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Selective recovery of indium from iron-rich solutions using an Aliquat 336 iodide supported ionic liquid phase (SILP)

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ABSTRACT

Selective recovery of valuable metals from secondary (waste) sources is essential for better resource efficiency. However, low-grade waste streams typically have complex and variable compositions and low concentrations of valuable metals. Therefore, development of novel technologies, able to deal with these complex and variable waste streams, is necessary. In this work, we present a process for the separation and purification of indium from iron-rich matrix solutions making use of a supported ionic liquid phase (SILP). The SILP used in this study was synthesized by impregnating Amberlite XAD-16N with the iodide form of the quaternary ammonium salt Aliquat 336. The SILP was characterized by infrared spectroscopy, elemental analysis, density, specific surface area and porosity and it was tested for the selective recovery of indium. Adsorption was preceded by the addition of an excess of iodide anions to the solution, to form indium iodide species, which were extracted to the ionic liquid of the SILP. A high selectivity for indium over iron could be achieved because iron iodide species are not stable in aqueous medium. The reaction kinetics and several adsorption parameters, including anion concentration, adsorbent mass, stripping and reusability of the adsorbent were investigated, using synthetic binary iron-indium solutions containing iron in large excess in comparison with indium, as is typically the case in low-grade ores or industrial process residues. Finally, the developed indium recovery process was validated on a real leachate of goethite residue. A pure indium solution of 49 mg L^{-1} was obtained with an indium-over-iron mass ratio of 7.9 and a selectivity factor equal to 5400.

1. Introduction

Many industrial metallurgical processes are designed to transform raw materials into marketable products, but unavoidably, they create waste along the flow sheet. Many industrial waste streams are stockpiled in landfills, leading to a loss of resources and vast areas of land being unavailable for other activities [1]. There is also the risk that the linings or dams of landfills or ponds get damaged, which may cause harmful material leaking into the environment [2]. Consequently, there is an increasing trend towards combined remediation and resource recovery strategies for landfills. In addition to reclamation of valuable land, future remediation costs can be drastically reduced and valuable resources may be unlocked. This way, treating waste becomes not only interesting from an ecological point of view, but also economically. Several waste streams are available as (low-grade) secondary sources for metal recovery, including metallurgical slags and sludges, mine tailings, acid mine drainage and industrial process residues, such as goethite. Goethite (FeOOH) is the main residue of the zinc industry produced during precipitation of iron. This precipitate is not suitable to

introduce in the steelmaking industry because of the zinc limitation of the blast furnace, being 0.01% maximum [3]. Due to the presence of undesirable elements in the goethite residue (Zn, Pb, Cd, As, S, etc.) and the large amount produced yearly, the disposal of goethite residue represents a serious environmental, social and economic challenge for zinc producers [3]. On the other hand, zinc refinery residues, like goethite or jarosite, might be a substantial source of indium [4–6], being one of Europe's critical metals as a consequence of its high supply risk and its high economic importance in several high- and green-technological applications [7]. Indium compounds are used in transparent electrodes of liquid crystal displays (LCDs) and plasma displays and as a semiconductor material in photovoltaic solar cells, light emitting diodes (LEDs) and lasers [8–10]. The average concentration of indium within the Earth's crust is only 0.05 mg kg^{-1} and since it only occurs in association with zinc (e.g. in sphalerite), copper (e.g. in chalcopyrite), iron or lead minerals and ores, it is always produced as a by-product [11–13]. In order to increase resource efficiency, the focus should be shifted from recovering metals from primary sources to secondary sources [14]. That is why it becomes more interesting to

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consider goethite residue from the zinc production as a valuable, alternative source for the production of indium. The main issue is that indium is typically present in minor amounts (ppm level) in these low-grade sources. Therefore, much attention is paid to the separation of indium from highly-concentrated contaminants, such as iron [15,16]. A multitude of techniques to recover indium already exist, such as solvent extraction [6,15,17–22], liquid membrane separation [23,24], vacuum chlorinated separation [25], vacuum carbon reduction [26], cation-exchange chromatography [27,28], adsorption using solvent impregnated resins [29–32] or biosorption [33,34]. Ionic liquids (ILs), which are solvents that consists entirely of ions, are considered to be particularly promising for indium recovery [35]. Several ionic liquids were reported to extract indium [36–38]. However, ionic liquids suffer from some drawbacks, like a high viscosity and a difficult separation from the aqueous phase [39]. On an industrial scale, it is much easier to handle solid particles than a viscous liquid. Also, small amounts of indium must be recovered from large volumes of aqueous streams having complex and variable compositions, a task for which adsorption chromatography is typically assumed to be more suitable over other techniques. The use of supported ionic liquid phases (SILPs), in which a thin ionic liquid layer is either covalently anchored or impregnated onto a solid support, is therefore an excellent technique to treat dilute solutions. The selectivity of the SILP for certain metals can be tuned by changing the nature of the ionic liquid impregnated onto the solid resin. The solid resin itself should therefore be porous (with a high surface area) and inert, such as polymeric resins (mostly based on styrene-divinylbenzene copolymers) [40–42], silica beads [43,44], activated carbon beads [43,45], cellulose beads [46], alumina beads [43], titania beads [43] or polymer-silica composite resins [47–49]. As adsorbent materials, SILPs may be used both in batch and column modes, thus having certain advantages over conventional solvent extraction systems, including a higher selectivity and recovery efficiency. Moreover, the SILP technique has a potential for industrial implementation because of the ease with which the indium rich (solid) phase and the indium depleted (aqueous) phase can be separated from each other [50]. The SILP technique has already been described in the literature for the recovery of indium [51,52]. However, in these papers, impurities (such as iron) are removed using a first column prior to indium recovery on a second column. This approach is only suitable for dilute iron solutions, not for solutions containing high iron concentrations, such as the leachates typically obtained from goethite residue, since the first column would saturate almost instantly. In order to achieve selectivity, a new SILP system needs to be developed, so that only indium and no iron is adsorbed. The observation that iron(III) iodide species do not occur in aqueous solution while indium(III) iodide species do, may be exploited to obtain selectivity for indium over iron [53]. This can be done by designing a SILP based on an anion-exchange extractant that comprises iodide anions, such as quaternary ammonium iodide salts. Indium(III) iodide complexes will be adsorbed, whereas, for the iron(III) cations, there is no driving force to interact with the SILP.

In this paper, we studied the selective recovery of indium from iron-rich solutions using Aliquat 336 in its iodide form ([A336][I]) impregnated on Amberlite XAD-16N, as SILP. In addition to the synthesis and characterization of the SILP, we report the parameter optimization experiments from synthetic aqueous mixtures, composed of iron in large excess compared to indium. Finally, the success of the SILP technological strategy was validated in the lab using a real goethite leachate.

2. Experimental

2.1. Chemicals and materials

Amberlite® XAD-16N (20–60 mesh, 200 Å mean pore size), Aliquat® 336 (88.2–93.0% quaternary content), acetone (> 99.5%), iron powder (> 99%, fine), deuterium oxide (99.9 atom% D), dideuterosulfuric acid

solution (99.5 atom% D) and iron(III) oxide ($\geq 99\%$, $< 5 \mu\text{m}$) were purchased from Sigma-Aldrich (Diegem, Belgium). Methanol (99.8%) was purchased from Acros Organics (Geel, Belgium). Potassium iodide (99.9%), sulfuric acid (> 95%), ethanol (99.99%) and sodium hydroxide (99.25%, pearls) were ordered from Fisher Scientific (Loughborough, UK). Iron(III) sulfate hydrate ($\geq 21\%$ Fe), citric acid (100.0%) and hydrochloric acid (37%) were purchased from VWR Chemicals (Leuven, Belgium). Acetonitrile (> 99.5%), hydrogen peroxide (> 35 wt%), calcium chloride dihydrate (> 99.5%) and 1000 $\mu\text{g mL}^{-1}$ ICP standard solutions were purchased from Chem-Lab nv (Zedelgem, Belgium). Phosphoric acid (85%) was obtained from Janssen Chimica (Beerse, Belgium). Anhydrous indium(III) sulfate (synthesis grade) was purchased from Merck Schuchardt OHG (Hohenbrunn, Germany) and anhydrous iron(III) chloride (99%) and calcium oxide (96%) were purchased from Riedel-De-Haën (Diegem, Belgium). Indium(III) chloride tetrahydrate (99.99%) was purchased from abcr GmbH (Karlsruhe, Germany). The silicone/isopropanol solution, used for TXRF analysis, was obtained from SERVA Electrophoresis GmbH (Heidelberg, Germany).

Amberlite® XAD-16N was purified before use (Section 2.4). All other chemicals were used without further purification. All solutions were prepared using 18.2 M Ωcm ultrapure water, produced by a Milli-Q® reference. Aliquat® 336 is a commercial mixture of quaternary ammonium compounds with methyltrioctylammonium chloride as the main component.

Goethite waste residue, kindly supplied by a Belgian zinc producer, was used as a representative low-grade waste material and a potential secondary indium source. The leachate preparation is described below.

