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„Heavy metal extraction from aqueous solutions using ionic liquids immobilized in polyvinyl alcohol-alginate- and polypropylene beads"

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1. Introduction

Heavy metals (HMs) in the aquatic environment have gained attention since the Industrial Revolution. Processes like fuel combustion or smelting lead to an emission of HMs into the environment, where the aquatic system represents one intermediate stop. Although HMs are not the only group of pollutants in waters (e.g. nutrients, pesticides or polycylic aromatic hydrocarbons to name a few), their behavior is different: Usually, natural processes do not eliminate those metals from the aquatic system and they are enriched in organic substances and minerals (Förstner et al. 2012). To prevent an impact on health, removal of those compounds could be necessary. One example is the contamination of drinking water with As, which is especially a problem in Bangladesh (Mohan et al. 2007). Methods like oxidation, precipitation, coagulation or filtration are used to remove or at least transform As into less toxic species. Low-cost, fast and efficient are the properties which are in particular relevant for use. The establishment of methods with those properties is for other HMs also of great importance.

1.1.   Metal extraction

The term "metal extraction" is affiliated with methods like ion exchange (Dabrowski et al. 2004) or extraction supported with various organic extractants (Danielsson et al. 1978, Tandy et al. 2004). Other, less famous tactics regarding metal extraction have been published like the use of supercritical CO_2 (Laintz et al. 1992) or adsorption on clay (Farrah et al. 1978). Either financial or toxicological reasons might limit the use of those methods, a solution for those boundaries could be the use of Ionic Liquids (ILs).

1.2.   Room Temperature Ionic Liquids (RTILs)

ILs are in general defined as salts, i.e. ionic compounds, in the liquid state. By the addition of the criterion of melting points below 100 °C, the term of room temperature ionic liquids (RTILs) is introduced (Janssen et al. 2015). The ions of those RTILs consist usually of cations, which are non-symmetrical and bulky organic compounds, e.g. imidazolium, pyrrolidinium, pyridinium, ammonium or phosphonium to name a few (Stojanovic et al. 2010) and various anions.

Due to the fact that RTILs are ionic compounds, this group of chemicals shares unique physical and chemical properties compared to other substances in the liquid state at room temperature. Many ILs have negligibly low vapor pressures and are in comparison to common organic solvents fairly non-flammable (Stojanovic et al. 2012). Those two properties make RTILs interesting solvents in synthesis and catalysis (Hallett et al. 2011) when it comes to the aspect of working safe and environmentally friendly. Many solvents which are used in synthesis and catalysis are first of all flammable, which puts the person using the solvent under risk, and second can lead to unwanted reactions in the atmosphere because of their volatility. According to the Austrian Federal Environment Agency, in 2008 163 kt of "non-methane volatile organic compounds" (NMVOCs) have been released in Austria, 59.4 % of those by the "use of solvents and other products" (Frischenschlager 2010) (Fig. 1).
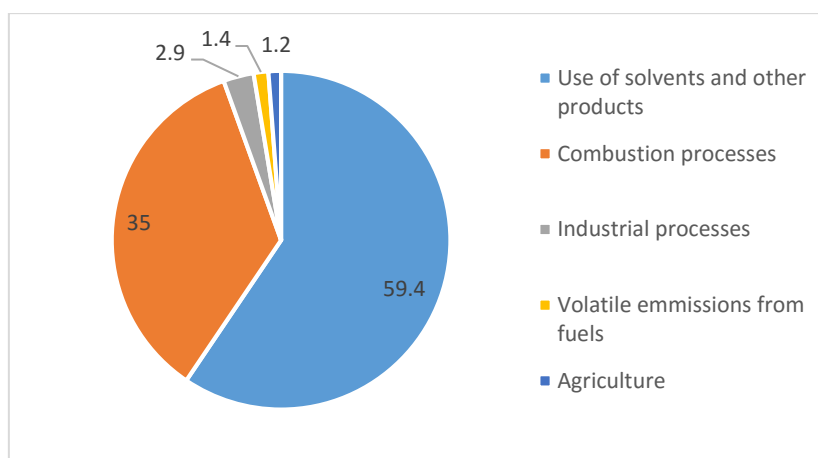
Fig. 1: Proportions in % of polluter groups which contributed to Austrian NMVOC-emissions (in total 163 kt) in 2008 (after Frischenschlager (2010))

1.3.   Task Specific Ionic Liquids (TSILs)

By smart synthesis, the properties of ILs can be shifted through grafting of functional groups, leading to task specific ionic liquids (TSILs) (H. Davis 2004). Many ILs have been designed for different applications, recent developments involve capturing of CO_2 (Raja Shahrom et al. 2016), desulfurization of liquid fuel (Kianpour et al. 2016), separation of n-decane/1-decene (Varyani et al. 2016) or a catalyst for the synthesis of polyvinyl butyral (Qin et al. 2016). The solubility of ILs can be altered as well, making them more hydrophobic (Visser et al. 2002) or more hydrophilic (Vafaeezadeh et al. 2012). Many researchers focus also on the capability of metal extraction from aqueous solutions using TSILs (Stojanovic et al. 2010, Zhang et al. 2011, Janssen et al. 2015, Leyma et al. 2016, Shen et al. 2016).

1.4.   Metal extraction using TSILs

The research on the use of ILs for the extraction of metals has become a hot topic. Recent studies involve the extraction of rare earth metals (Kubota et al. 2016, Shen et al. 2016), Plutonium (Rout et al. 2016), Uranyl complexes (Wu et al. 2016) or heavy metals with toxicological relevance due to their release into the environment (Haixia et al. 2007, Martinis et al. 2008, Escudero et al. 2013).

Because of the ionic nature of ILs, the metal extraction mechanisms are different to the mechanisms known from molecular liquids. Electro neutrality has to be kept in mind while proposing metal extraction mechanisms. Regardless of the mode by which the metal enters the IL phase, the net charge of the aqueous and IL phases cannot change (Janssen et al. 2015). Basically, there are three different types of mechanisms which can lead to an extraction of metals to ionic liquids: Neutral extraction, Neutral coextraction or Ion exchange.

Neutral extraction occurs, when the metal ion forms a complex with an anion and this complex transits into the IL. The reactions can also be assisted by a ligand, which supports the transition into the IL. In the following equations, M^+ denotes a metal ion, X^- an anion, L a ligand, C^+ the cation of the IL and A^- the anion of the IL. Components are either in the aqueous phase denoted with (aq) or in the IL phase denoted with (IL):

$$M^+(aq) \, + \, X^-(aq) \, \rightarrow \, [M \cdot X] \, (IL)$$

$$M^+(aq) \, + L(aq) + \, X^-(aq) \, \rightarrow \, [M \cdot L \cdot X] \, (IL)$$
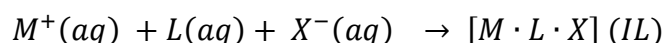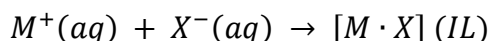
The neutral coextraction mechanism is more or less a special case of the neutral extraction mechanism: A simultaneous transfer of cations and anions into the IL occurs, which preserves electro neutrality.

$$M^+(aq) \, + \, X^-(aq) \, \rightarrow M^+(IL) \, + \, X^-(IL)$$

$$M^+(aq) \, + L(aq) \rightarrow [M \cdot L]^+(aq) + X^-(aq) \rightarrow [M \cdot L]^+(IL) + X^-(IL)$$
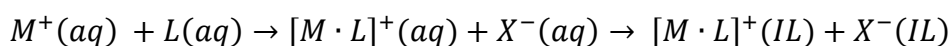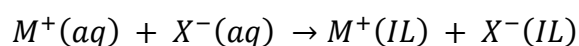
Third and last possible mechanism is the ion exchange mechanism, where the cation of the IL transits into the aqueous phase simultaneously while the metal ion transits into the IL.

$$M^+(aq) \; + \; C^+(IL) \; \rightarrow \; M^+(IL) \; + \; C^+(aq)$$

$$M^+(aq) \; + L(aq) \rightarrow [M \cdot L]^+(aq) + C^+(IL) \rightarrow \; [M \cdot L]^+(IL) + C^+(aq)$$
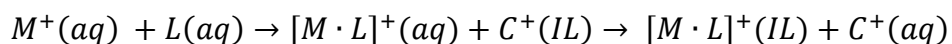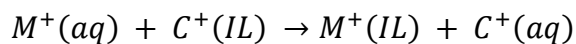
Besides one of the two neutral extraction and one of the two neutral coextraction mechanisms, all of the possible mechanisms mentioned above involve the use of a supporting ligand or the transition of the cation of the IL into the aqueous phase. If those conditions are unwanted, a combination of mechanisms can be induced, by e.g. the introduction of the anion of the IL as a chelating ligand, which could result in the following mechanism:

$$A^-(IL) + X^-(aq) \; \rightarrow \; A^-(aq) + X^-(IL)$$

$$M^+(aq) + A^-(aq) \; \rightarrow \; [M \cdot A] \, (IL)$$
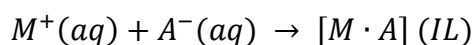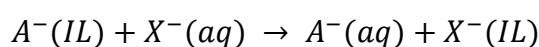
The proposed mechanism would result in a very environmentally-friendly metal extraction. The ligand or the cation of the IL would not leach into the aqueous phase, which could have an impact due to toxicological reasons. Specific TSILs with a hydrophobic cation and an anion, which is hydrophilic enough to transit into the aqueous phase and contains a functional group for the complexation of a metal ion, which could afterwards transit back as a complex into the IL can be synthesized for this application. Other combinations of mechanisms, which lead back to one of those three stated fundamental reactions, are potential pathways, including the combination of two or more reactions leading to an extraction as shown for 1-octyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl] imid, [C_8mim][NTf_2] (Dietz 2006).

1.5.   Toxicity of ILs

The use of ILs is usually supported in literature with the argument that these chemicals are, in comparison to e.g. organic solvents, environmentally friendly. However, a problem which has to be faced when it comes to metal extraction processes is the toxicity of the IL itself. Just like any other chemical, every IL has to be tested for its toxicological effects towards different targets, although general trends have been observed.

If the anion of an IL contains fluorine, it can show toxic effects caused by hydrolysis (Cho et al. 2008), resulting in free fluoride anions which have different modes of toxic interactions

(Camargo 2003, Barbier et al. 2010). Taking a look at cations of ILs, an effect called the "alkyl length chain effect" has been described: Cations, which consist of alkyl chains, show an increase in toxicity when the chain length is increased; this is caused by inhibitory effects or the interaction of the cation with anionic sites of enzymes or lipid bilayers of biological membranes (Stock et al. 2004, Docherty et al. 2005, Stolte et al. 2007). This observation makes the design of several TSILs a double-edged sword, e.g. if the cation is supposed to be hydrophobic: By the increase of the length of alkyl chains of the cation, the polarity decreases, but at the same time the toxicity is increased. This is particularly interesting, because it has been reported that the modification of the hydrophobicity can have an impact on the extraction mechanism (Rout et al. 2015). An approach for a compromise if the hydrophobicity is lowered could be the introduction of an immobilizing agent, which keeps the IL in a defined matrix (Zhang et al. 2011).

1.6.   Immobilization

ILs have been immobilized in different ways for many purposes, e.g. ILs on magnetic nanoparticles (Dadhania et al. 2015) or as peroxometalate-based polymers as catalysts (Doherty et al. 2015), on β-cyclodextrin/attapulgite for the detection of insecticides (Yang et al. 2016) or in PVA-alginate gel beads for mercury extraction (Zhang et al. 2011).

