecht, Belgium). Sodium hydroxide ( $\geq$ 97%), calcium chloride dihydrate ( $\geq$ 99%) and potassium chloride ( $\geq$ 99%) were delivered by VWR Chemicals (Leuven, Belgium). Chloroform (>99%) was purchased from Rathburn Chemicals Ltd. (Walkerburn, UK).



Fig. 1 – Schematic drawing of the continuous setup for metal extraction and IL regeneration.

1-Palmitoyl-2-oleyl-sn-glycero-3-[phospho-rac-(1-glycerol)] (sodium salt) (POPG) was purchased from Genzyme Pharmaceuticals (Liestal, Switzerland) and L- $\alpha$ -phosphatidylcholine (Egg, Chicken) (EggPC) was from Avanti Lipids (Alabaster, AL, USA). MilliQ water ( $\geq$ 18.2M $\Omega$ cm) used throughout the synthesis and extraction/regeneration experiments utilized and was obtained by a Millipore MilliQ<sup>®</sup> biocel, which used a Q-grade<sup>®</sup> column.

#### 2.2. Synthesis of the ionic liquid [P<sub>8888</sub>][oleate]

For this research the IL was synthesized on a larger scale than previously reported. (Parmentier et al., 2015a) First, oleic acid (57.98 mL, 0.231 mol) was mixed with an excess of NaOH (12.74 g, 0.319 mol) dissolved in 800 mL MilliQ water at 45  $^{\circ}$ C for 3 h in a 1 L flask. Afterwards, [P<sub>8888</sub>][Br] (100 g, 0.177 mol) was added to the reaction mixture and the mixture was stirred for an additional 6 h at 75  $^\circ\text{C}.$  The organic phase was then washed multiple times with water ( $6 \times 500 \text{ mL}$ ) and remaining water was removed by a rotary evaporator (BUNCHI Rotavapor® R-3) and a vacuum oven at 50°C to obtain a slightly yellow viscous liquid as product (135.1g). The yield was 99%. The bromide content was 5 µg mL<sup>-1</sup>. The IL was determined by <sup>1</sup>H NMR (Bruker 400 MHz, CDCl<sub>3</sub>,  $\delta$ /ppm) and the following data was obtained:  $\delta = 0.88$  (m, 15H), 1.26 (m, 54H), 1.48 (m, 14H), 1.60 (m, 2H), 1.99 (m, 4H), 2.17 (t, 2H), 2.37 (m, 8H), 5.32 (m, 2H). MS (ESI) was run and the following data was obtained:  $[P_{8888}(C_{32}H_{68}P)]^+ m/z = 483.6$  (calculated value m/z = 483.9) and  $[oleate (C_{18}H_{33}O_2)]^- m/z = 281.3$  (calculated m/z = 281.5).

#### 2.3. Experimental setup

Fig. 1 presents a schematic drawing of the continuous setup, in which one can observe two mixer-settler extractors placed in series. The solutions are pumped into the extractors using 8 mm outer diameter pipes. *Masterflex L/S* pumps were set for the first experiment at 15 mL min<sup>-1</sup> to get an accurately regulated flow of IL, aqueous metal solution and stripping solution in the set up. This flow rate made sure that the IL had a contact time of more than 4 min with the aqueous metal salt solution Download English Version:

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