2.2. Equipment and analysis

Fourier Transform Infrared (FTIR) spectra were recorded between 4000 and 400 cm^{-1} on a Bruker Vertex 70 spectrometer equipped with a platinum ATR module. CHN elemental analyses were performed using a Thermo Scientific Interscience Flash 2000 CHN(SO) elemental analyzer. A Quantachrome Instruments NOVA 2000e volumetric adsorption analyzer was used to record nitrogen adsorption-desorption isotherms at 77 K. From these, the specific surface area of the SILP material, its pore volume and pore size distribution were calculated, based on the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) method, respectively. Prior to the measurements, the SILP material was degassed under vacuum for 29 h at 100 °C. A Mettler-Toledo pH meter with a Hamilton Slimtrode pH electrode was used for pH measurements. The densities of the SILP materials were measured using an AccuPyc II 1340 pycnometer with a helium gas displacement system. To efficiently separate the precipitates from solution, an Eppendorf 5804 centrifuge with an A-4-44 swing-bucket rotor was used at 4000 rpm for 10 min. The metal content of the aqueous solutions was measured using a Perkin Elmer Optima 8300 Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES), equipped with an axial/radial dual plasma view. Appropriate dilutions were made with 5 wt% hydrochloric acid. Calibration curves, based on five standard solutions of known concentration (0.02, 0.10, 0.25, 1.00 and 10.00 mg L^{-1}), were constructed for all elements in the analysis. Gallium (5 mg L^{-1}) was added as an internal standard to each calibration and sample solution, except for the goethite solutions, where scandium (5 mg L^{-1}) was used as an internal standard. Quality control samples were measured before and after measuring the sample series. All ICP-OES spectra were measured in triplicate. The absence of chloride anions after the metathesis reaction (Section 2.4) was qualitatively confirmed using a benchtop Bruker S2 Picofox Total Reflection X-Ray Fluorescence (TXRF) spectrometer equipped with a molybdenum X-ray source at 50 kV voltage and 600 μA current. Samples for analysis were prepared by mixing the aqueous phase (500 μL) or the organic phase (100 mg) in a polypropylene Eppendorf microtube either with ultrapure water (500 μL) or ethanol (900 μL), respectively. Quartz

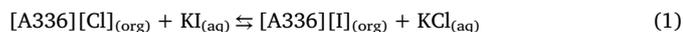
plates, precoated with a Serva® silicone/isopropanol solution (10 µL) were used for the analysis. After drying for 5 min at 60 °C, the sample (3 µL) was dropped on the quartz plate and dried again for 30 min at 60 °C. Each analytical sample was prepared in duplicate and measured for 500 s. A Büchi Rotavapor R-300 rotary evaporator was used to remove excess solvent from the IL phase or the SILP adsorbent particles. A Thermo Scientific MaxQ 2000 orbital shaker was used for all shaking experiments at 175 rpm. The concentration of ionic liquid in the aqueous phase was determined using quantitative ¹H NMR spectroscopy. ¹H NMR spectra were recorded on a Bruker Ascend spectrometer operating at 400 MHz (1024 scans, d1 = 3 s) by adding 10 µL of a 10% methanol standard solution (diluted in deuterium oxide) to 500 µL sample. The SpinWorks software package was used for analysis of the spectra. The technological flow sheet has been drawn using the web-based application draw.io. All experiments were performed at room temperature.

2.3. Selective hydrolysis precipitation of iron

A possible way to separate indium from iron is to selectively precipitate iron by hydrolysis. A first attempt was performed by adding 20 µL H₂O₂ to 10 mL of a binary iron-indium solution at pH 1, containing 7 061 mg L⁻¹ of iron(III) and 69 mg L⁻¹ of indium(III) (sulfate medium). The pH of the solution was adjusted to 3.5 using NaOH 1.0 mol L⁻¹, added dropwise to the solution while stirring vigorously to minimize local excess of base. The precipitate was separated from the solution by centrifugation for 10 min at 4000 rpm and decantation. The residual iron and indium contents in the aqueous phase were measured by ICP-OES. An optimized method consisted of adding CaO particles to the iron-indium solution, instead of NaOH. In addition, solid Fe₂O₃ particles (25 mg) were added to the solution, to act as seeds for iron hydroxide precipitates.

2.4. Synthesis of the [A336][I] and [A336][Cl] SILP

The first step in the [A336][I] SILP synthesis was the anion-exchange metathesis reaction of the ionic liquid with a KI solution to replace the chloride anions of the ionic liquid with iodide anions:



[A336][Cl] (75 g) was first diluted in acetonitrile (30 mL) to enhance phase separation after which it was combined with a 500 g L⁻¹ KI solution (75 mL) (step 1). After stirring the mixture for 2 h in a separatory funnel, the aqueous phase was separated from the organic phase (step 2). Steps 1 and 2 were repeated three more times (the fourth time using only 25 mL of a 500 g L⁻¹ KI solution). To confirm whether all the chloride ions in the [A336][Cl] had been exchanged by iodide anions, both the aqueous and the ionic liquid phase were qualitatively analyzed by TXRF. After quantitatively transferring the [A336][I] ionic liquid to a round-bottom flask and rinsing the separatory funnel twice with acetonitrile (10 mL), the acetonitrile was removed by using a rotary evaporator. After that, the ionic liquid phase became very viscous (to even solid). A 50 g L⁻¹ KI solution (50 mL) was added to the ionic liquid to saturate it with an aqueous phase. After phase separation, the remaining aqueous phase was separated from the organic phase, rendering the [A336][I] ionic liquid ready for impregnation.

Prior to impregnating the solid Amberlite XAD-16N particles with the [A336][I], the Amberlite particles were purified. Sodium chloride salts, contained in Amberlite to retard bacterial growth, were washed out by adding ethanol (250 mL) to the Amberlite XAD-16N resin (200 g) and shaking for 2 h at 170 rpm. It was important to shake rather than to stir, since stirring would damage the beads. Subsequently, the ethanol and dissolved salts were removed from the particles by filtration and the resin was washed twice with a small amount of ultrapure water and once with ethanol. Finally, the ethanol was evaporated and

the solid particles were equilibrated to air.

Physical impregnation was performed by combining [A336][I] (75 g) and the washed Amberlite XAD-16N (75 g) in acetone (375 mL). The mixture was shaken for 24 h, after which the acetone was removed using a rotary evaporator. Then, the SILP was washed three times with ultrapure water (500 mL), each time separating the SILP from the aqueous solution by using a vacuum filtration system. Residual water was removed from the wet SILP by drying in a vacuum oven at 45 °C for 48 h. The SILP was equilibrated to air for another 24 h. The SILP material was characterized by infrared spectroscopy, CHN elemental analysis, density and nitrogen adsorption-desorption isotherms for determination of the specific surface area, the pore volume and the pore size distribution. The characteristic peaks of the FTIR spectrum of the [A336][I] SILP are: 2955 cm⁻¹, 2923 cm⁻¹ and 2855 cm⁻¹ (C–H stretches); 1602 cm⁻¹, 1510 cm⁻¹, 1485 cm⁻¹, 1469 cm⁻¹ and 1456 cm⁻¹ (C=C aromatic ring stretches); 1376 cm⁻¹ (C–H bend); 1117 cm⁻¹ (C–N stretch tertiary amine); 989 cm⁻¹, 900 cm⁻¹, 830 cm⁻¹, 795 cm⁻¹ and 709 cm⁻¹ (aromatic C–H out-of-plane bends). The aromatic peaks arise from the Amberlite XAD-16N support material.

Analogously, an [A336][Cl] SILP was synthesized for comparison. The synthesis procedure was identical to the one described above for the [A336][I] SILP, with the exception that [A336][Cl] was used as such, without exchanging the chloride for the iodide anion. The characteristic peaks of the FTIR spectrum of the [A336][Cl] SILP are similar compared to the peaks of the [A336][I] SILP.

2.5. Adsorption parameters optimization

Metal ion stock solutions were prepared by dissolving the chloride or sulfate metal salts in ultrapure water and acidifying using concentrated HCl or H₂SO₄ solutions, respectively. The pH of the solutions was adjusted by adding a 10 mol L⁻¹ NaOH solution or an 8 mol L⁻¹ acid solution (hydrochloric or sulfuric acid, depending on the counter anion of the synthetic leachate). Since there is no proton or hydroxyl exchange occurring during reaction, buffering the system would only lead to unnecessary addition of chemicals and therefore also an unnecessary cost. Unless stated otherwise, adsorption experiments proceeded as follows. In closed glass vials, SILP particles (100 mg) were added to a binary iron-indium mixture containing In(III) (49 ± 10 mg L⁻¹ for chloride solutions and 65 ± 6 mg L⁻¹ for sulfate solutions) and Fe(III) (10 764 mg L⁻¹ for chloride solutions and 6860 ± 871 mg L⁻¹ for sulfate solutions). The initial pH of the aqueous solutions was 1.0. Reduction of iron(III) to iron(II) was accomplished by the addition of iron powder (300 mg). The adsorption experiments were maintained for 30 min by shaking the solutions at 175 rpm and room temperature. After adsorption, the SILP adsorbent was separated from the liquid by means of a 0.45 µm syringe filter.

Adsorption efficiencies (%A) were calculated using Eq. (2).

$$\%A = \frac{C_i - C_f}{C_i} \cdot 100 \quad (2)$$

where C_i is the initial metal concentration in solution and C_f is the final metal concentration in solution. To confirm that the removal of metal ions from the aqueous solution resulted from adsorption on the [A336][I] SILP and not from precipitation, a blank (without SILP) was always recorded and the more general term “metal removal percentage” is reported on the Y-axis of the graphs. Since the added iron powder dissolves to an unknown and variable extent during each of the adsorption experiments, it was difficult to calculate the adsorption amount from the initial iron concentration. Therefore, results for iron are not presented in the adsorption graphs.

2.6. Stripping parameters optimization

Stripping tests were performed by first loading the SILP using the

optimized adsorption procedure: adding iron powder (300 mg) to a binary iron-indium sulfate solution (10 mL) of pH 1, reacting for 5 min, adding 5 mol L⁻¹ KI (1 mL) and [A336][I] SILP (100 mg) and shaking for 30 min (Section 3.3). Consequently, the loaded SILP (139 ± 1 mg) was contacted with a certain stripping solution (10 mL) for 40 min. Ultrapure water and solutions of different acids (H₂SO₄, HCl, H₃PO₄ and citric acid) in different concentrations were tested for their stripping potential. To separate the SILP from the excess iron powder after the adsorption step, the aqueous solution and the SILP are decanted out of the glass container onto a paper filter, while holding a magnet to the bottom of the container. The magnet prevents the excess iron powder from being poured out. The SILP was washed twice on top of the filter with ultrapure water (twice 5 mL), except for the sample where ultrapure water was investigated as a stripping agent.