1.7.   Immobilization in Polypropylene

Polypropylene (PP) (Fig. 2) has beneficial features: Low density, high thermal stability and resistance to many corrosives (Karger-Kocsis 2012). Very little studies have been published working on the subject of immobilization in polypropylene in general, involving a work on green tea extracts in films (de Dicastillo et al. 2013) or the enzyme β-galactosidase in membranes (Vasileva et al. 2012). Ramenskaya et al. (2012) worked on the immobilization of ILs on various polymer films, amongst others on polypropylene, showing no satisfactory results with the setup used.
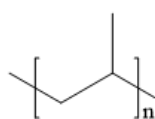
Fig. 2: Structure of polypropylene.

1.8.   Immobilization in Alginate

Alginate gel entrapment is a common technique for immobilization in general, which has been developed for enzymes and might be a possible technique for ILs as well. The big advantages of using alginate as an immobilization agents include mild conditions, a single-step process and simplicity for synthesis; the agent to be immobilized is simply mixed with a sodium alginate solution and afterwards immersed in a hardening solution containing e.g. Ca^{2+} (Fig. 3). Disadvantages which have to be faced using this technique are low stability of the gel and high porosity (Smidsrød et al. 1990).

Calcium alginate beads have already been used for metal extraction, either as pure beads (Esposito et al. 2002, Papageorgiou et al. 2006) or as a supporting matrix for the immobilization of e.g. a white-rot fungus (Kacar et al. 2002, Lai et al. 2008). ILs have also been immobilized in alginate beads (Guibal et al. 2009). If those beads are supposed to be used as a supporting matrix for heavy metal extraction from aqueous solutions, one has to keep in mind that their stability might be limited (Guibal et al. 2009, Cruz et al. 2013) which could lead to a release of ILs into the environment in particular when degradation occurs.
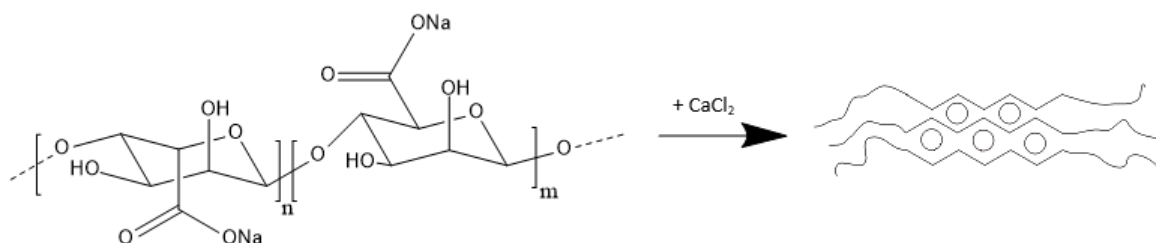
Fig. 3: Formation of the so called "Egg-Box Structure" of sodium alginate by the addition of calcium chloride, redrawn after Grant et al. (1973).

1.9.   Immobilization in Polyvinyl alcohol

Polyvinyl alcohol (PVA) is a water-soluble polymer (Moulay 2015). If the polymer was supposed to be used in aqueous solutions, stabilization steps are necessary. A method which has been described for the immobilization of the enzyme β-galactosidase is freezing and thawing of PVA beads or crosslinking with boric acid (Fig. 4) (Ariga et al. 1989). The preparation of PVA beads has shown another problem: Since it represents a sticky material, the beads tend to agglomerate.
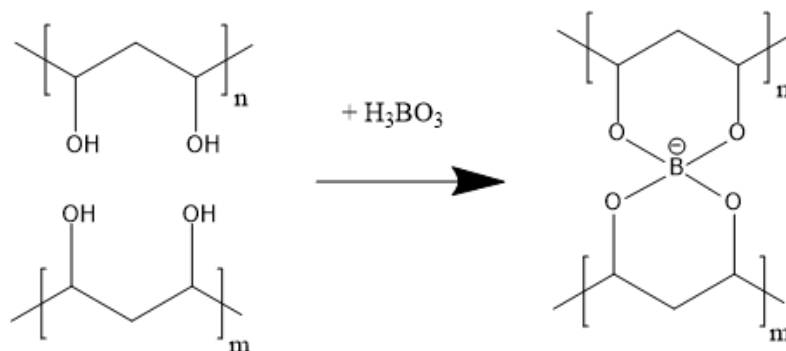
Fig. 4: Crosslinking reaction of PVA with boric acid, redrawn after Zain et al. (2011).

Agglomeration can be suppressed by using a hybrid PVA and alginate method by taking advantage of the faster reaction of the formation of the alginate gel with Ca^{2+}. This prevents agglomeration caused by the relatively slow crosslinking reaction of PVA and boric acid (Wu et al. 1992). Using the PVA-alginate method, one IL has already been immobilized by Zhang et al. (2011). Due to observed instability of these beads, additional hardening steps were proposed to adjust their physical properties, e.g. treatment in a KH_2PO_4-solution (Bae et al. 2015) or in a Na_2SO_4-solution (Fig. 5) (Zain et al. 2011).
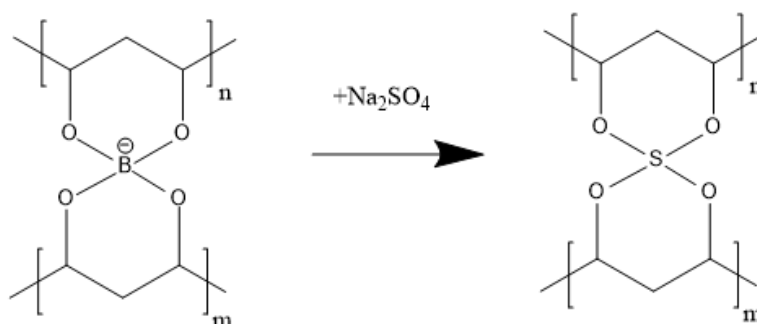
Fig. 5: Substitution of borate in PVA, crosslinked with boric acid, by sodium sulfate, redrawn after Zain et al. (2011).

1.10. Mercury (Hg)

Compared to other metals, Hg is a very special element: It is the only liquid metal at room temperature. It is produced mostly from cinnabar (HgS) and forms alloys with many metals called amalgams. The saturated vapor pressure in air amounts to 15 mg/m^3 at 20 °C. Hg (0) is dissolvable in HNO_3 and does not dissolve in HCl nor H_2SO_4 (Riedel et al. 2011).

According to the United Nations Environment Programme Global Mercury Assessment 2013, Hg is a threat to environmental and human health. In 2010, approximately 1960 tons of Hg have been emitted by human activity. Artisanal and small-scale gold mining and coal burning are contributing with 37 % and 24 %, respectively, which make up almost for two thirds of the emissions (UNEP 2013). Most of the Hg emissions are attributable to anthropogenic sources, re-emissions or re-mobilizations (Fig. 6).
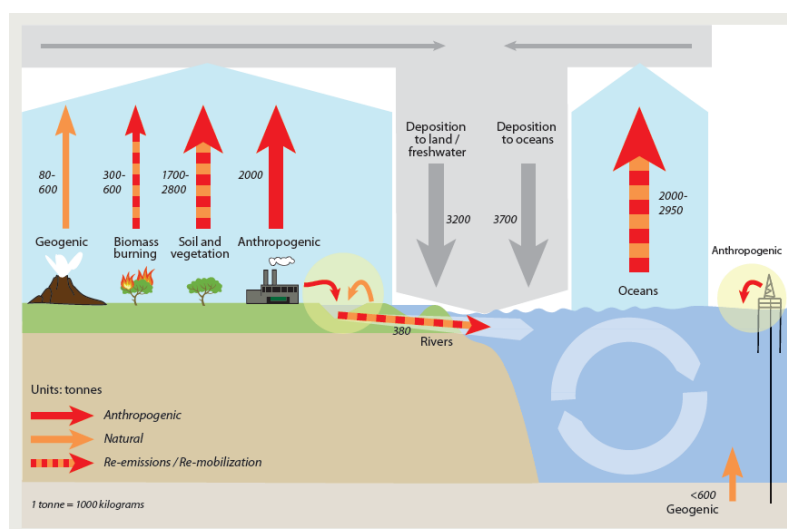
Fig. 6: Anthropogenic sources, natural sources and re-emissions or re-mobilizations of Hg (Figure from (UNEP 2013) © United Nations Environment Programme, 2013, with kind permission by the United Nations Environment Programme)

Metallic mercury, as well as its organic and inorganic compounds are toxic (Riedel et al. 2011, Rice et al. 2014). Inhaled Hg (0) vapors can easily enter the body through the lungs (Rice et al. 2014). Inorganic Hg salts are better watersoluble than elemental Hg and living organisms can be exposed to it through ingestion (Magos et al. 2006). Sulfate-reducing bacteria can synthesize methylmercury (MeHg) from Hg^{2+} ions under anoxic conditions (Compeau et al. 1985), which can be bioaccumulated along the food chain (Mahaffey 1999). Hence, consumption of fish may lead to an exposure of organic Hg for humans. Dimethylmercury is probably the most toxic Hg compound. Dermal contact of minimum amounts of a few microliters can cause death in humans (Joshi et al. 2012). The probably most famous disease caused by heavy metal pollution in general is the Minamata disease, which occurred in the 1950s in Japan. The consumption of Hg contaminated fish by local population caused the Minamata disease, which was officially recognized in over 2000 patients and killed over 1000 of those (Harada 1995). In addition to the environmental aspect, a reduction of Hg emissions at the present time could also lead to economic benefits by avoidance of health impacts (Giang et al. 2016).

1.11. Platinum (Pt)

The natural abundance of Pt is low compared to other precious metals .To obtain pure Pt, a separation of the other platinum group metals (Ru, Rh, Pd, Os, Ir) for purification is necessary as they usually occur in paragenesis (Bernardis et al. 2005). Pt is dissolvable in aqua regia and many of its salts have a characteristic color (Riedel et al. 2011).

In literature, two main sources of Pt in the environment have been discussed: Pt (0) as mechanical friction from automobile catalytic converters (Zereini et al. 1997) as well as hospital effluents, which contain Pt originating from drugs (Kümmerer et al. 1999).

Studies have shown that Pt particles which are released from automobile exhaust catalysts are potentially bioavailable (Artelt et al. 1999) and that Pt has toxic effects on living organisms (Gagnon et al. 2006). Cancerostatic Platinum compounds (CPCs) like cisplatin, carboplatin or oxaliplatin are excreted for the most part via the urine as the original compounds or transformed into other chemical species by patients after administration (Hann et al. 2003, Lenz et al. 2005, Lenz et al. 2007). It is obvious that the release of CPCs can have an impact on living organisms by interacting with DNA (Blommaert et al. 1995, Takahara et al. 1995, Woynarowski et al. 2000).

1.12. Motivation and goals of this work

As already indicated, the emission of heavy metals like Hg or Pt into the environment is a problem because of their toxicity to living organisms. Successful experiments using ILs for heavy metal extraction from aqueous solutions have already been published, but only a negligible amount make the so called leaching, the partly dissolution of ILs in the water phase, a subject of discussion. Because of the toxic potential of ILs, the release of those into the water phase has to be considered with great caution. A possible method to evaluate the quantitative extent of this leaching process, the measurement of dissolved organic carbon (DOC) in the water phase after extraction experiments has been in use, similar to the stand-alone leaching experiments described by Platzer et al. (2015) in which leaching was investigated independently of the metal extraction process. In addition, the evaluation of dissolved nitrogen (DN) would give a better insight in leaching processes, if the IL under investigation contained nitrogen.