The stripping kinetics were assessed by contacting the loaded SILP (125 ± 1 mg) with different volumes of 0.1 mol L⁻¹ H₂SO₄ for several reaction times (between 1 min and 2 h). The stripping efficiency (%S) was calculated by Eq. (3):

$$\%S = \frac{C_s \cdot V_s}{C_i \cdot V_i - C_a \cdot V_a} \cdot 100 \quad (3)$$

with C_s , C_i and C_a being the elemental concentration in the stripping solution, the initial solution and the solution after adsorption, respectively, and V_s , V_i and V_a being the volume of the stripping solution, the initial solution and the solution after adsorption, respectively. Up-concentration of the final product was performed by contacting the loaded SILP twice with a small volume (2 mL) of stripping solution for 40 min.

The selectivity of the recovery process quantifies the preferential uptake of the target element (indium) compared to the interfering matrix element(s) (mainly iron in this case) and is calculated using Eq. (4).

$$S = \frac{\frac{C_{In,s}}{C_{Fe,s}}}{\frac{C_{In,i}}{C_{Fe,i}}} \quad (4)$$

with $C_{In,s}$ and $C_{Fe,s}$ being the indium and iron concentration in the stripping solution, respectively, and $C_{In,i}$ and $C_{Fe,i}$ being the indium and iron concentration of the initial goethite leachate, respectively.

2.7. SILP reusability study

The reusability of the SILP was tested by performing five subsequent (optimized) adsorption – washing – stripping cycles from a binary iron-indium solution. A washing step (twice with 5 mL ultrapure water) was included between the adsorption and the stripping cycle to remove residual (iron-rich) solution from the SILP.

2.8. Indium recovery from an actual goethite residue leachate

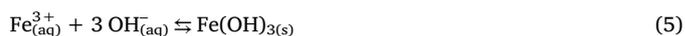
The [A336][I] SILP performance was also tested on an actual goethite residue leachate. Goethite residue (400 g) with a moisture content of 50 wt% was first dried in an oven at 70 °C for 20 h, followed by leaching by addition of 3 mol L⁻¹ H₂SO₄ (600 mL) to the dried goethite and shaking for 24 h at 65 °C. After cooling down to room temperature, the mixture was filtered using a glass filter with a pore size of 10–16 μm. The pH of the goethite residue leachate had a value of 0.1. The metal content was determined by ICP–OES.

3. Results and discussion

3.1. Assessment on the effectiveness and selectivity of the hydrolysis precipitation of iron

Industrial process residues like goethite from the zinc industry are generally composed of a large matrix of major compounds, such as iron

derivatives, typically in combination with other impurities. By conventional leaching methods, these interfering elements end up in the leachate solutions, severely complicating the subsequent separation and purification of the valuable metals, like indium, that are contained in these leachates as well. To simplify the leachate matrix, the selective precipitation of iron from solution, prior to the isolation of pure indium, was studied. By increasing the pH to a level where iron forms hydrolysis products, but indium does not, most iron might selectively precipitate, thus being separated from the pregnant leaching solution. The essential hydrolysis reaction taking place is:



Iron in goethite residue is partly present as Fe(II) and partly as Fe(III). Since the solubility product of Fe(OH)₃ ($K_{\text{sp}} = 6 \cdot 10^{-38}$) is smaller than the solubility product of Fe(OH)₂ ($K_{\text{sp}} = 2 \cdot 10^{-15}$), it is essential for an efficient hydrolysis precipitation step to first oxidize Fe(II) to Fe(III) [54,55]. This can be achieved by adding a small amount of an oxidizing agent (H₂O₂) to the solution. H₂O₂ was chosen because it has a high standard reduction potential and it will not contaminate the sample with other metal ions. The following redox reaction takes place:



As can be seen from Eq. (6), the oxidation of Fe(II) to Fe(III) results in the consumption of hydroxide anions and thus in a pH decrease. Therefore, by measuring the pH in situ, one can ensure that all Fe(II) is oxidized to Fe(III).

In a first attempt, the pH of the binary iron-indium solution containing 7 061 mg L⁻¹ of iron and 69 mg L⁻¹ of indium (sulfate salts) was increased to 3.5 using a 1.0 mol L⁻¹ NaOH solution after addition of a small amount of H₂O₂. Even though the synthetic solutions only contained iron as Fe(III), H₂O₂ was added to mimic the matrix from a real goethite leachate since iron is present in goethite residue partially as Fe(III) and partially as Fe(II). Near quantitative (99.8 wt%) removal of iron was achieved. However, co-precipitation of indium occurred as well (90.6 wt%). Since this method was not selective, a second attempt was made by adding CaO particles instead of a NaOH solution to the iron-indium solution. CaO reacts with water forming Ca(OH)₂, which is also a strong base. However, since this reaction is indirect, local excesses of hydroxide ions are minimized. Unfortunately, the solubility of CaO (or Ca(OH)₂) in water is very low, so that addition of CaO resulted in only a small increase of the solution pH, not sufficient to hydrolyze the present iron ions. In the last attempt, solid Fe₂O₃ particles were added to the system, aimed to act as seeds for the formation of Fe(OH)₃ hydrolysis precipitates. This, however, did not improve the results. In addition to the co-precipitation of indium, the pH increase required for the hydrolysis precipitation of iron consumes considerable amounts of chemicals, especially because the solution needs to be acidified again for further processing. Therefore, A conclusion was made that precipitation is not the preferred technique to separate small amounts of indium from a large matrix of iron in an efficient and selective way and that there is need for an alternative system. This led us to the development of an indium selective SILP system.

3.2. Synthesis of the [A336][I] and [A336][Cl] SILP

Different combinations of solid supports and ionic liquids are possible when synthesizing SILPs. Due to its large specific surface area (800 m² g⁻¹), medium pore size (20 nm) [56] and inert behavior towards metal adsorption, Amberlite XAD-16N was selected as the solid support [57]. This is a nonionic macroporous resin consisting of a styrene – divinylbenzene copolymer. Aliquat 336 (chloride) was selected as the ionic liquid because it is one of the cheapest commercially available ionic liquids and a known extractant for indium(III) [36]. Alternatively, the iodide form of Aliquat 336 was also studied, although this chemical is more expensive and the preparation of the SILP is more

elaborate compared to the commercially available chloride form. The synthesis of the [A336][I] SILP is described in detail in the experimental section (Section 3.2) and consists of a two-step process containing a metathesis and an impregnation step. The synthesis of the [A336][Cl] SILP followed a similar process, but did not require the metathesis step. Aliquat 336, both in its chloride and iodide form, could directly be impregnated onto the support.

Since iodide is lower in the Hofmeister series (more chaotropic) than chloride, the metathesis reaction of [A336][Cl] and KI proceeded very effectively [58]. Three contact times were required for a full exchange of chloride to iodide anions. The success of the metathesis reaction in the ionic liquid was confirmed after the fourth metathesis step by analyzing the chloride content of both the aqueous and the ionic liquid phase using TXRF. From a qualitative TXRF analysis, it was confirmed that no chloride was detectable in neither the aqueous nor the ionic liquid phase. Since emulsification occurred with ultrapure water, it was necessary to saturate the ionic liquid using a 50 g L⁻¹ KI solution prior to the impregnation step. The evaporation step after the impregnation reaction was performed slowly, in order to ensure a homogeneous SILP.

The presence of quaternary ammonium groups on the SILP was proven using FTIR spectroscopy (Section 2.4). Further evidence for the successful impregnation of [A336][I] on the Amberlite resin is provided by CHN elemental analyses of the corresponding materials (Table 1). The most characteristic element is nitrogen since this element is only present in the ionic liquid. By evaluating the differences in nitrogen content, one can clearly see that the Amberlite solid support was successfully impregnated with the [A336][I]. The actual amount of ionic liquid impregnated on the solid support is hard to quantify, since Aliquat 336 is a mixture of compounds. However, from the estimated molar ratio of octyl to decyl groups (2:1), an approximate evaluation of the impregnation efficiency is possible [59]. The percentage of ionic liquid impregnated into the resin was calculated by Eq. (7):

$$\%_{IL} = \frac{C_{N,SILP} - C_{N,support}}{C_{N,IL}} \cdot 100 = \frac{1.2 \text{ wt\%} - 0.1 \text{ wt\%}}{2.4 \text{ wt\%}} \cdot 100 = 46 \text{ wt\%} \quad (7)$$

where C_N refers to the nitrogen concentration in either the SILP, support (Amberlite XAD-16N) or ionic liquid ([A336][I]).

In addition, textural properties of the SILP material were examined by nitrogen physisorption measurements. The obtained isotherms showed a subtle evolution from hysteresis loop type IV for the washed Amberlite XAD-16N resin to hysteresis loop type V adsorption for the [A336][I] SILP material. This indicates that the employed Amberlite resin is largely macroporous and by impregnating the pores with ionic liquid, the SILP material has less porous volume (*vide infra*) and weak adsorbate-adsorbent interactions remain [60]. In our interpretation, this means that the overall metal uptake mechanism from the aqueous phase to the SILP phase is mainly driven by interaction with the ionic liquid layer. The total pore volume of the SILP material (0.88 cm³ g⁻¹) is considerably smaller than the total pore volume of the washed solid support before impregnation (2.03 cm³ g⁻¹). However, the average pore radius of the SILP material (15.3 nm) is larger than of the washed solid support before impregnation (4.4 nm). This is the result of the ionic liquid only being deposited in a thin layer on the surface of the solid support and therefore covering the smallest pores completely, but not the larger ones, resulting to an increase in average pore radius.

Table 1

CHN elemental analysis results for pure Amberlite XAD-16N, [A336][I] and [A336][I] SILP.

	Pure Amberlite XAD-16N	[A336][I]	[A336][I] SILP
C (wt%)	35.4 ± 1.0	64.8 ± 4.7	76.0 ± 0.1
H (wt%)	3.8 ± 1.2	12.2 ± 1.1	9.4 ± 0.2
N (wt%)	0.1 ± 0.1	2.4 ± 0.2	1.2 ± 0.0

From area-volume data derived from the nitrogen adsorption-desorption isotherms, it appeared that the specific surface area of the solid support decreased drastically after impregnation with the ionic liquid: from 939 m² g⁻¹ for the washed Amberlite XAD-16N to 115 m² g⁻¹ for the SILP material. Thus, the surface of the support was largely covered with a layer of material with a less pronounced surface structure. The same observation has been described in a related work on SILP materials and is an additional indication that the impregnation succeeded well [43].