The aim of this work was the immobilization of TSILs in polypropylene- and polyvinyl alcohol beads, to identify their potential to extract different Hg and Pt species from aqueous solutions regarding the extraction capacity and leaching of ILs, to pinpoint optimal reaction conditions and to monitor the stripping of extracted heavy metals. Four different Aliquat 336©-based TSILs were synthesized and characterized in our lab during former studies (Stojanovic et al. 2010, Leyma et al. 2016) and have shown their potential for successful heavy metal extraction in preliminary liquid-liquid extraction experiments: Tricaprylylmethylammonium thiosalicylate ([A336][TS]), Tricaprylylmethylammonium 2-(methylthio)benzoate ([A336][MTBA]), Tricaprylylmethylammonium 2-(ethylthio)benzoate ([A336][ETBA]) and Tricaprylylmethylammonium 2-(propylthio)benzoate ([A336][PTBA]) (Fig. 7).
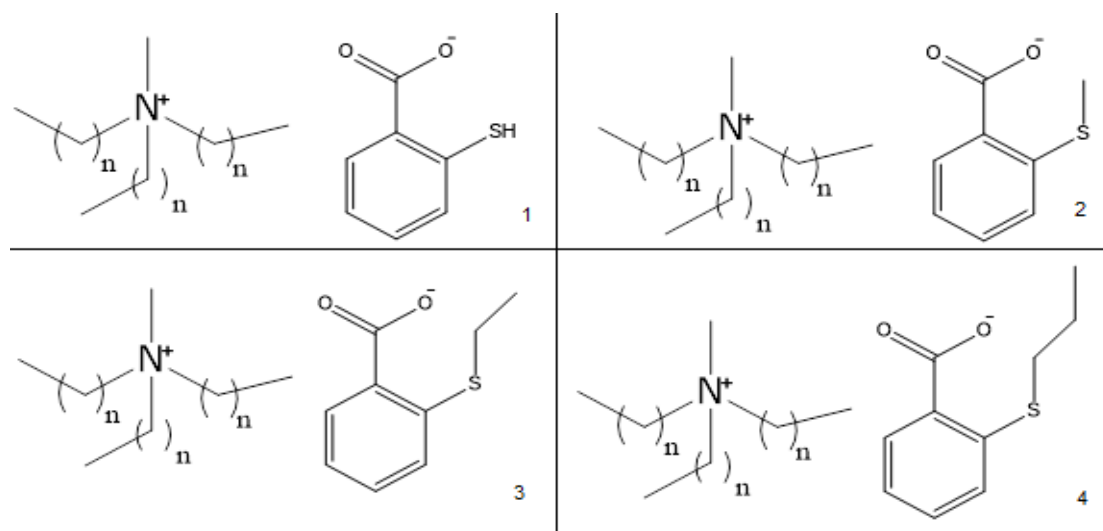
Fig. 7: Structures of the used ILs.

1: [A336][TS]. 2: [A336][MTBA]. 3: [A336][ETBA]. 4: [A336][PTBA]. n=8 or 10, predominantly 8.

PP beads containing approximately 3 % of [A336][TS] and [A336][MTBA] respectively, were provided by Borealis, Linz, Austria. [A336][TS], [A336][MTBA], [A336][ETBA] and [A336][PTBA] in PVA-alginate beads were manufactured for this work in our lab following Zhang et al. (2011), after enhancing the stability of the beads by developing an additional preparation routine following Zain et al. (2011).

The experiments should give insights on the stability of the beads, influence of bead mass, pH, species, anion content and duration on the extraction of Hg and Pt. Loading capacities were evaluated as well as the release of the extracted heavy metals. By determination of DOC and DN values, a first approximation of which bead compounds dissolved into the aqueous solution was performed.

2. Materials and methods

2.1. Chemicals and apparatus

The ILs [A336][TS], [A336][MTBA], [A336][ETBA] and [A336][PTBA] were successfully synthesized and characterized at our Institute for prior studies (Stojanovic et al. 2010, Leyma et al. 2016). Polyvinyl alcohol (PVA) (99+ % hydrolyzed, avg. molecular weight 146,000 – 186,000), sodium alginate, boric acid (BioReagent), sodium sulfate (p.a.), hydrochloric acid (traceselect®), sodium hydroxide and nitric acid (traceselect®) were obtained from Sigma-Aldrich, Germany. Calcium chloride dihydrate (p.a.) was obtained from Fisher Scientific, UK. Mercury extraction experiments were performed using either $Hg(NO_3)_2$ or $HgCl_2$ solutions. A 10 mg/L Hg^{2+} as $Hg(NO_3)_2$ stock-solution in 5 % HNO_3 was prepared by dilution of a "Mercury standard for AAS" (1000 ± 4 mg/L) (traceCERT®), obtained by Sigma-Aldrich, Germany, with 5 % HNO_3 solution. Two additional stock-solutions containing 10 mg/L Hg^{2+} were prepared by dissolving $HgCl_2$ (99.5+ %), obtained by Sigma-Aldrich, Germany, in either 5 % HNO_3 or 3 % HCl. For Pt extraction experiments, a stock-solution containing 10 mg/L Pt^{4+} was prepared using a "Platinum standard solution, 1,000 mg/l Pt in 10% hydrochloric acid AVS TITRINORM® standard for AAS", which consisted of hexachloroplatinic acid in 10 % HCl, obtained from VWR, which was diluted with Millipore water. Further dilutions were performed using Millipore water. (SP-4-2)-diamminedichloroplatinum(II) (cisplatin), cis-diammine(cyclobutane-1,1-dicarboxylate-O,O')platinum(II) (carboplatin) and [(1R,2R)-cyclohexane-1,2-diamine](ethanedioato-O,O')platinum(II) (oxaliplatin) solids were dissolved in acidified Millipore water (as described further below) in our laboratory for extraction experiments. The three compounds were previously synthesized according to literature at the Institute of Inorganic Chemistry, University of Vienna. For dilutions, double deionized water (18.2 MΩ cm) was used from a Milli-Q installation by Millipore. pH values have been adjusted with diluted HNO_3, HCl or NaOH using an EcoSense® pH100 pH electrode. Pt concentrations of the extraction solutions were determined by GF-AAS using a PinAAcle 900Z (Perkin Elmer) instrument. The determination of Hg concentrations of extraction solutions was performed by CV-AAS using a FIMS 400 Mercury Analysis System (PerkinElmer). The measurement of dissolved organic carbon (DOC) and dissolved nitrogen (DN) of the extracting solutions was performed by a TOC-VCPH total organic carbon analyser and a TMN-1 total nitrogen measuring unit by Shimadzu. Determinations of concentrations of all extraction solutions

were performed by calibration with external standards. Polypropylene (PP) beads, consisting of PP-blockpolymers, polyethylene and elastomers and PP beads with an additional content of 3 % [A336][TS] or [A336][MTBA] were obtained from Borealis AG, Linz. Abbreviations for the "PP beads" used are as follows: PP-beads without IL: PP. PP-beads containing 3 % [A336][TS]: PP/TS. PP-beads containing 3 % [A336][MTBA]: PP/MTBA.

2.2.   Immobilization of ILs in PVA-alginate

A method for PVA-alginate production, which has been modified after Zhang et al. (2011) and Zain et al. (2011), was performed for the immobilization of ILs in PVA-alginate: 4.0 g PVA and 0.68 g sodium alginate were weighed in a 250 mL beaker. Following, 50 mL Millipore water were added into the beaker, which was covered with aluminum foil and put into a boiling water bath. Vigorous stirring was carried out with a magnetic stirrer; after 1 h, the mixture was allowed to cool down to below 40 °C. 0.13 g of either [A336][TS], [A336][MTBA], [A336][ETBA] or [A336][PTBA] were added to the mixture and steadily stirred for 6 h at room temperature to adjust the content of IL in the mixture to approximately 3 %. PVA-alginate beads containing no IL were synthesized as well for comparison. A first hardening solution was prepared by adding and dissolving 100 g of H_3BO_3 in 1.5 L of Millipore water, resulting in a supersatured boric acid solution. Thereafter, 45 g of $CaCl_2 \cdot 2\ H_2O$ were added to the supersaturated boric acid solution. The shaping of the beads was performed as follows: The blend containing the IL was drawn up using a syringe with Luer lock and beads formed by squeezing the mixture through a needle (0.90 x 40 mm) into the stirred $H_3BO_3/CaCl_2$-solution, causing a hardening of the blend. After the final drop had been immersed, the beads were stirred for 24 h. The beads were rinsed afterwards twice with 250 mL Millipore water and transferred into 500 mL of a Na_2SO_4-solution for 30 min. A proper concentration of the Na_2SO_4-solution to increase the stability of the beads was determined in an additional experiment (see below). Finally, the beads were rinsed again twice with 250 mL Millipore water, dried over night at 60 °C in a drying oven and stored in PP-tubes until further usage. The abbreviations for beads consisting of PVA-alginate, either pure or with IL are as follows: Polyvinyl alcohol-alginate beads without IL: PVA. Polyvinyl alcohol-alginate beads containing 3 % [A336][TS]: PVA/TS. Polyvinyl alcohol-alginate beads containing 3 % [A336][MTBA]:

PVA/MTBA. Polyvinyl alcohol-alginate beads containing 3 % [A336][ETBA]: PVA/ETBA. Polyvinyl alcohol-alginate beads containing 3 % [A336][PTBA]: PVA/PTBA.

2.3.   Stability of PVA-alginate beads experiments

Due to stability issues of the PVA-alginate beads, as observed in first experiments and as mentioned by Zain et al. (2011), an appropriate concentration of Na_2SO_4 in the hardening solution had to be determined. PVA/MTBA beads were prepared and hardened in a 0.5 M, 1.0 M, 1.4 M, 1.5 M and a supersaturated Na_2SO_4 solution (200 g Na_2SO_4 in 0.5 L Millipore water) for 30 min. An additional experiment was performed in a supersaturated Na_2SO_4 solution (same amounts as used before) for 24 h. Stability was determined by stirring of 0.5 g beads for 24 h in 40 mL Millipore water (pH was adjusted to 3.5 using HCl) in Erlenmeyer flasks, following a measurement of the DOC in the Millipore water.

2.4.   Extraction experiments

For Hg extraction experiments, feed solutions containing 100 µg/L Hg^{2+} in form of $Hg(NO_3)_2$ or $HgCl_2$ were prepared from stock solutions. For Pt extraction experiments, feed solutions containing 1 mg/L Pt^{4+} in form of hexachloroplatinic acid were prepared from a stock solution. Extracting experiments with CPCs cisplatin, carboplatin and oxaliplatin were conducted by dissolving the compounds in acidified Millipore water (100 µL HCl per 1 L Millipore water) to reach concentrations of 1 mg/L Pt^{4+}. Extracting experiments were started within 25-30 min from the moment the dissolving of the CPCs was completed. Due to product supply problems, PVA-alginate extraction experiments with carboplatin were conducted using a 0.65 mg/L Pt^{4+} solution.

All extraction experiments were conducted in 100 mL Erlenmeyer flasks on a magnetic stirrer (140 rpm, 21-22 °C), using 40 mL of the prepared feed solution at a defined pH containing the respective heavy metal species in the defined concentration and a defined mass of beads. To evaluate the eventual loss of metal due to precipitation or wall-adsorption during the experiment, the feed solution without the addition of beads was tested as "blank" in the same way as the experiments using beads. The extraction- as well as the blank experiments were conducted in triplicates. During the experiment "Time dependency of PVA/TS, PVA/MTBA,

PVA/ETBA, PVA/PTBA and PVA on Hg^{2+} extractions" (described below), one of the PVA/TS triplicates was shattered after the 3rd hour, the experiment was continued for PVA/TS beads in duplicates. pH values of the feed solutions were adjusted with diluted NaOH and HNO$_3$ for Hg(NO$_3$)$_2$ extraction experiments, for HgCl$_2$ and all Pt extraction experiments pH values were adjusted with diluted NaOH and HCl. For the time of the experiments flasks were covered with aluminum foil. After the pursued time of the experiment samples were taken out of the flasks using syringes; the samples were filtered through 0.2 µm PTFE pre syringe filters (VWR) and the metal concentration as well as DOC concentrations were determined immediately. If Hg concentrations exceeded the calibration, appropriate dilutions were performed using 2 % HNO$_3$.

The use of triplicates made it possible to use statistics to detect outliers. For this purpose, Dixon's Q test has been used at 95 % confidence.

The extraction capacity (%) was recalculated for each experiment basing on the remaining heavy metal concentration in the blank solutions. If one of the triplicates containing beads showed a higher concentration than the blank solutions (resulting in a negative extraction value), it was not taken into account. If two or three of the replicates containing beads showed higher concentrations than blank solutions, the experiment was classified as "no extraction observed" (labelled with two asterisks **). The following extraction experiments were conducted:

2.4.1. Mercury extraction experiments

Application of PP/TS, PP/MTBA and PP for Hg^{2+} extractions: 3 g of PP/TS, PP/MTBA and PP were stirred in a 100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ solution at pH 3.5 for 24 h.

Bead mass impact of PP/TS and PP on Hg^{2+} extractions: 0.1 g, 1 g, 2 g, 3 g and 4 g of PP/TS and PP were stirred in a 100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ solution at pH 3.5 for 24 h.

Bead mass impact of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA on Hg^{2+} extractions: 0.01 g, 0.05 g, 0.1 g and 0.2 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ solution at pH 3.5 for 24 h.

pH impact on Hg^{2+} extractions with PP/TS and PP: 3 g of PP/TS and PP were stirred in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH 3.5, 4.0 and 5.0 for 24 h.

pH impact on Hg^{2+} extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.2 g of PVA/TS and PVA and 0.05 g of PVA/MTBA, PVA/ETBA and PVA/PTBA were stirred in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH 3.5, 4.0 and 5.0 for 24 h.

Species impact of Hg^{2+} on extractions with PP/TS: 3 g of PP/TS were stirred in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ or $HgCl_2$ solution (latter in either 5 % HNO_3 or 3 % HCl) at pH 3.5 for 24 h.

Species impact of Hg^{2+} on extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.2 g of PVA/TS and PVA and 0.05 g of PVA/MTBA, PVA/ETBA and PVA/PTBA were stirred in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ or $HgCl_2$ solution (latter in either 5 % HNO_3 or 3 % HCl) at pH 3.5 for 24 h.

Time dependency of Hg^{2+} extractions with PP/TS and PP: 3 g of PP/TS and PP were stirred in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH 3.5, samples were taken every hour for 12 h and a final one in the end after 24 h.

Time dependency of Hg^{2+} extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.2 g of PVA/TS and PVA and 0.05 g of PVA/MTBA, PVA/ETBA and PVA/PTBA were stirred in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH 3.5, samples were taken every 2 hours for 11 h and a final one in the end after 24 h.

2.4.2. Platinum extraction experiments

Bead mass impact of PP/TS, PP/MTBA and PP on Pt^{4+} extractions: 0.1 g, 0.5 g, 1 g, 2 g, 3 g and 4 g of PP/TS, PP/MTBA and PP were stirred in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH 3.0 for 24 h.

Bead mass impact of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA on Pt^{4+} extractions: 0.01 g, 0.05 g, 0.1 g, 0.15 g and 0.2 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH 3.0 for 24 h.

pH impact on Pt^{4+} extractions with PP/TS, PP/MTBA and PP: 3 g of PP/TS, PP/MTBA and PP were stirred in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH 3.0, 4.0, 5.0 and 6.0 for 24 h.

pH impact on Pt^{4+} extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH 3.0, 4.0, 5.0 and 6.0 for 24 h.

pH impact on Pt^{4+} (cisplatin) extractions with PP/TS, PP/MTBA and PP: 3 g of PP/TS, PP/MTBA and PP were stirred in a 1 mg/L Pt^{4+} as cisplatin solution at pH 3.0, 6.0, and 9.0 for 24 h.

pH impact on Pt^{4+} (cisplatin) extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 1 mg/L Pt^{4+} as cisplatin solution at pH 3.0, 6.0, and 9.0 for 24 h.

pH impact on Pt^{4+} (carboplatin) extractions with PP/TS, PP/MTBA and PP: 3 g of PP/TS, PP/MTBA and PP were stirred in a 1 mg/L Pt^{4+} as carboplatin solution at pH 3.0, 6.0, and 9.0 for 24 h.

pH impact on Pt^{4+} (carboplatin) extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 0.65 mg/L Pt^{4+} as carboplatin solution at pH 3.0, 6.0, and 9.0 for 24 h.

pH impact on Pt^{4+} (oxaliplatin) extractions with PP/TS, PP/MTBA and PP: 3 g of PP/TS, PP/MTBA and PP were stirred in a 1 mg/L Pt^{4+} as oxaliplatin solution at pH 3.0, 6.0, and 9.0 for 24 h.

pH impact on Pt^{4+} (oxaliplatin) extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 1 mg/L Pt^{4+} as oxaliplatin solution at pH 3.0, 6.0, and 9.0 for 24 h.

Time dependency of Pt^{4+} extractions with PP/TS, PP/MTBA and PP: 3 g of PP/TS, PP/MTBA and PP were stirred in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH 3.0, samples were taken every hours for 9 h and a final one in the end after 24 h.

Time dependency of Pt^{4+} extractions PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA were stirred in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH 3.0, samples were taken every 2 hours for 9 h and a final one in the end after 24 h.

2.5.   Stripping experiments

To check the reusability of the beads, an intermediate step in which extracted metals are released from the beads, so called "stripping", is necessary. Stripping was achieved in the conducted experiments by using a 0.5 M HNO_3 solution, in which the beads were stirred. The progress of the stripping process could be observed by measuring the metal concentration in the HNO_3 solution. Following stripping experiments were conducted:

Stripping of Hg^{2+} from PP/TS, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 3 g and 6 g of PP/TS, 3 g of PP, 0.2 g of PVA/TS and PVA and 0.05 g of PVA/MTBA, PVA/ETBA and PVA/PTBA, which were loaded previously in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution for 24 h, were stirred in a 0.5 M HNO_3 solution for 24 h.

Stripping of Pt^{4+} from PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA: 3 g of PP/TS, PP/MTBA and PP and 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA, which were loaded previously in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution for 24 h, were stirred in a 0.5 M HNO_3 solution for 24 h.

Stripping experiments without measurable quantities were classified as "no stripping observed" (labelled with three asterisks ***).

2.6.   Leaching

Leaching was assessed by the measurement of DOC and DN from the extraction solutions after the experiment was finished. For all bead mass impact on Hg^{2+} extraction experiments, only DOC has been measured. In this series of experiments, DN was not evaluated because of the use of nitrogen containing compounds ($Hg(NO_3)_2$, HNO_3) resulting in meaningless data. By subtraction of the DOC for beads without IL from the DOC for beads containing IL, a first approximation to the order of magnitude of leaching was possible by partitioning in an IL and polymer share. For the bead mass impact on Pt^{4+} extraction experiments, DOC and DN has been evaluated, since no nitrogen containing chemicals were used. The only nitrogen source in the used experimental setup for Pt extractions was the cation of the IL, a further segmenting of the IL share on DOC into cationic IL ([A336]) and anionic IL ([TS], [MTBA], [ETBA] or [PTBA]) share was possible by recalculation of the DN into cationic IL share on DOC and subtraction of the result and the polymer share on DOC from the total IL share on DOC. If the DOC values of

beads containing no IL were higher than the beads containing ILs, or if subtraction of the cationic IL share on DOC and the polymer share on DOC exceeded total DOC, no further recalculation was possible (labelled with one asterisk *).

2.7.   Loading

A value, which helps to determine the efficiency of the extraction is the loading capacity. Since the loading capacity might depend on the concentration of the feed solution, which changes over time in extraction experiments, the term "loading" is used. This term is also used in the case of possibly uncompleted extractions. To calculate the loading, the following formula was used:

$$\frac{\left(\Delta c_{IL}[\mu g/L] - \Delta c_{pure}\,[\mu g/L]\right) * 0{,}04\ L}{Bead\ mass\,[g] * 0{,}03} = Loading$$

Δc_{IL} stands for the difference in metal concentrations between the start and the end of the experiment using beads containing IL, Δc_{pure} stands for the difference in metal concentrations between the start and the end of the experiment using beads containing no IL, 0.04 L is the volume of the feed solution and 0.03 is the percentage of IL in the beads. A loading range was determined by two calculations, using the highest possible value for c_{IL} (mean value + SD) and the lowest possible value for c_{IL} (mean value – SD). Loadings were evaluated as µg Hg^{2+} or mg Pt^{4+} per g of IL.

2.8.   Change in bead mass

After the "Time dependency of Hg^{2+} extractions with PP/TS and PP" and "Time dependency of Hg^{2+} extractions with PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA" experiments, the bead mass was determined after the experiment was over. The beads were dried for several hours in a drying oven at 60 °C and afterwards weighed on a balance.

3. Results

3.1. Stability of PVA-alginate beads

DOC values as an indicator for the stability of beads stirred in a slightly acidic aqueous solution at pH = 3.5 are shown in Fig. 8. The use of a 1.5 M Na_2SO_4 solution for 30 min resulted in the lowest DOC concentration of 138.5 mg/L. Therefore this concentration was chosen for the hardening steps of the subsequent production of PVA-alginate beads.
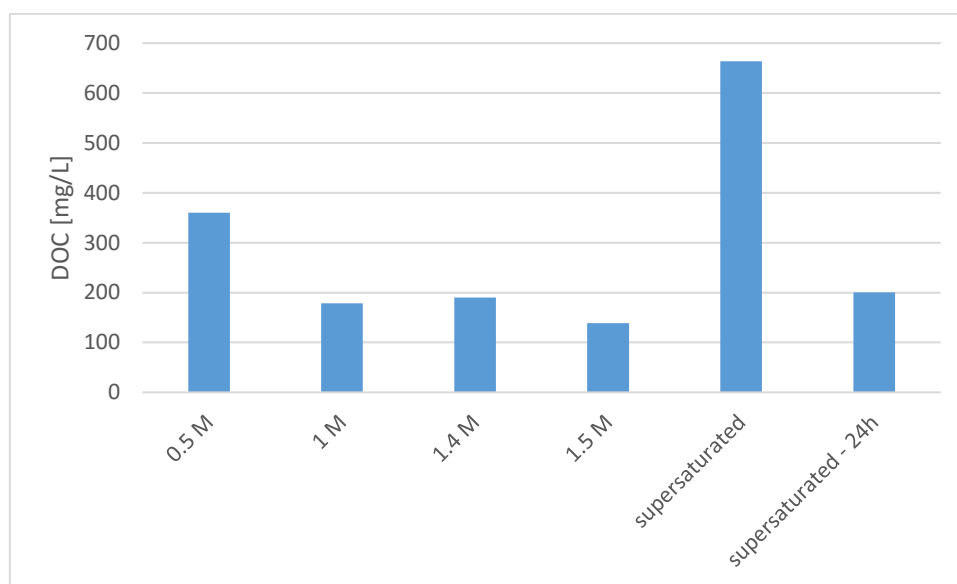
Fig. 8: DOC of 0.5 g PVA/MTBA beads, stirred in Millipore water (pH = 3.5) for 24 h, hardened previously in 0.5 L of various concentrated Na_2SO_4-solutions for 30 min (and in one case for 24 h) (n=1).