The FTIR spectrum of the [A336][Cl] SILP also indicated the presence of the quaternary ammonium groups (Section 2.4). The CHN analysis of the [A336][Cl] SILP material indicated that the material consisted of 80.7 ± 0.2 wt% C, 10.7 ± 0.1 wt% H and 1.4 ± 0.0 wt% N. The percentage of IL compared to the total mass of the SILP is 52.4 wt%. The specific surface area of the [A336][Cl] SILP was 32.0 m² g⁻¹, the total pore volume of the [A336][Cl] SILP is 0.29 cm³ g⁻¹ with average pore radius of 183 Å and the N₂ adsorption measurements indicated a type III adsorption-desorption loop.

The [A336][I] SILP has a density of 1.0788 ± 0.0015 g cm⁻³ at 24.60 °C and the [A336][Cl] SILP has a density of 0.9893 ± 0.0004 g cm⁻³ at 25.57 °C. When comparing these values to the specific gravity (which is very comparable to the density) of the Amberlite XAD-16N resin and the density of Aliquat 336 in its chloride form, being 1.015–1.025 [57] and 0.8860 g cm⁻³ [61], respectively, and taking into account that the density is expected to increase when exchanging the chloride anion for the iodide anion, it is clear that this is another indication of the successful impregnation of both SILP materials.

3.3. Adsorption parameters optimization

First, the [A336][Cl] SILP (250 mg) was tested for its indium adsorption by varying the chloride concentration in a single-element indium chloride solution (10 mL, 94 mg L⁻¹ In(III)). The influence of different chloride concentrations was investigated by varying the amount of CaCl₂·2H₂O. For the 2 h lasting experiment, the initial pH value of the solutions was 2.0. As can be seen from Fig. 1, the indium adsorption efficiency increases with increasing chloride concentration due to a change in speciation. At a certain chloride concentration, several indium(III) chloride species are present and the predominant species can change when changing the chloride concentration [62]. InCl₃ is extracted to the SILP and forms the [InCl₄]⁻ complex with a chloride anion provided by the SILP [62]. At a chloride concentration of 8 mol L⁻¹, the indium adsorption efficiency reaches 100%. To achieve a 95% indium adsorption efficiency, a 5 mol L⁻¹ chloride solution is sufficient.

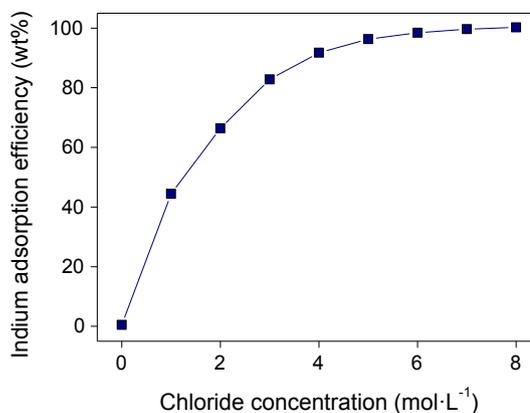


Fig. 1. [A336][Cl] SILP adsorption efficiency from a single-element indium solution as function of the chloride concentration in the feed (10 mL solution, 94 mg L⁻¹ In(III), 0–8 mol L⁻¹ Cl⁻, 250 mg SILP, 2 h adsorption, initial pH 2).

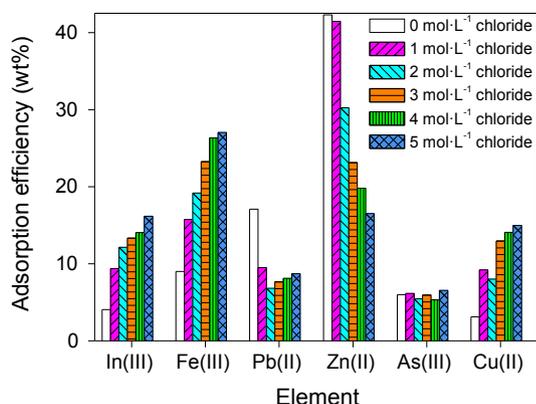


Fig. 2. [A336][Cl] SILP adsorption efficiency from a multi-element solution as function of the chloride concentration in the feed (40 mL multi-element solution, 53 mg L⁻¹ In(III), 0–5 mol L⁻¹ Cl⁻, 5 g SILP, 24 h adsorption, initial pH 2).

With the aim of investigating the influence of other metal ions on the indium adsorption efficiency, a similar experiment was repeated using a multi-element solution containing In(III) (53 mg L⁻¹), Fe(III) (10 764 mg L⁻¹), Pb(II) (269 mg L⁻¹), Zn(II) (1502 mg L⁻¹), As(III) (480 mg L⁻¹) and Cu(II) (41 mg L⁻¹); all present in concentration levels resembling a potential goethite leachate. The amount of SILP (5 g in 40 mL solution) was increased compared to the previous experiment to prevent saturation of the SILP by the competing metal ions. The chloride concentration was again varied using CaCl₂·2H₂O and for the 24 h lasting experiment, the initial pH of the solutions was kept at a constant value of 2.0. As shown in Fig. 2, the indium adsorption efficiency increases with increasing chloride concentration. However, other elements (such as Fe(III) and Cu(II)) follow the same trend. These metals are co-adsorbed to the [A336][Cl] SILP because they form anionic metal chloride complexes similar to those of indium, resulting in contamination of the SILP and reduced indium uptake. Especially the adsorption of iron is a problem, given its high concentration in solution. Selective stripping is not an option, as fast saturation of the SILP would occur first, thus impeding the uptake of indium. Various methods were attempted to reduce co-adsorption of iron (including the removal of iron by hydrolysis precipitation and the reduction of Fe(III) to Fe(II) prior to adsorption, see Section 3.1), but none of these approaches provided a solution to the problem of SILP saturation when applied to solutions with a large iron matrix. Therefore, the [A336][Cl] SILP was not suitable to selectively recover indium from iron-rich solutions.

Because of the unsatisfying results with the [A336][Cl] SILP and based on the knowledge that indium(III) easily forms iodide species (either InI₃ or negatively charged [InI₄]⁻ complexes), whereas iron does not [53], the [A336][I] SILP was studied instead of the [A336][Cl] SILP. By adding an excess of iodide ions to the aqueous feed, indium(III) iodide species are formed, which are adsorbed to the [A336][I] SILP. Iron, on the other hand, either in its ferric or ferrous state, does not form iodide species and is therefore not extracted to the [A336][I] SILP. Importantly, since I⁻ can be oxidized by Fe(III) to I₃⁻, Fe(III) first had to be reduced to Fe(II), thus improving the selectivity for indium and avoiding oxidation of I⁻ to I₃⁻. This was done by exploiting the following comproportionation reaction with iron powder:



In the experiments, iron powder (300 mg) was added to the binary iron-indium solution (10 mL) to reduce the present Fe(III) to Fe(II). In a laboratory environment, iron powder was used as the reducing agent, but on industrial scale, it would be possible to significantly reduce the cost by using iron scrap instead. An excess of Fe powder is required to avoid re-oxidation of Fe(II) to Fe(III) by dissolved oxygen originating from the air. In a later stage, the excess can be recovered and reused.

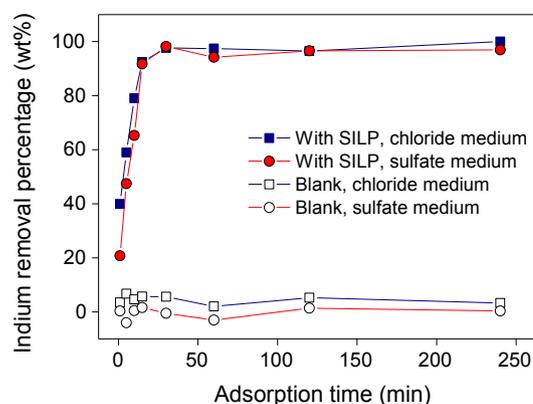


Fig. 3. [A336][I] SILP adsorption kinetics from a binary iron-indium solution in chloride and sulfate media (10 mL solution, 49 ± 10 mg L⁻¹ In(III) and 10 764 mg L⁻¹ Fe(III) (chloride), 65 ± 6 mg L⁻¹ In(III) and 6860 ± 871 mg L⁻¹ Fe(III) (sulfate), 0.45 mol L⁻¹ KI, 100 mg SILP, 1–240 min adsorption, initial pH 1).

Since the main issue in the selective recovery of indium from goethite is the large presence of iron, parameter optimization was conducted on binary iron-indium solutions, composed by iron in major excess compared to indium.

Firstly, the adsorption kinetics were investigated. After shaking the mixture (10 mL solution and 300 mg Fe powder) for 5 min, 5 mol L⁻¹ KI (1 mL) and SILP (100 mg) were added to the mixture while the reaction time was recorded. Both chloride and sulfate media were tested in order to study the influence of the anion on the indium adsorption efficiency. Nitrate media would oxidize I⁻ to I₃⁻ and was therefore not considered. From Fig. 3, it can be seen that the removal of indium from solution was negligible if no [A336][I] SILP was added to the solution (blank). This means that indium removal resulted completely from adsorption and not from another process such as precipitation. The kinetics experiment showed that near complete adsorption of indium (> 95 wt%) was already achieved after 20 min, both from chloride and sulfate media. This indicates that the formation of the indium(III) iodide species proceeded efficiently, regardless of the counter anion present. To ensure that equilibrium conditions were reached, a 30 min adsorption time was used in the following adsorption experiments.