3.2. Mercury extraction

3.2.1. Application of PP/TS, PP/MTBA and PP for Hg^{2+} extractions

In an initial experiment at pH=3.5, the extraction potential of PP/TS and PP/MTBA beads was supposed to be evaluated. As illustrated in Fig. 9, PP/TS beads showed a high affinity to Hg with an extraction capacity of 75.8 ± 8.9 %. PP/MTBA beads (7.2 ± 2.1 %) showed no significant difference in extraction capacity compared to PP beads without IL (6.9 ± 1.2 %). Because of this result, no PP/MTBA beads were used in further Hg extraction experiments.
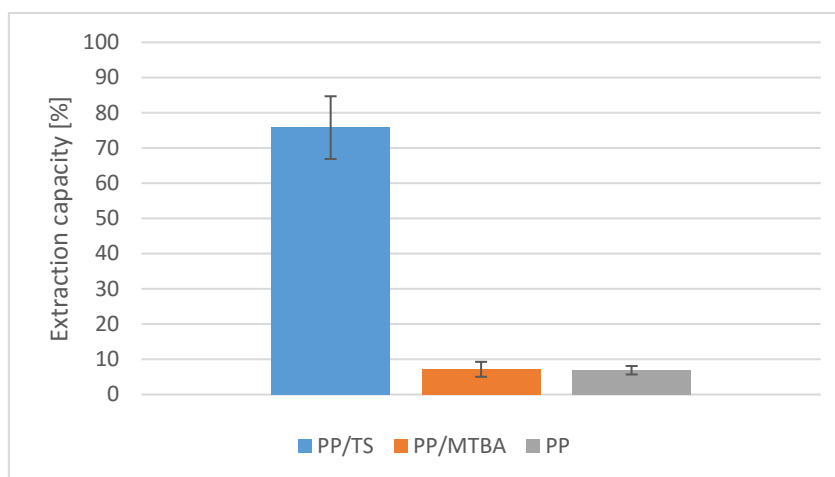
Fig. 9: Mean values ± SD for the extraction capacity of 3g PP/TS, PP/MTBA and PP in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH=3.5 (n=3).

3.2.2. Bead mass impact of PP/TS, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA on Hg^{2+} extractions and loading

Capacity experiments were conducted and showed that increasing the bead mass did not necessarily improve the extraction capacity of Hg, especially for ILs immobilized in PVA-alginate (Fig. 11). The best extraction capacities were gained using 0.05 g for PVA/MTBA, PVA/ETBA, PVA/PTBA, displaying extraction rates of 83.1 ± 0.9 %, 87.2 ± 0.6 % and 91.1 ± 0.4 %, respectively. For PVA/TS and PVA 0.2 g gave best results, showing 87.3 ± 1.0 % and 51.5 ± 3.8 % respective extraction capacities. Therefore further Hg extraction experiments were conducted with the bead masses defined as optimal in this experiment. 2 g PP/TS (93.3 ± 3.5 %) and PP (37.9 ± 10.8 %) as well as 4 g PP/TS (96.3 ± 0.3 %) and PP (15.6 ± 1.9 %) showed significantly better extraction results than 3g of the respective beads (Fig. 10). Anyway, all PP experiments were conducted using 3 g, because the results of this capacity experiment were not known at the time when PP experiments started.
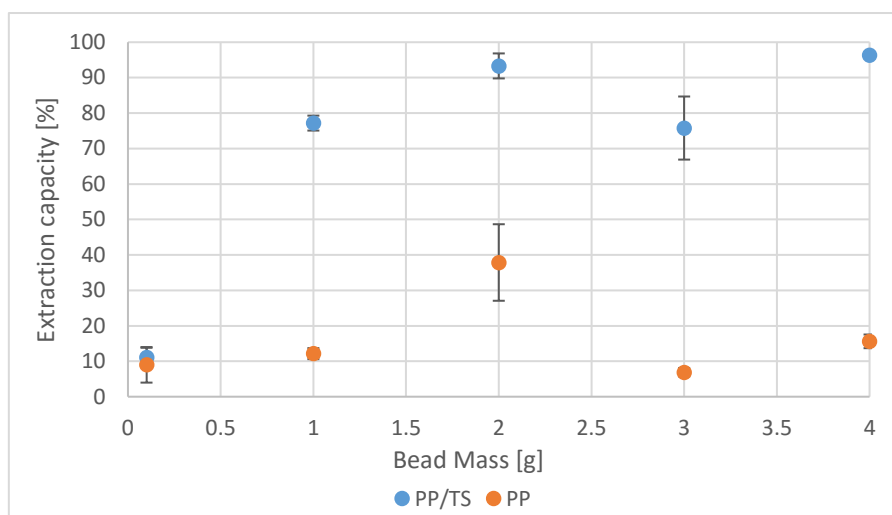
Fig. 10: Mean values ± SD for the extraction capacity of various bead masses of PP/TS and PP in a 100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ solution at pH=3.5 after 24 h(n=3).
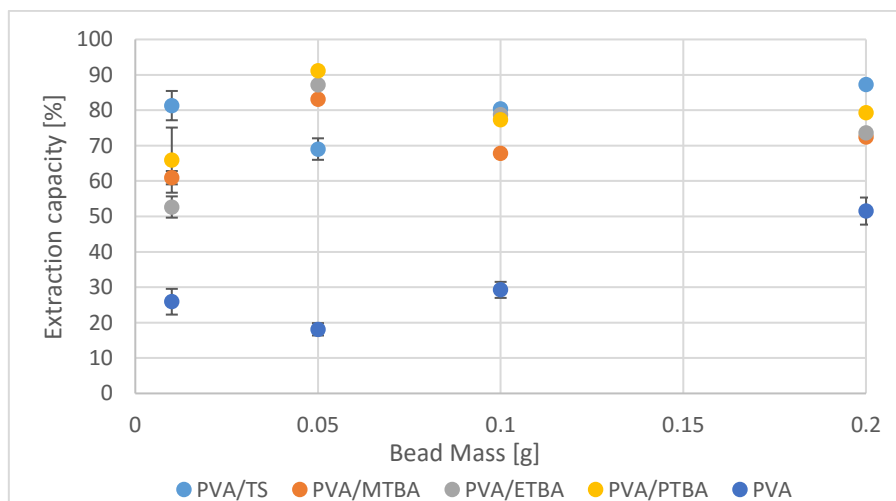
Fig. 11: Mean values ± SD for the extraction capacity of various bead masses of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ solution at pH=3.5 after 24 h (n=3).

The loading has been calculated for this set of experiments, as shown in Table 1 – 5. A trend of decreased loading with increasing bead mass is visible. The highest loading of PP/TS beads was observed at 0.1 g (62.9 – 125.3 µg Hg^{2+}/g IL). For PVA beads containing IL, the dimension of loadings is similar when comparing between same bead masses: 0.01 g and 0.05 g display loadings of over a thousand µg Hg^{2+}/g IL, 0.1 g loadings of several hundred µg Hg^{2+}/g IL and 0.2 g between 100 and 200 µg Hg^{2+}/g IL.

Table 1: Loading ranges of PP/TS for Hg extractions (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5 after 24 h) (n=3).

PP/TS [g]	Loading range [µg Hg^{2+}/g IL]
0.1	62.9 – 125.3
1	57.8 – 62.3
2	27.8 – 31.5
3	28.4 – 36.8
4	23.0 – 23.1

Table 2: Loading ranges of PVA/TS for Hg extractions (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5 after 24 h) (n=3).

PVA/TS [g]	Loading range [µg Hg^{2+}/g IL]
0.01	5750 – 6680
0.05	1380 – 1560
0.1	693 – 701
0.2	188 - 198

Table 3: Loading ranges of PVA/MTBA for Hg extractions (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5 after 24 h) (n=3).

PVA/MTBA [g]	Loading range [µg Hg^{2+}/g IL]
0.01	3720 – 4140
0.05	1850 – 1900
0.1	520 – 531
0.2	110 - 116

Table 4: Loading ranges of PVA/ETBA for Hg extractions (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5 after 24 h) (n=3).

PVA/ETBA [g]	Loading range [µg Hg^{2+}/g IL]
0.01	2660 – 3340
0.05	1970 – 2010
0.1	659 – 693
0.2	117 – 121

Table 5: Loading ranges of PVA/PTBA for Hg extractions (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5 after 24 h) (n=3).

PVA/PTBA [g]	Loading range [µg Hg^{2+}/g IL]
0.01	3860 – 6900
0.05	2090 – 2120
0.1	645 – 666
0.2	146 - 154

3.2.3. pH impact on Hg^{2+} extractions with PP/TS, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

The pH dependency of the extraction capacity of Hg was evaluated for PP (Fig. 12) and for PVA-alginate (Fig. 13) beads. The highest extraction capacity for PP/TS was observed at pH=3.5 with 75.8 ± 8.9 %. PP displayed at pH=3.5 (6.90 ± 1.20 %) and pH=5.0 (5.67 ± 3.40 %) highest extraction capacities. PVA/TS and PVA/PTBA showed an insignificant change when comparing pH=3.5 with 87.3 ± 1.0 % and pH=4.0 with 86.0 ± 0.4 % for PVA/TS and pH=3.5 with 79.3 ± 0.8 % and pH=4.0 with 80.0 ± 0.5 % for PVA/PTBA. The highest extraction capacity for PVA/MTBA was observed at pH=3.5 with 72.4 ± 0.5 %, while for PVA/ETBA this was the case at pH=4.0 with 82.3 ± 2.4 %. Raising the pH to pH=5.0 lead to an improved extraction capacity for pure PVA, which was also the highest of all in this set of experiments with with 89.0 ± 0.4 %.

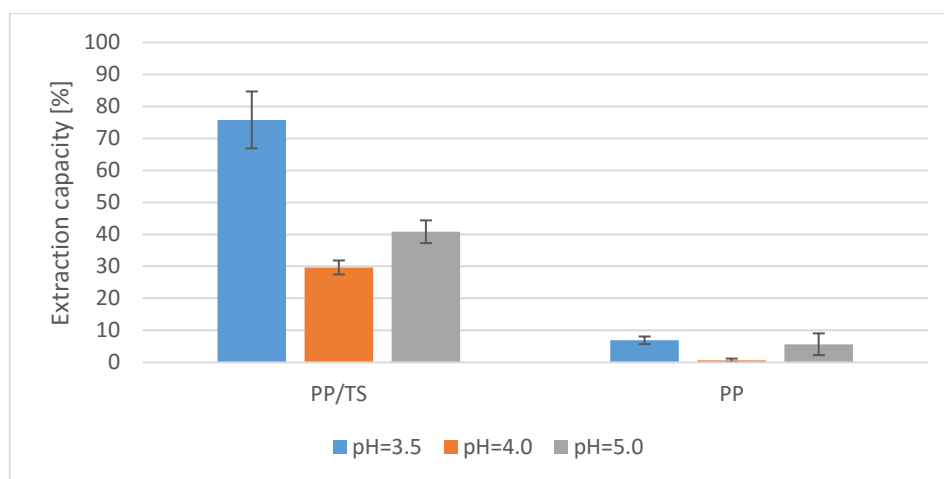*Fig. 12: Mean values ± SD for the extraction capacity of 3 g PP/TS and PP in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH=3.5, 4.0 and 5.0 (n=3).*

Fig. 13: Mean values ± SD for the extraction capacity of 0.2 g PVA/TS and PVA and 0.05 g PVA/MTBA, PVA/ETBA and PVA/PTBA in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH=3.5, 4.0 and 5.0 (n=3).