Then, the influence of the KI concentration on the indium removal percentage was studied, again both in chloride and sulfate media. The results of this experiment are presented in Fig. 4. The addition of iodide to the aqueous solution appeared necessary to adsorb indium from

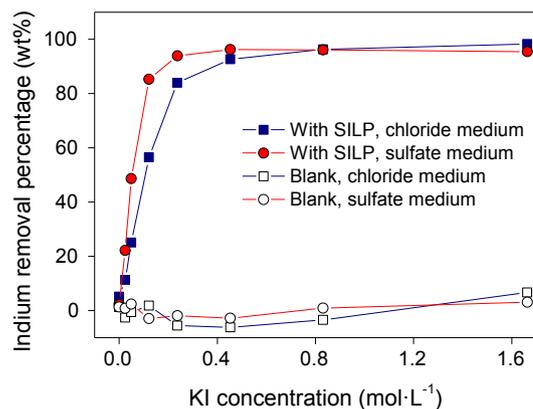


Fig. 4. Influence of the KI concentration on the indium removal percentage using an [A336][I] SILP in sulfate medium (10 mL solution, 49 ± 10 mg L⁻¹ In(III) and 10 764 mg L⁻¹ Fe(III) (chloride), 65 ± 6 mg L⁻¹ In(III) and 6860 ± 871 mg L⁻¹ Fe(III) (sulfate), 0–1.67 mol L⁻¹ KI, 100 mg SILP, 30 min adsorption, initial pH 1).

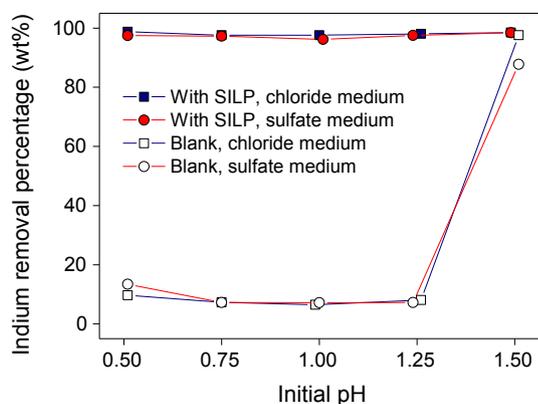


Fig. 5. pH influence on the indium adsorption efficiency using an [A336][I] SILP, both from chloride and sulfate media (10 mL solution, $49 \pm 10 \text{ mg L}^{-1}$ In(III) and 10764 mg L^{-1} Fe(III) (chloride), $65 \pm 6 \text{ mg L}^{-1}$ In(III) and $6860 \pm 871 \text{ mg L}^{-1}$ Fe(III) (sulfate), 0.45 mol L^{-1} KI, 100 mg SILP, 30 min adsorption, initial pH 0.5–1.5).

solution. By adding additional iodide ions to the aqueous feed, the formation of the indium iodide species, which are the ones being adsorbed to the [A336][I] SILP, is enhanced. A minimum KI concentration of 0.4 mol L^{-1} was required to attain almost quantitative recovery of indium. Due to the increasing salt matrix, which interfered with the spectral lines during the metal content determination by ICP–OES, the data were corrected using the gallium internal standard in this experiment. No significant difference was observed between the data for sulfate and chloride media.

The indium adsorption process by the [A336][I] SILP was independent of the solution initial pH, both in chloride and sulfate media, as shown in Fig. 5. A 98% removal efficiency was observed for initial pH values ranging from 0.5 to 1.5. However, the blank measurements also pointed out the importance of keeping the initial pH below 1.25. Above that pH, indium was completely removed from solution, even without addition of SILP. The indium removal might be due to co-precipitation with iron hydrolysis products, of which the formation is aided by the presence of solid iron powder particles. Since the reaction is pH independent (below a certain pH value), it is of more interest to report the initial pH than the equilibrium pH. No proton or hydroxyl exchange occurs during reaction and therefore the initial pH and equilibrium pH will be very similar. Even if small changes in pH would occur, this would have no effect on the results as the adsorption efficiency remains the same at all pH values, as can be seen in Fig. 5. The idea of this paper is to implement this system on a real life situation, namely to recover indium out of a real goethite leachate. In industry, a column setup is preferred as this can be used in a continuous way. However, in column setups, it is very difficult to regulate the pH during adsorption (on the column) and therefore it is more interesting to know the initial pH of the solution, especially with the knowledge that no proton or hydroxyl exchange takes place and therefore the pH will not fluctuate during adsorption. This is why initial pH values are reported instead of equilibrium pH values.

Given the similar adsorption behavior from chloride and sulfate environment, only sulfate solutions were considered for further experiments. The main reason is that sulfuric acid is a more interesting leaching agent on industrial scale, both from an economic and environmental point of view. Sulfuric acid is a simple, inorganic acid that is less corrosive and volatile than hydrochloric acid and can be obtained at a much lower cost than nitric acid.

As a final parameter, the adsorption capacity of the [A336][I] SILP was investigated. This information is especially useful if one wants to use the SILP materials in a column configuration. The results of this experiment are shown in Fig. 6. As expected, the higher the added amount of SILP, the higher the indium adsorption. An amount of

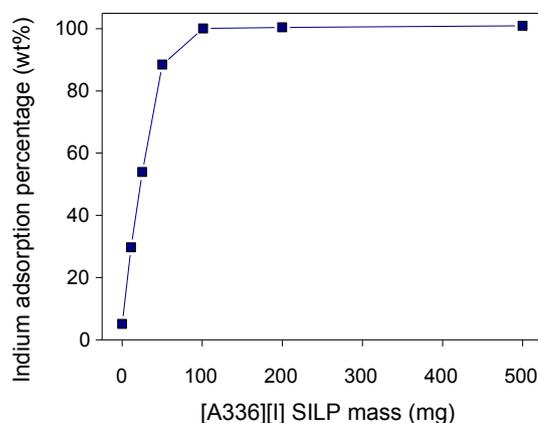


Fig. 6. Influence of the amount of [A336][I] SILP on the indium adsorption efficiency from a binary iron-indium solution (10 mL solution, 69 mg L^{-1} In(III) and $6860 \pm 871 \text{ mg L}^{-1}$ Fe(III) (sulfate), 0.45 mol L^{-1} KI, 0–500 mg SILP, 30 min adsorption, initial pH 1).

100 mg of [A336][I] SILP was sufficient to obtain quantitative indium recovery from the binary iron-indium sulfate solution (containing 69 mg L^{-1} of indium).

3.4. Stripping parameters optimization

Based on the extraction mechanism, In(III) could in principle be stripped with water. However, due to the easy hydrolysis of In(III) at high pH, it is advisable to use a slightly acidic solution. Different acids in different concentrations have been tested for their stripping potential. Fig. 7 represents the indium concentration in several stripping solutions, obtained by stripping the loaded and washed [A336][I] SILP with 10 mL of the respective acid in a certain concentration. In none of the stripping solutions, the iron concentration exceeded 3 mg L^{-1} (most of them being under 2 mg L^{-1}). An acid concentration of 0.1 mol L^{-1} was determined to be optimal for all stripping solutions. At lower acidity, an insufficient amount of protons are available to prevent hydrolysis of In(III). At higher acid concentrations, two factors might play a role in the decreasing stripping efficiency. Firstly, the presence of coordinating anions might cause the re-adsorption of other anionic indiate complexes. Secondly, the addition of ions might increase the ionic strength, hence increasing the activity of the free iodide in the strip solution, again resulting in complex formation of the iodide with In(III) and re-adsorption onto the SILP. After evaluation of different acids, H_2SO_4 (0.1 mol L^{-1}) was selected as the most suitable stripping agent. Other stripping solutions could be used, but since adsorption occurs from sulfate media too, it was better to exploit the same anion during

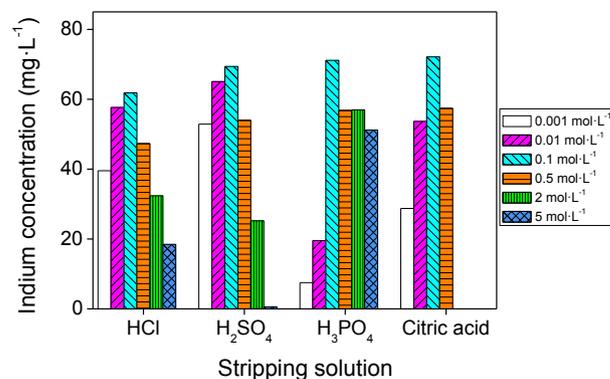


Fig. 7. Indium concentration in several stripping solutions using different acids in different concentrations (optimal adsorption parameters, 10 mL stripping solution, 40 min stripping time, $0.001\text{--}5 \text{ mol L}^{-1}$ acid concentration).

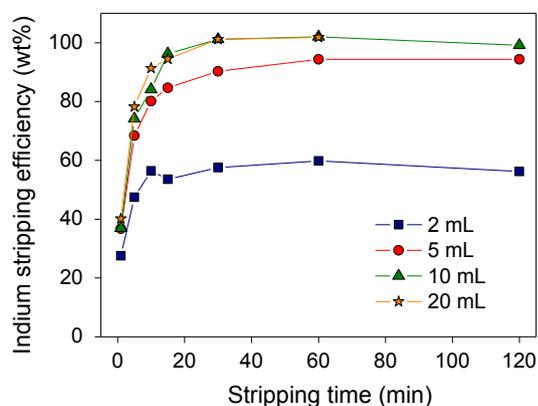


Fig. 8. Influence of the stripping time on the indium stripping efficiency for different volumes of the $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ stripping solution (optimal adsorption parameters, 2–20 mL stripping solution, 1–120 min stripping time, 0.1 mol L^{-1} acid concentration).

stripping. This way, anion cross-over during multiple adsorption – washing – stripping cycles can be avoided.

The influence of the stripping solution volume and time on the indium stripping efficiency is shown in Fig. 8. After 30 min of stripping, equilibrium was reached and the maximum amount of indium desorbed from the SILP. With regard to the stripping solution volume, there is a trade-off between absolute indium concentration and relative indium stripping efficiency. If 2 mL of $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ would be employed, the stripping efficiency equals 60%, whereas this is increased to 100% by employing 10 mL of the same stripping solution. However, when only 2 mL of stripping solution volume is used, the indium concentration in the loaded stripping solution is more than twice as high compared to the concentration in 10 mL of the same stripping solution. Therefore, the effect of using two stripping cycles with a small volume of stripping solution (2 mL each time) was also studied (*vide infra*).

The iron content in the stripping solutions was also measured. For every stripping solution volume, the same amount of iron was stripped from the [A336][I] SILP, resulting in a larger iron concentration for the 2 mL stripping solution volume (25 mg L^{-1}) than for the 20 mL stripping solution volume (3 mg L^{-1}), due to a dilution effect. Compared to the indium concentrations, being 178 mg L^{-1} and 31 mg L^{-1} , respectively, the iron concentrations are very low. Moreover, since the iron concentration in the stripping solutions remained constant over all stripping times, a conclusion was made that the iron present in the stripping solution just resulted from physical contamination of the SILP by the leaching solution. This would mean that the iron concentration could be decreased even more by washing the SILP more thoroughly after adsorption. After stripping the SILP with 2 mL of a $0.1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution, the SILP was used again in a second stripping cycle to strip the indium that was not stripped in the first cycle. This way, a total recovery efficiency of 96.5% was obtained while generating a more valuable product compared to a one-stage stripping step using a larger volume of stripping solution. The indium concentration in the pregnant stripping solution was more than 8 times higher than the iron concentration and a selectivity factor of 847 was reached. At this point, we have shown that the [A336][I] SILP system is very efficient to selectively recover indium from a synthetic iron-rich solution.

3.5. SILP reusability

The indium recovery efficiency was determined for five subsequent adsorption-washing-stripping cycles. The column plot in Fig. 9 clearly indicates that the [A336][I] SILP can be reused several times. As expected, there seemed to be no need to regenerate the SILP material with fresh KI solution between subsequent adsorption cycles, since iodide anions are not readily exchanged for other anions present in the

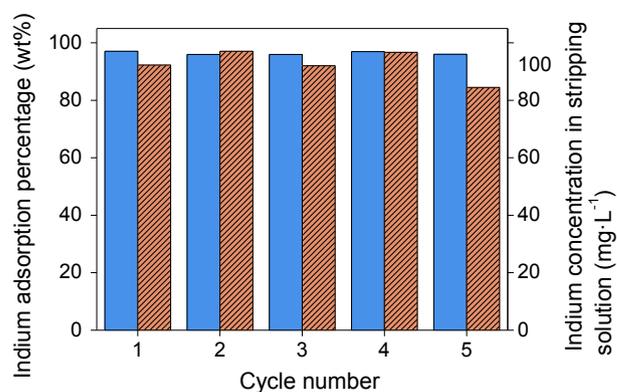


Fig. 9. Column plot of the indium adsorption efficiency (full bars, left Y-axis) and indium concentration in the stripping solution (dashed bars, right Y-axis) over five subsequent adsorption-washing-stripping cycles using the optimal parameters.

aqueous medium (due to its position in the Hofmeister series, Section 3.2). On average, a $96.4 \pm 0.6 \text{ wt}\%$ adsorption efficiency was achieved for the recovery of indium from the iron-rich iron-indium solution and the average indium concentration in the final stripping solutions was $92.5 \pm 5.1 \text{ mg L}^{-1}$. The larger variation on the stripping results compared to the adsorption results might be explained because the same feed solution was used for each adsorption step, while the stripping step was always preceded by a number of manual operations, including a washing step, a transfer of loaded SILP to another vial, etc. Slight variations in these physical handlings have probably caused the higher experimental variability in the stripping results.

Since the ionic liquid is physically impregnated on the solid support, it is important to monitor the loss of the ionic liquid to the aqueous phase, as this can drastically affect the economics of the process. The loss of ionic liquid to the aqueous phase depends on a variety of factors, such as the water solubility of the ionic liquid, the morphology of the porous compound or the characteristics of the aqueous solution (pH, salt concentration, etc.). The solubility of Aliquat 336 into the aqueous phase was reported to be as low as 0.08 g per 100 mL [63]. Also the loss of Aliquat 336 from impregnated resins was determined to be low [64–66]. By exchanging the chloride anion of Aliquat 336 to the more hydrophobic iodide anion, the water solubility is expected to decrease even more. The concentration of Aliquat 336 iodide in the aqueous phase was determined by performing an experiment in deuterated medium using the optimized parameter setup and analyzing the organic content of the aqueous solution after adsorption, the washing solution and the loaded stripping solution by ^1H NMR spectroscopy. By comparing the organic content in the aqueous phases with the organic content on the SILP after washing, stripping and adsorption (Section 3.2), it was concluded that the loss of the ionic liquid to the aqueous phase was in general very limited. For the washing solution and the loaded stripping solution, the loss of ionic liquid to the aqueous phase was determined to be 0.05% and 0.19%, respectively. The loss of ionic liquid to the aqueous phase after adsorption could not be determined as the losses were too low to be quantitatively determined.

3.6. Indium recovery from a real goethite leachate

In order to evaluate the SILP's true potential for the recovery of indium from a typical iron-rich industrial process residue, the optimized adsorption-washing-stripping procedure, based on the binary iron-indium synthetic solution, was applied to a real goethite leachate. The composition of the leachate is presented in Table 2. The indium content in the goethite leachate was very low compared to the remarkably high iron content, resulting in a greater difference than with the synthetic iron-rich solutions.

Table 2
Elemental concentrations of the goethite leachate.

Element	Concentration (mg L ⁻¹)	Element	Concentration (mg L ⁻¹)
Fe	36 230	Cr	108
Zn	17 481	In	53
Al	1915	Ga	37
Cu	1280	Sn	19
As	888	Ni	17
Mg	833	Pb	17
Mn	781	Sb	12
Ca	524	Co	3
K	197	Ge	2
Cd	138	Ba	1
Ti	124	Ce	0

Because many contaminating elements are present in the real leachate compared to the synthetic iron-indium solution, an additional screening test was performed, varying the added amount of iron powder, the amount of SILP and the volume of the 5 mol L⁻¹ KI solution added to the leaching solution. In addition to this, the washing step was improved by washing three times with water (10 mL) for 10 min. Increasing the KI concentration in the reaction mixture did not have a positive influence on the results, so this parameter is not further discussed. The amount of iron powder was either 300 mg or 600 mg and the amount of SILP was either 100 mg or 500 mg. For each of the parameter sets, the elemental concentration of the resulting stripping solution is presented in Table 3. The elements which are not shown, were not detected in the stripping solution.

The best process appears to be the one where 300 mg of iron powder and 500 mg of SILP were added to the feed solution. Although the adsorption percentage from the actual goethite leachate was only 65.8%, the applied method resulted in a relatively pure indium solution containing 49 mg L⁻¹ of In, 8 mg L⁻¹ of Cu and only 6 mg L⁻¹ of Fe. This corresponds to an indium-over-iron mass ratio of 7.9 and a selectivity factor equal to 5414 for the [A336][I] SILP process applied on the real goethite leachate. In conclusion, the presented method is very selective, especially when comparing these values to the respective concentrations in the original leachate (Table 2).

A flowsheet for the recovery of indium from a dilute indium – iron solution, such as a goethite type of leachate, is presented in Fig. 10. The proposed flowsheet is based on a batch process. If this flowsheet would be transformed into a flowsheet for a column setup, some process steps could be eliminated. If, for instance, two columns would be placed in

series, with the first column containing solid iron particles (to reduce iron(III) to iron(II)) and the second column containing the SILP, the ‘filtration + magnet’ step would no longer be necessary since no solid iron particles would be in contact with the SILP particles. The only necessity is a regular refill of the first column with iron scrap. Also, the adsorption, washing and stripping steps may seem as separate steps within the process, but in practice, there is no need to transfer the SILP particles from one column to another. A final, important aspect of the flowsheet is the iodide recovery step. Due to its high price, the systematic addition of potassium iodide to the system would result in fairly high operating costs. In order to obtain a cost-effective process, the iodide from the indium-depleted solutions should be recovered. According to a patented procedure, this can be achieved by another column, containing a polyhalide anion-exchange resin material [67]. The procedure involves the liberation of iodine by oxidation of aqueous iodide through reaction with the reactive halogen (chlorine or bromine) that is available on the polyhalide anion-exchange resin. The liberated iodine then displaces the corresponding halogen in the anion-exchange resin and can be recovered from the resin by a simple solvent such as ethanol, acetone or aqueous sodium hydroxide.

4. Conclusions

A novel flowsheet is proposed for the selective recovery of indium from iron-rich solutions such as goethite residue from the zinc industry. The developed system, based on the SILP technology, appeared to be highly selective. First, an [A336][Cl] SILP was made by physical impregnation of Amberlite XAD-16N with the corresponding ionic liquid. However, it appeared that, besides indium, large amounts of iron (and other contaminants present in a multi-element solution) adsorbed to the SILP as well, leading to immediate saturation of the SILP at the expense of the indium recovery efficiency. By switching to an [A336][I] SILP, co-adsorption of iron could be avoided, since iron does not form iodide species and therefore does not interact with the SILP material. The [A336][I] SILP adsorption procedure was fully optimized and quantitative adsorption was reached for 10 mL of a binary iron-indium solution by addition of 300 mg of iron powder to reduce iron(III) to iron(II), addition of 1 mL of potassium iodide (5 mol L⁻¹) to form the indium(III) iodide species, adding 100 mg of SILP and contacting for 30 min. A two-step stripping procedure, each time with 2 mL of a 0.1 mol L⁻¹ H₂SO₄ solution for 40 min, was determined to be optimal to recover and concentrate the adsorbed indium(III) ions. The SILP system is reusable

Table 3
Elemental composition of stripping solutions for four different parameter sets, varying the added amount of SILP (100 or 500 mg) and iron powder (300 or 600 mg).