3.2.4. Species impact of Hg^{2+} on extractions with PP/TS, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

The results for different Hg- species using PP/TS are depicted in Fig. 14. They clearly show a smaller extraction capacity for PP/TS of 36.5 ± 0.1 % for $HgCl_2$ in HCl compared to Hg^{2+} solutions where NO_3^- was the dominant anion. PVA/TS extraction capacities were less dependent on the Hg species than the other PVA-alginate beads (Fig. 15): Slightly increased extraction capacities for $HgCl_2$ in 5 % HNO_3 (90.9 ± 0.5 %) and in 3 % HCl (90.5 ± 0.1 %) were determined when comparing to $Hg(NO_3)_2$ in 5 % HNO_3. The other PVA-alginate beads displayed highest extraction capacities when using $Hg(NO_3)_2$ in 5 % HNO_3: 72.4 ± 0.5 % for PVA/MTBA, 73.6 ± 0.4 % for PVA/ETBA, 79.3 ± 0.8 % for PVA/PTBA and 51.5 ± 3.8 % for PVA. Only PVA/PTBA displayed a significant impact on the extraction capacity when changing the dilution acid of $HgCl_2$: The extraction capacity in 5 % HNO_3 was at 67.7 ± 1.7 % while in 3 % HCl it decreased to 63.5 ± 1.0 %.
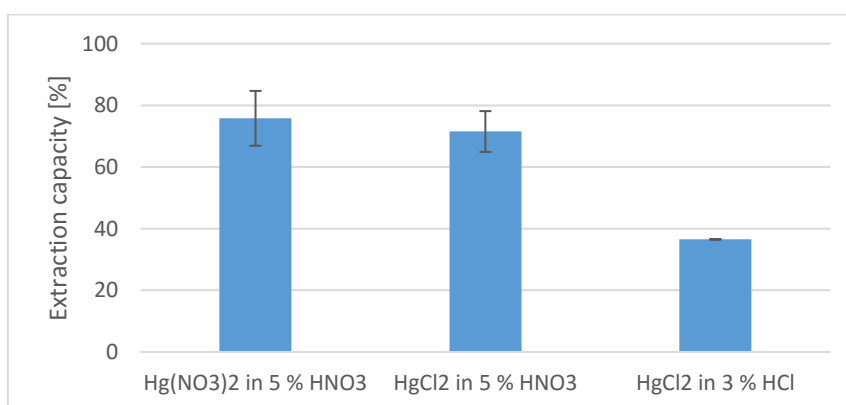
Fig. 14: Mean values ± SD for the extraction capacity of 3 g PP/TS in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ in 5 % HNO_3, $HgCl_2$ in 5 % HNO_3 and $HgCl_2$ in 3 % HCl solution at pH=3.5 (n=3).
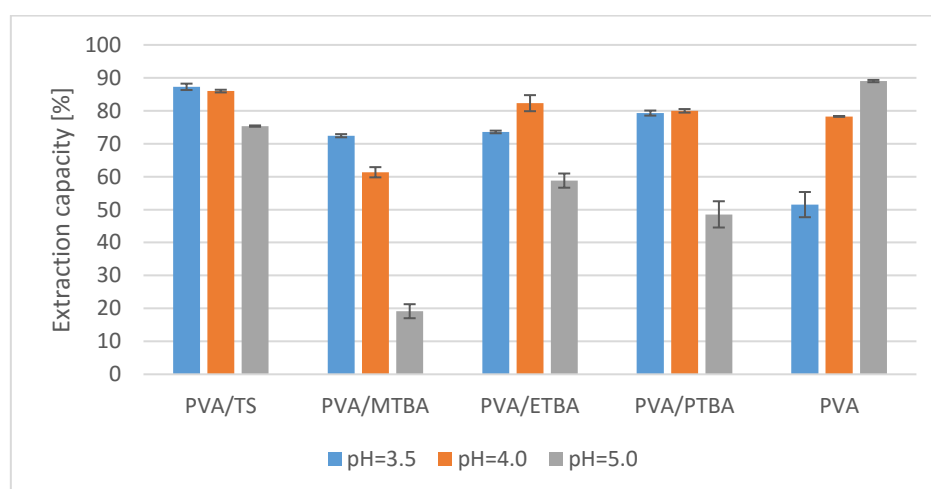

Fig. 15: Mean values ± SD for the extraction capacity of 0.2 g PVA/TS and PVA and 0.05 g PVA/MTBA, PVA/ETBA and PVA/PTBA in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ in 5 % HNO_3, $HgCl_2$ in 5 % HNO_3 and $HgCl_2$ in 3 % HCl solution at pH=3.5 (n=3).

3.2.5. Time dependency of Hg^{2+} extractions with PP/TS, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

The results of the time dependent extraction experiments are depicted in Figures 16&17. The extraction with PP/TS could be observed as slow and steady rising to 39.5 ± 3.8 % after 12 hours and to 68.3 ± 10.1 % after 24 hours. The extraction capacity of PP beads was observed to be constantly low, no significant change was detectable leading to a final extraction capacity of 7.2 ± 4.8 %. The behavior of PVA-alginate beads is more complex: PVA/TS rises rapidly and reaches a steady state after 7 hours (84.0 ± 2.7 %), following an unobserved increase after the 11th hour which was measured with 93.6 ± 2.6 % in the end after 24 hours. In the case of PVA/MTBA and PVA/ETBA, a steady state is reached between the 7th and 9th hour with extraction capacities of approximately 42 % and 53 %, respectively. A significant increase of the extraction capacity is observable at the 11th hour, the values after 24 hours are for PVA/MTBA 68.8 ± 0.9 % and for PVA/ETBA 58.4 ± 0.7 %. PVA/PTBA did not display a steady state, the extraction capacity was at 72.7 ± 0.8 % after 24 h. For PVA, the steady state sets in already after 5 hours and lasts to the 9th hour with an extraction capacity approximately 35 %, although a slight increase after 7 hours (38.0 ± 0.8 %) is observed which decreases afterwards. The extraction capacity of PVA is in the end at 48.8 ± 0.5 %.
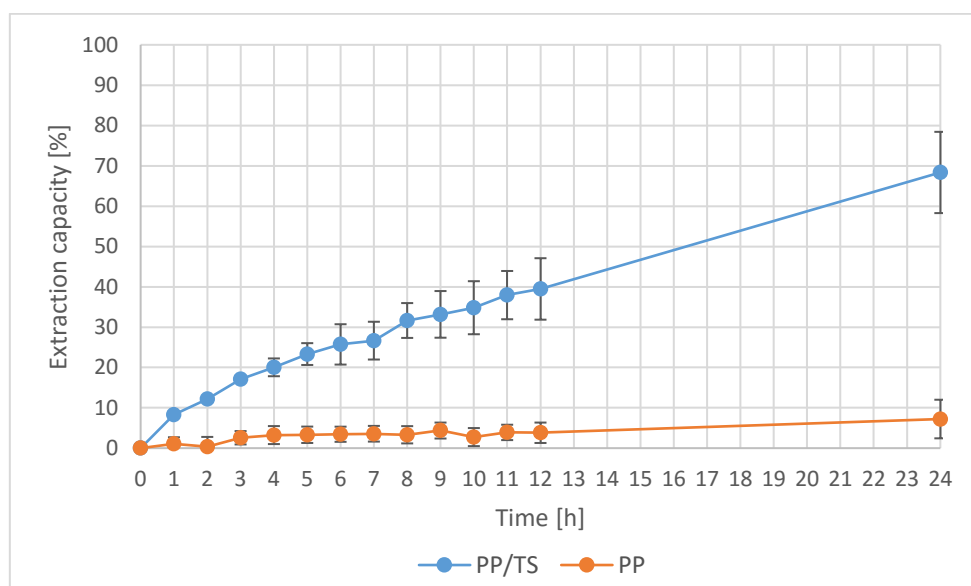
Fig. 16: Mean values ± SD for the extraction capacity of 3 g PP/TS and PP in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution at pH=3.5 during 24 h (n=3).
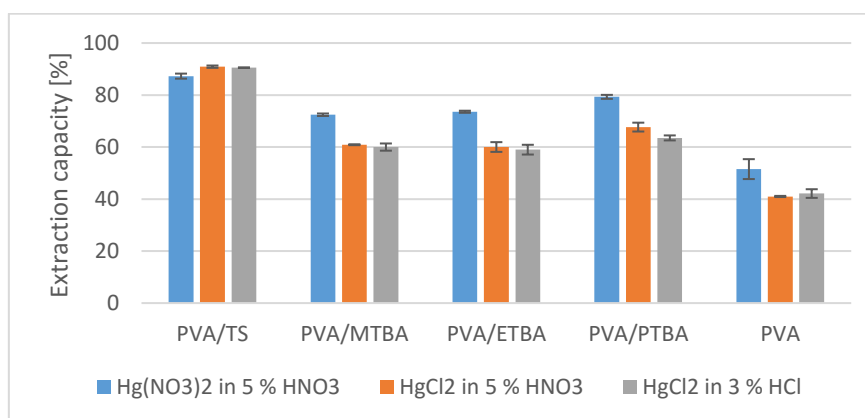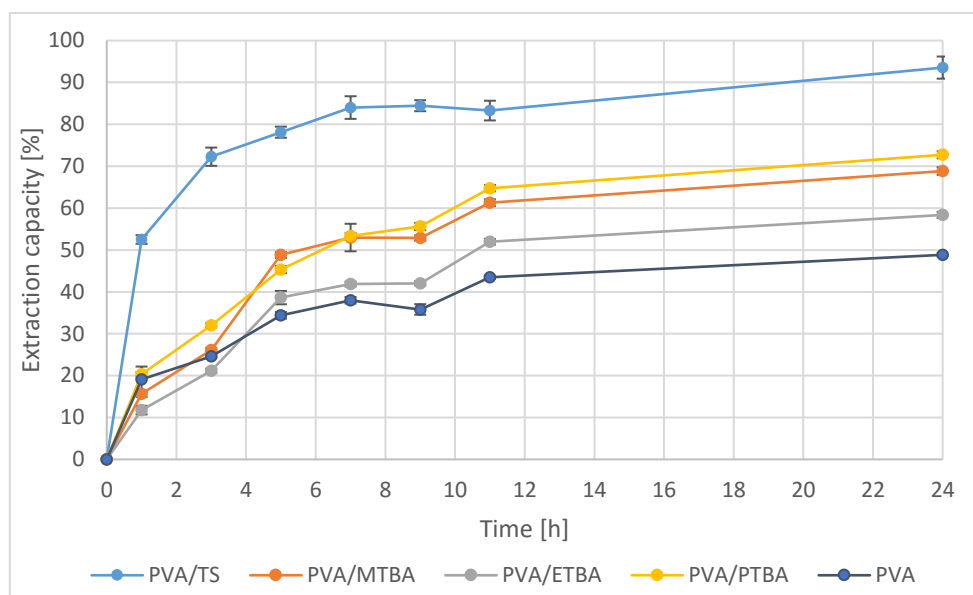
Fig. 17: Mean values ± SD for the extraction capacity of 0.2 g PVA/TS and PVA and 0.05 g PVA/MTBA, PVA/ETBA and PVA/PTBA in a 100 µg/L Hg²⁺ as Hg(NO₃)₂ solution at pH=3.5 during 24 h (n=3, for PVA/TS after 3 hours n=2).

3.2.6. Leaching of PP/TS, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA for Hg²⁺ extractions

DOC has been measured at the end of the capacity experiments. PP/TS featured with 3 g beads after 24 h a peak in the DOC value (10.8 ± 0.4 mg/L) (Fig. 18). The DOC values for PP were below the LOD of 0.6 mg/L. DOC of the PVA-alginate beads increased with higher bead mass, beads with immobilized ILs showed a similar trend (Fig. 19) of increasing DOC with increasing bead mass. Highest DOC values were measured at 0.2 g, for PVA/TS with 79.5 ± 1.4 mg/L, PVA/MTBA with 92.2 ± 3.2 mg/L, PVA/ETBA with 86.7 ± 2.5 mg/L, PVA/PTBA 73.7 ± 0.8 mg/L and PVA with 77.0 ± 3.9 mg/L. DN values have not been interpreted for this set of experiments, therefore only a separation of polymer and IL was possible. According to the recalculation results, the total DOC of PP/TS beads consisted exclusively of [A336][TS] (Table 6). PVA-alginate beads showed a different behavior: The origin of total DOC was for the most part the immobilization matrix (Table 7 - 10). A trend of increased leaching with higher bead mass is visible for PVA/MTBA and PVA/ETBA, for PVA/TS one exception occurs at 0.05 g with no detectable IL leaching. PVA/PTBA beads were the only beads, which did not display any leaching of the IL at all from 0.05 g onwards.
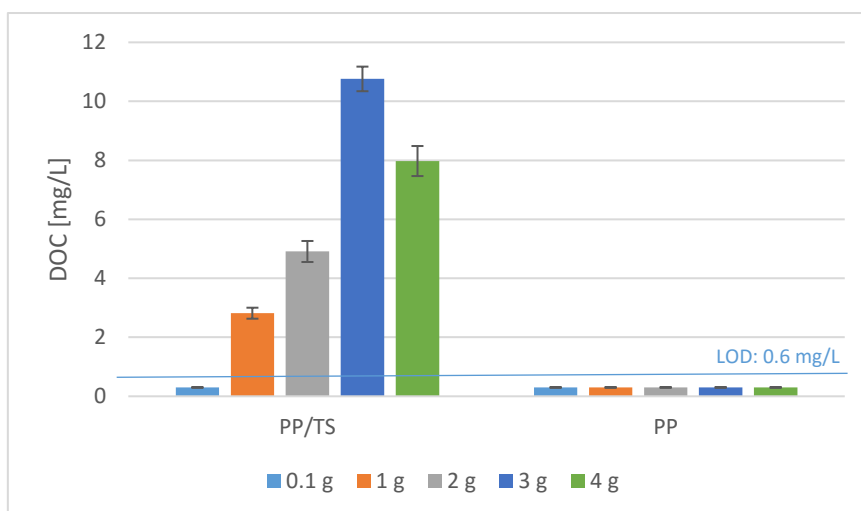
Fig. 18: Mean values ± SD for the DOC of various bead masses of PP/TS and PP in a 100 µg/L Hg²⁺ as Hg(NO₃)₂ solution at pH=3.5 after 24 h of extraction (n=3).
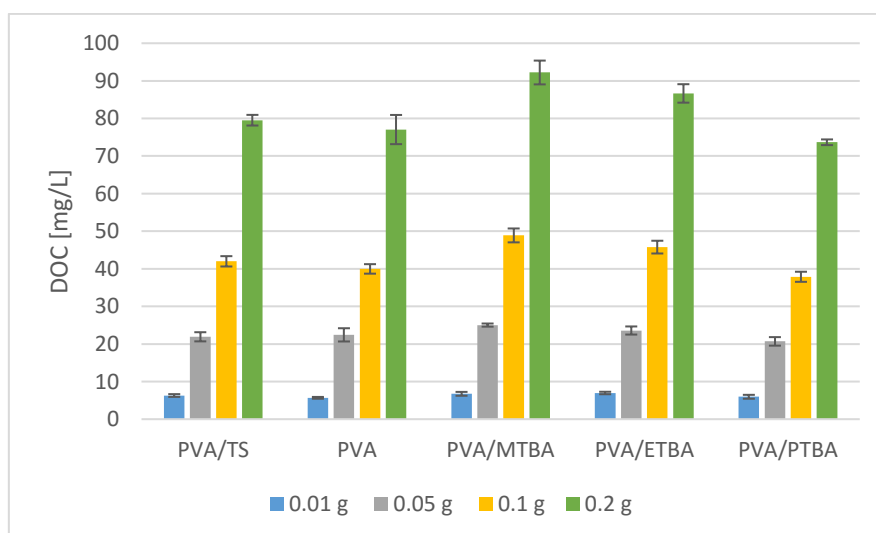
Fig. 19: Mean values ± SD for the DOC of various bead masses of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 100 µg/L Hg²⁺ as Hg(NO₃)₂ solution at pH=3.5 after 24 h of extraction (n=3).

Table 6: Mean values ± SD for the total DOC and the share of DOC derived from PP and [A336][TS] after 24 hours of Hg-extraction (100 µg/L Hg²⁺ as Hg(NO₃)₂ at pH=3.5) (n=3).

Bead mass [g]	Total DOC [mg/L]	DOC from PP [mg/L]	DOC from [A336][TS] [mg/L]
0.1	< 0.6	< 0.6	< 0.6
1	2.8 ± 0.2	< 0.6	2.8 ± 0.2
2	4.9 ± 0.4	< 0.6	4.9 ± 0.4
3	10.8 ± 0.4	< 0.6	10.8 ± 0.4
4	8.0 ± 0.5	< 0.6	8.0 ± 0.5

*Table 7: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][TS] after 24 hours of Hg-extraction (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336][TS] [mg/L]
0.01	6.3 ± 0.4	5.6 ± 0.2	0.7 ± 0.4
0.05	21.9 ± 1.2	22.4 ± 1.8	*
0.1	42.0 ± 1.4	40.0 ± 1.3	2.0 ± 1.9
0.2	79.5 ± 1.4	77.1 ± 3.9	2.4 ± 4.1

Table 8: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][MTBA] after 24 hours of Hg-extraction (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5) (n=3).

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336][MTBA] [mg/L]
0.01	6.7 ± 0.5	5.6 ± 0.2	1.1 ± 0.5
0.05	25.0 ± 0.4	22.4 ± 1.8	2.6 ± 1.8
0.1	48.9 ± 1.9	40.0 ± 1.3	8.9 ± 2.3
0.2	92.2 ± 3.2	77.1 ± 3.9	15.1 ± 5.0

Table 9: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][ETBA] after 24 hours of Hg-extraction (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5) (n=3).

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336][ETBA] [mg/L]
0.01	7.0 ± 0.3	5.6 ± 0.2	1.4 ± 0.4
0.05	23.6 ± 1.1	22.4 ± 1.8	1.2 ± 2.1
0.1	45.8 ± 1.7	40.0 ± 1.3	5.8 ± 2.1
0.2	92.2 ± 2.5	77.1 ± 3.9	15.1 ± 4.6

*Table 10: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][PTBA] after 24 hours of Hg-extraction (100 µg/L Hg^{2+} as Hg(NO$_3$)$_2$ at pH=3.5) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336][PTBA] [mg/L]
0.01	6.0 ± 0.5	5.6 ± 0.2	0.4 ± 0.5
0.05	20.7 ± 1.1	22.4 ± 1.8	*
0.1	37.9 ± 1.3	40.0 ± 1.3	*
0.2	73.7 ± 0.8	77.1 ± 3.9	*

3.2.7. Stripping of Hg^{2+} from PP/TS, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

Stripping experiments showed in general low recoveries (Fig. 20). Because no detectable Hg could be stripped from 3 g of PP/TS beads, which had been loaded with Hg^{2+} before, an additional experiment using 6 g PP/TS beads was performed. In that experiment 3.37 ± 1.05 % of the initially loaded Hg could be recovered from the beads. Stripping of PP beads showed

no detectable quantities of Hg in the stripping acid. Stripping of PVA/TS showed similar results like PVA beads with rates of 0.791 ± 0.141 % and 0.533 ± 0.222 %, respectively. 5.27 ± 1.58 % was stripped of PVA/ETBA and 6.12 ± 3.89 % of PVA/PTBA. Best results were achieved for the stripping of PVA/MTBA beads where 11.2 ± 1.7 % of Hg could be recovered.
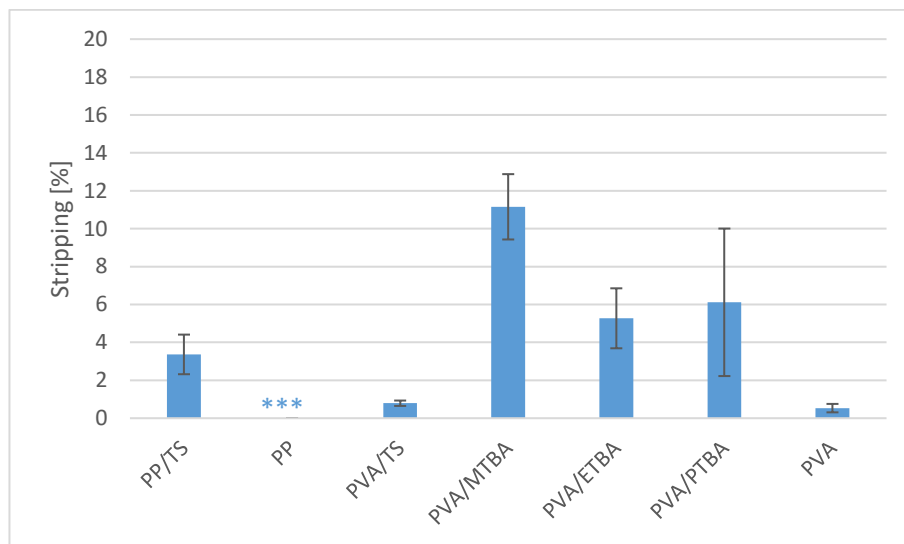
*Fig. 20: Mean values ± SD for the Hg^{2+}-stripping of 6 g of PP/TS, 3 g of PP, 0.2 g of PVA/TS and PVA and 0.05 g of PVA/MTBA, PVA/ETBA, PVA/PTBA in a 0.5 M HNO3 solution after 24 h which have been loaded previously in a 100 µg/L Hg^{2+} as $Hg(NO_3)_2$ solution for 24 h (n=3). *** = No stripping observed.*