	100 mg of SILP		500 mg of SILP	
	Element	Concentration (mg L ⁻¹)	Element	Concentration (mg L ⁻¹)
300 mg of iron powder	Fe	18	Fe	6
	Zn	0	Zn	0
	Al	1	Al	1
	Cu	14	Cu	8
	As	3	As	2
	Ca	1	Ca	1
	K	1	K	2
	Ti	1	Ti	1
	In	1	In	49
600 mg of iron powder	Fe	11	Fe	262
	Zn	0	Zn	0
	Al	1	Al	3
	Cu	0	Cu	0
	As	1	As	6
	Ca	1	Ca	1
	K	1	K	1
	Ti	0	Ti	1
	In	27	In	43

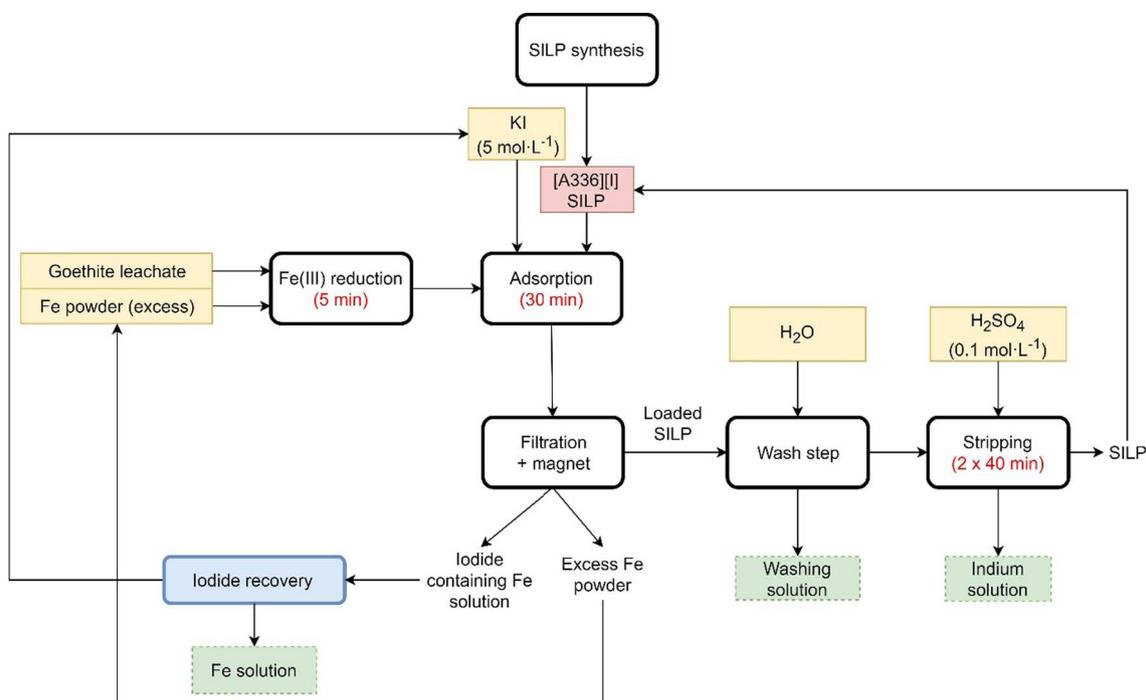


Fig. 10. Proposed flowsheet for the selective recovery of indium from an iron-rich matrix solution using an [A336][I] SILP in batch mode (2-column figure).

in multiple cycles without losses of adsorption or stripping efficiencies and without the need to regenerate the SILP adsorbent with a fresh potassium iodide solution. As a proof-of-concept, the procedure was tested on a real goethite leachate. A pure indium solution of 49 mg L⁻¹ was obtained with an indium-over-iron mass ratio of 7.9 and a selectivity factor equal to 5400. Only copper and iron were identified as minor contaminants in the final stripping solutions, demonstrating the high potential of the developed flowsheet for the recovery of small amounts of indium from a goethite leachate by the [A336][I] SILP.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- [1] J. Esteban-Altabella, F.J. Colomer-Mendoza, A. Gallardo-Izquierdo, Simulation of the behavior of a refuse landfill on a laboratory scale, *J. Environ. Manage.* 204 (2017) 144–151.
- [2] W.M. Mayes, I.T. Burke, H.I. Gomes, Á.D. Anton, M. Molnár, V. Feigl, É. Ujaczki, Advances in understanding environmental risks of red mud after the Ajka Spill, Hungary, *J. Sust. Metall.* 2 (2016) 332–343.
- [3] M. Pelino, C. Cantalini, C. Abbruzzese, P. Plescia, Treatment and recycling of goethite waste arising from the hydrometallurgy of zinc, *Hydrometallurgy* 40 (1996) 25–35.
- [4] A.M. Alfantazi, R.R. Moskalyk, Processing of indium: a review, *Miner. Eng.* 16 (2003) 687–694.
- [5] A. Di Maria, K. Van Acker, Turning industrial residues into resources: an environmental impact assessment of goethite valorization, *Engineering* 4 (2018) 421–429.
- [6] S. Nusen, T. Chairuangstri, Z. Zhu, C.Y. Cheng, Recovery of indium and gallium from synthetic leach solution of zinc refinery residues using synergistic solvent extraction with LIX 63 and Versatic 10 acid, *Hydrometallurgy* 160 (2016) 137–146.
- [7] Study on the review of the list of Critical Raw Materials, EU Publications,

- [8] Y. Li, Y. Tao, F. Zhu, M. Liao, F. Xiong, X. Deng, Distribution and existing state of indium in the Gejiu Tin polymetallic deposit, Yunnan Province, SW China, *Chin. J. Geochem.* 34 (2015) 469–483.
- [9] Critical Materials Strategy. U.S. Department Of Energy, 2010.
- [10] Y.J. Kim, C.W. Hwang, M.H. Jeong, T.S. Hwang, Design of flow through continuous deionization system for indium recovery, *Sep. Purif. Technol.* 176 (2017) 200–207.
- [11] J.C.Ø. Andersen, R.J. Stickland, G.K. Rollinson, R.K. Shail, Indium mineralisation in SW England: host parageneses and mineralogical relations, *Ore Geol. Rev.* 78 (2016) 213–238.
- [12] M. Martin, E. Janneck, R. Kermer, A. Patzig, S. Reichel, Recovery of indium from sphalerite ore and flotation tailings by bioleaching and subsequent precipitation processes, *Miner. Eng.* 75 (2015) 94–99.
- [13] X. Li, C. Wei, Z. Deng, C. Li, G. Fan, H. Rong, F. Zhang, Extraction and separation of indium and copper from zinc residue leach liquor by solvent extraction, *Sep. Purif. Technol.* 156 (2015) 348–355.
- [14] J. Geldermann, L.M. Kolbe, A. Krause, C. Mai, H. Militz, V.-S. Osburg, A. Schöbel, M. Schumann, W. Toporowski, S. Westphal, Improved resource efficiency and cascading utilisation of renewable materials, *J. Clean. Prod.* 110 (2016) 1–8.
- [15] J. Chang, L.B. Zhang, Y. Du, J.H. Peng, G.Y. Hu, J. Chen, C. Srinivasakannan, Separation of indium from iron in a rotating packed bed contactor using Di-2-ethylhexylphosphoric acid, *Sep. Purif. Technol.* 164 (2016) 12–18.
- [16] M.C.B. Fortes, J.S. Benedetto, Separation of indium and iron by solvent extraction, *Miner. Eng.* 11 (1998) 447–451.
- [17] L. Wang, M. Lee, Recovery of indium from secondary resources by hydro-metallurgical method, *J. Kor. Inst. Resour. Recycl.* 22 (2013) 3–10.
- [18] J. Yang, T. Retegan, B.-M. Steenari, C. Ekberg, Recovery of indium and yttrium from Flat Panel Display waste using solvent extraction, *Sep. Purif. Technol.* 166 (2016) 117–124.
- [19] C. Lupi, D. Pilone, In(III) hydrometallurgical recovery from secondary materials by solvent extraction, *J. Environ. Chem. Eng.* 2 (2014) 100–104.
- [20] M. Matsumiya, M. Sumi, Y. Uchino, I. Yanagi, Recovery of indium based on the combined methods of ionic liquid extraction and electrodeposition, *Sep. Purif. Technol.* 201 (2018) 25–29.
- [21] S. Nishihama, T. Hirai, I. Komasa, Separation and recovery of gallium and indium from simulated zinc refinery residue by liquid–liquid extraction, *Ind. Eng. Chem. Res.* 38 (1999) 1032–1039.
- [22] J. Ruan, Y. Guo, Q. Qiao, Recovery of indium from scrap TFT-LCDs by solvent extraction, *Proc. Environ. Sci.* 16 (2012) 545–551.
- [23] R. Guerriero, L. Meregalli, X. Zhang, Indium recovery from sulphuric solutions by supported liquid membranes, *Hydrometallurgy* 20 (1988) 109–120.
- [24] K. Kondo, M. Matsumoto, Separation and concentration of indium (III) by an emulsion liquid membrane containing diisostearylphosphoric acid as a mobile carrier, *Sep. Purif. Technol.* 13 (1998) 109–115.
- [25] E. Ma, R. Lu, Z. Xu, An efficient rough vacuum-chlorinated separation method for the recovery of indium from waste liquid crystal display panels, *Green Chem.* 14 (2012) 3395–3401.
- [26] Y. He, E. Ma, Z. Xu, Recycling indium from waste liquid crystal display panel by vacuum carbon-reduction, *J. Hazard. Mater.* 268 (2014) 185–190.
- [27] K. Kawazu, H. Kakiyama, Cation-exchange chromatography of bismuth(III), Luxembourg, 2017.

- cadmium(II), indium(III) and zinc(II) ions with hydrochloric acid in aqueous acetone solution, *J. Chromatogr. A* 151 (1978) 339–345.
- [28] J. Roosen, S. Mullens, K. Binnemans, Multifunctional alginate–sulfonate–silica sphere-shaped adsorbent particles for the recovery of Indium(III) from secondary resources, *Ind. Eng. Chem. Res.* 56 (2017) 8677–8688.
- [29] H. Li, J. Liu, L. Zhu, X. Gao, S. Wei, L. Guo, S. Zhang, X. Liu, Recovery of Indium(III) from a hydrochloric acid medium with two types of solvent impregnated resins containing sec-octylphenoxy acetic acid, *Solvent. Extr. Res. Dev., Jpn.* 21 (2014) 147–161.
- [30] J.S. Liu, H. Chen, Z.L. Guo, Y.C. Hu, Selective separation of In(III), Ga(III), and Zn (II) from dilute solution using solvent-impregnated resin containing Di(2-ethylhexyl) phosphoric acid, *J. Appl. Polym. Sci.* 100 (2006) 253–259.
- [31] S. Wei, J. Liu, S. Zhang, X. Chen, Q. Liu, L. Zhu, L. Guo, X. Liu, Stoichiometry, isotherms and kinetics of adsorption of In(III) on Cyanex 923 impregnated HZ830 resin from hydrochloric acid solutions, *Hydrometallurgy* 164 (2016) 219–227.
- [32] Y. Yuan, J. Liu, B. Zhou, S. Yao, H. Li, W. Xu, Synthesis of coated solvent impregnated resin for the adsorption of indium (III), *Hydrometallurgy* 101 (2010) 148–155.
- [33] M.A. Meyers, H.A.C. Benavides, S.P. Brühl, H.A. Colorado, E. Dalgaard, C.N. Elias, R.B. Figueiredo, O. Garcia-Rincon, M. Kawasaki, T.G. Langdon, Proceedings of the 3rd Pan American Materials Congress, Springer International Publishing, 2017.
- [34] Y. Konishi, N. Saito, A. Higashi, Indium recovery method, JP5968320B2, 2016.
- [35] P. Rdzanek, J. Marszałek, W. Kamiński, Biobutanol concentration by pervaporation using supported ionic liquid membranes, *Sep. Purif. Technol.* 196 (2018) 124–131.
- [36] C. Deferm, M. Van de Voorde, J. Luyten, H. Oosterhof, J. Franssaer, K. Binnemans, Purification of indium by solvent extraction with undiluted ionic liquids, *Green Chem.* 18 (2016) 4116–4127.
- [37] F. Kubota, Y. Shimobori, Y. Koyanagi, K. Nakashima, K. Shimojo, N. Kamiya, M. Goto, Extraction behavior of indium with TOPO into ionic liquids, *Solvent Extr. Res. Dev.* 16 (2009) 151–155.
- [38] T. Vander Hoogerstraete, B. Onghena, K. Binnemans, Homogeneous Liquid-liquid extraction of metal ions with a functionalized ionic liquid, *J. Phys. Chem. Lett.* 4 (2013) 1659–1663.
- [39] D. Shanthana Lakshmi, A. Figoli, G. Fiorani, M. Carraro, L. Giorno, E. Drioli, Preparation and characterization of ionic liquid polymer microspheres [PEEKWC/DMF/CYPHOS IL 101] using the phase-inversion technique, *Sep. Purif. Technol.* 97 (2012) 179–185.
- [40] S. Bao, W. Hawker, J. Vaughan, Scandium loading on chelating and solvent impregnated resin from sulfate solution, *Solvent Extr. Ion Exch.* 36 (2018) 100–113.
- [41] X. Sun, Y. Ji, J. Chen, J. Ma, Solvent impregnated resin prepared using task-specific ionic liquids for rare earth separation, *J. Rare Earth.* 27 (2009) 932–936.
- [42] A. Arias, I. Saucedo, R. Navarro, V. Gallardo, M. Martínez, E. Guibal, Cadmium(II) recovery from hydrochloric acid solutions using Amberlite XAD-7 impregnated with a tetraalkyl phosphonium ionic liquid, *React. Funct. Polym.* 71 (2011) 1059–1070.
- [43] J. Lemus, J. Palomar, M.A. Gilarranz, J.J. Rodriguez, Characterization of supported ionic liquid phase (SILP) materials prepared from different supports, *Adsorption* 17 (2011) 561–571.
- [44] A. Riisager, K.M. Eriksen, P. Wasserscheid, R. Fehrmann, Propene and 1-octene hydroformylation with silica-supported, ionic liquid-phase (SILP) Rh-phosphine catalysts in continuous fixed-bed mode, *Catal. Lett.* 90 (2003) 149–153.
- [45] A. Weiß, M. Munoz, A. Haas, F. Rietzler, H.-P. Steinrück, M. Haumann, P. Wasserscheid, B.J.M. Etzold, Boosting the activity in supported ionic liquid-phase-catalyzed hydroformylation via surface functionalization of the carbon support, *ACS Catal.* 6 (2016) 2280–2286.
- [46] C. Lee, B. Sandig, M.R. Buchmeiser, M. Haumann, Supported ionic liquid phase (SILP) facilitated gas-phase enzyme catalysis – CALB catalyzed transesterification of vinyl propionate, *Catal. Sci. Technol.* 8 (2018) 2460–2466.
- [47] A. Zhang, Q. Hu, Z. Chai, Synthesis of a novel macroporous silica-calix[4]arene-crown polymeric composite and its adsorption for alkali metals and alkaline-earth metals, *Ind. Eng. Chem. Res.* 49 (2010) 2047–2054.
- [48] A. Zhang, Y. Wei, H. Hoshi, M. Kumagai, Synthesis of a novel silica-based macroporous polymer containing TODGA chelating agent and its application in the chromatographic separation of Mo(VI) and Zr(IV) from diethylene-triaminepentaacetic acid, *Sep. Sci. Technol.* 40 (2005) 811–827.
- [49] A. Zhang, E. Kuraoka, M. Kumagai, Preparation of a novel macroporous silica-based 2,6-bis(5,6-diisobutyl-1,2,4-triazine-3-yl)pyridine impregnated polymeric composite and its application in the adsorption for trivalent rare earths, *J. Radioanal. Nucl. Chem.* 274 (2007) 455–464.
- [50] C. Araneda, C. Fonseca, J. Sapag, C. Basualto, M. Yazdani-Pedram, K. Kondo, E. Kamio, F. Valenzuela, Removal of metal ions from aqueous solutions by sorption onto microcapsules prepared by copolymerization of ethylene glycol dimethacrylate with styrene, *Sep. Purif. Technol.* 63 (2008) 517–523.
- [51] K. Inoue, M. Nishiura, H. Kawakita, K. Ohto, H. Harada, Recovery of indium from spent panel of liquid crystal display panels, *Kagaku Kogaku Ronbun.* 34 (2008) 282–286.
- [52] K. Inoue, S. Alam, Hydrometallurgical recovery of indium from flat-panel displays of spent liquid crystal televisions, *JOM* 67 (2015) 400–405.
- [53] H.M. Irving, F.J.C. Rossotti, J.G. Drysdale, Solvent extraction of indium, *Nature* 169 (1952) 619.
- [54] W.M. Haynes, CRC Handbook of Chemistry and Physics, 92nd ed., CRC Press, 2011.
- [55] L.G. Sillén, A.E. Martell, J. Bjerrum, Stability Constants of Metal-ion Complexes, Chemical Society, 1964.
- [56] S. Bao, Y. Tang, Y. Zhang, L. Liang, Recovery and separation of metal ions from aqueous solutions by solvent-impregnated resins, *Chem. Eng. Technol.* 39 (2016) 1377–1392.
- [57] Rohm and Haas Company, Amberlite XAD-16 Product Data Sheet, Philadelphia, USA, 2003.
- [58] D. Dupont, D. Dupuydt, K. Binnemans, Overview of the effect of salts on biphasic ionic liquid/water solvent extraction systems: anion exchange, mutual solubility, and thermomorphic properties, *J. Phys. Chem. B* 119 (2015) 6747–6757.
- [59] M. Halpern, What is Aliquat 336 and Adogen 464 HF? Let's clear up the confusion, PTC Organics Inc., 2012.
- [60] S. Brunauer, L.S. Deming, W.E. Deming, E. Teller, On a theory of the van der Waals adsorption of gases, *J. Am. Chem. Soc.* 62 (1940) 1723–1732.
- [61] Y. Litaïem, M. Dhahbi, Measurements and correlations of viscosity, conductivity and density of an hydrophobic ionic liquid (Aliquat 336) mixtures with a non-associated dipolar aprotic solvent (DMC), *J. Mol. Liq.* 169 (2012) 54–62.
- [62] C. Deferm, B. Onghena, T. Vander Hoogerstraete, D. Banerjee, J. Luyten, H. Oosterhof, J. Franssaer, K. Binnemans, Speciation of indium(III) chloro complexes in the solvent extraction process from chloride aqueous solutions to ionic liquids, *Dalton Trans.* 46 (2017) 4412–4421.
- [63] J. Xu, R. Paimin, W. Shen, X. Wang, An investigation of solubility of aliquat 336 in different extracted solutions, *Fibers Polym.* 4 (2003) 27–31.
- [64] N. Kabay, Ö. Solak, M. Arda, Ü. Topal, M. Yüksel, A. Trochimczuk, M. Streat, Packed column study of the sorption of hexavalent chromium by novel solvent impregnated resins containing aliquat 336: effect of chloride and sulfate ions, *React. Funct. Polym.* 64 (2005) 75–82.
- [65] I. Pérez-Silva, M.T. Ramírez-Silva, C.A. Galán-Vidal, G.A. Álvarez-Romero, J.A. Rodríguez, M.E. Pérez-Hernández, Evaluation of the use of solvent impregnated resins in the analysis of salbutamol in human urine followed by capillary electrophoresis, *React. Funct. Polym.* 105 (2016) 89–94.
- [66] W. Wei, D.H.K. Reddy, J.K. Bediako, Y.-S. Yun, Aliquat-336-impregnated alginate capsule as a green sorbent for selective recovery of gold from metal mixtures, *Chem. Eng. J.* 289 (2016) 413–422.
- [67] J.F. Mills, Recovery of iodine from aqueous iodide solutions, US Patent US3050369A, 1962.