3.3. Platinum extraction

3.3.1. Bead mass impact of PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA on Pt^{4+} extractions

Extraction experiments for Pt showed that the capacity reaches from 2 g onwards approximately 90 % for PP beads with immobilized ILs (Fig. 21). The extraction capacity of 3 g, which was used in the following experiments, was for PP/TS 87.7 ± 2.2 % and for PP/MTBA beads 85.9 ± 2.0 %. Extraction of pure PP beads was low, peaking at 1 g with 2.90 ± 0.50 %. PVA-alginate beads with immobilized ILs reach extraction capacities of approximately 90 % from 0.1 g onwards (Fig. 22). 0.1 g of PVA-alginate beads were used in the following experiments, displaying extraction capacities of   89.4 ± 1.0 % for PVA/TS, 90.0 ± 0.9 % for PVA/MTBA, 90.1 ± 0.3 % for PVA/ETBA and 89.1 ± 0.1 % for PVA/PTBA. The highest extraction efficiency for pure PVA beads was observed at 0.1 g with 12.5 ± 0.8 % and 0.2 g with 13.2 ± 1.1 %.
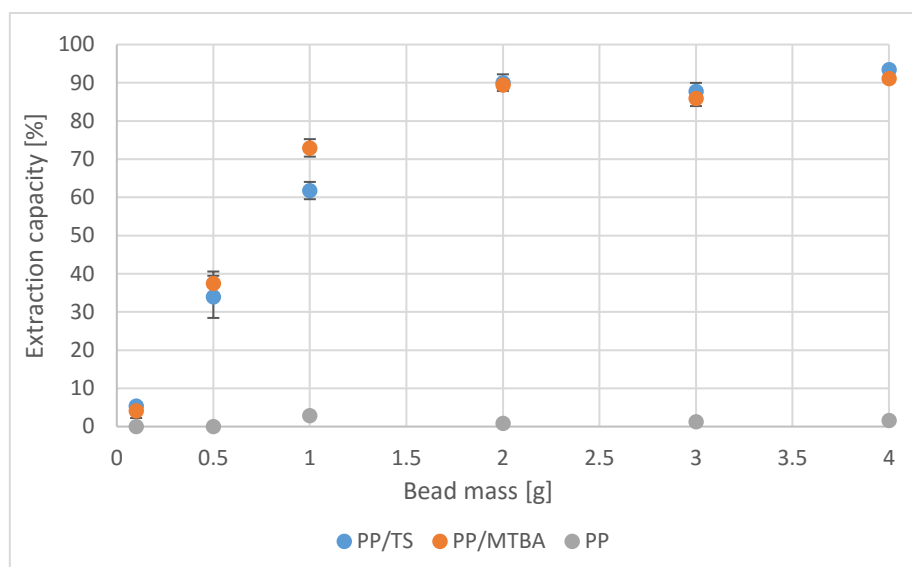
Fig. 21: Mean values ± SD for the extraction capacity of various bead masses of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution at pH=3.0 after 24 h (n=3).

Fig. 22: Mean values ± SD for the extraction capacity of various bead masses of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution at pH=3.0 after 24 h (n=3).

The loading results for this set of data display that PP/TS (Table 11) and PP/MTBA (Table 12) show similar trends: 0.1 g and 0.5 g displaying highest loadings of almost or over 1 mg Pt^{4+}/g IL, following a continuous decrease till 3 g and increasing slightly at 4 g. The loading results for PVA beads (Table 13 - 16) show that all used PVA-alginate beads display loadings of over 1 mg Pt^{4+}/g IL at 0.01 g, 0.05 g and 0.1 g. An increase in bead mass results in a decreased loading, lowest loadings were observed at 0.2 g.

Table 11: Loading ranges of PP/TS for Pt extractions (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0 after 24 h) (n=3).

PP/TS [g]	Loading range [mg Pt^{4+}/g IL]
0.1	0.131 – 0.862
0.5	0.80 – 1.12
1	0.748 – 0.807
2	0.519 – 0.545
3	0.271 – 0.272
4	0.325 – 0.329

Table 12: Loading ranges of PP/MTBA for Pt extractions (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0 after 24 h) (n=3).

PP/MTBA [g]	Loading range [mg Pt^{4+}/g IL]
0.1	0.39 -1.45
0.5	0.99 – 1.43
1	0.893 – 0.952
2	0.524 – 0.533
3	0.261 – 0.264
4	0.317 – 0.319

Table 13: Loading ranges of PVA/TS for Pt extractions (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0 after 24 h) (n=3).

PVA/TS [g]	Loading range [mg Pt^{4+}/g IL]
0.01	3.02 – 3.21
0.05	1.82 – 1.85
0.1	1.01 – 1.04
0.15	0.766 – 0.778
0.2	0.495 – 0.515

Table 14: Loading ranges of PVA/MTBA for Pt extractions (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0 after 24 h) (n=3).

PVA/MTBA [g]	Loading range [mg Pt^{4+}/g IL]
0.01	2.35 – 2.40
0.05	2.04 – 2.05
0.1	1.02 – 1.05
0.15	0.753 – 0.764
0.2	0.479 – 0.488

Table 15: Loading ranges of PVA/ETBA for Pt extractions (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0 after 24 h) (n=3).

PVA/ETBA [g]	Loading range [mg Pt^{4+}/g IL]
0.01	2.59 – 3.17
0.05	1.99 – 2.05
0.1	1.03 – 1.04
0.15	0.739 – 0.743
0.2	0.479 – 0.526

Table 16: Loading ranges of PVA/PTBA for Pt extractions (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0 after 24 h) (n=3).

PVA/PTBA [g]	Loading range [mg Pt^{4+}/g IL]
0.01	2.12 – 2.47
0.05	2.03 – 2.06
0.1	1.02 – 1.02
0.15	0.739 – 0.742
0.2	0.523 – 0.526

3.3.2. pH impact on Pt^{4+} extractions with PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

The results for PP beads are depicted in Fig. 23. The highest extraction capacity for PP beads containing ILs was observed at pH=3.0 with 87.7 ± 2.2 % for PP/TS and 85.9 ± 2.0 % for PVA/MTBA. Pure PP beads extracted most Pt at pH=4.0 (4.23 ± 0.83 %), while no extraction could be observed at higher pH values. A pH increase to 4.0 and higher resulted for both PP/TS and PP/MTBA beads in lowered extraction capacities by more than half. Except for PVA/TS, the other immobilized ILs displayed a similar behavior when comparing PVA-alginate beads containing ILs (Fig. 24): The highest extraction capacity was observed at pH=3.0 with 88.9 ± 0.4 % for PVA/MTBA, 86.0 ± 0.7 % for PVA/ETBA and 87.0 ± 0.3 % for PVA/PTBA. PVA/TS showed similar extraction capacities when comparing pH=3.0 (93.3 ± 0.5 %) and pH=4.0 (93.6 ± 0.6 %). A trend of decreasing extraction capacity with higher pH is observed for PVA-alginate beads containing ILs. In contrast, pure PVA beads extracted at pH=6.0 most of the Pt with an efficiency of 16.2 ± 3.2 %, no extraction was observed at pH=5.0.

Fig. 23: Mean values ± SD for the extraction capacity of 3 g of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH=3.0, 4.0, 5.0 and 6.0 after 24 h (n=3). ** = No extraction observed.
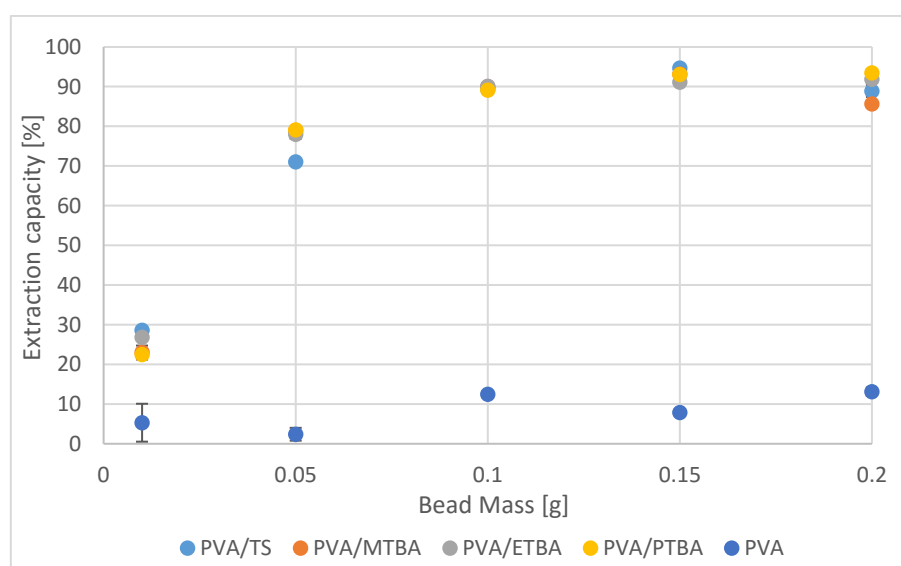

Fig. 24: Mean values ± SD for the extraction capacity of 0.1 g PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH=3.0, 4.0, 5.0 and 6.0 after 24 h (n=3). ** = No extraction observed.

3.3.3. pH impact on Pt^{4+} (CPCs) extractions with PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

The extraction of various CPCs showed the following results: Cisplatin was only extracted at pH=3.0 by PP/TS and PP/MTBA beads with extraction capacities of 3.40 ± 1.26 % and 4.46 ± 2.21 %, respectively (Fig. 25). Pure PP beads did not extract cisplatin at any of the tested pH values. For PVA beads, highest extraction efficiencies were observed in general at pH=6.0, overall PVA (38.7 ± 2.0 %) and PVA/ETBA (36.3 ± 1.6 %) displayed the highest values (Fig. 26). No extraction was observed at pH=9.0 for PVA/TS.

*Fig. 25: Mean values ± SD for the extraction capacity of 3 g of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as cisplatin solution at pH=3.0, 6.0 and 9.0 after 24 h (n=3). ** = No extraction observed.*

*Fig. 26: Mean values ± SD for the extraction capacity of 0.1 g PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as cisplatin solution at pH=3.0, 6.0 and 9.0 after 24 h (n=3). ** = No extraction observed.*

Carboplatin was not extracted at any of the tested pH values by PP/TS and PP/MTBA beads, pure PP beads extracted only at pH=6.0 with 1.96 ± 0.04 % (Fig. 27). The highest extraction capacities were observed at pH=9.0 for all PVA-alginate beads with approximately 5 to 7 % (Fig. 28). PVA/PTBA displayed a comparatively high extraction capacity at pH=3.0 with 3.44 ± 2.11 %. No extraction of carboplatin was observed at pH=3.0 for PVA/TS, PVA/MTBA and PVA/PTBA beads.

*Fig. 27: Mean values ± SD for the extraction capacity of 3 g of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as carboplatin solution at pH=3.0, 6.0 and 9.0 after 24 h (n=3). ** = No extraction observed.*

*Fig. 28: Mean values ± SD for the extraction capacity of 0.1 g PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 0.65 mg/L Pt^{4+} as carboplatin solution at pH=3.0, 6.0 and 9.0 after 24 h (n=3). ** = No extraction observed.*

PP/TS showed no affinity towards oxaliplatin at all (Fig. 29). PP/MTBA beads extracted oxaliplatin only at pH=6.0 with 1.59 ± 0.44 %, while PP beads extracted at pH=6.0 with 3.25 ± 1.51 % and peaked at pH=9.0 with 47.2 ± 8.4 %. All PVA-alginate beads showed highest extraction efficiencies at pH=3.0 with 10.4 ± 1.0 % for PVA/TS, 10.3 ± 1.0 % for PVA/MTBA, 8.30 ± 0.85 % for PVA/ETBA, 9.11 ± 0.50 % for PVA/PTBA and 8.31 ± 0.32 % for PVA (Fig. 30).

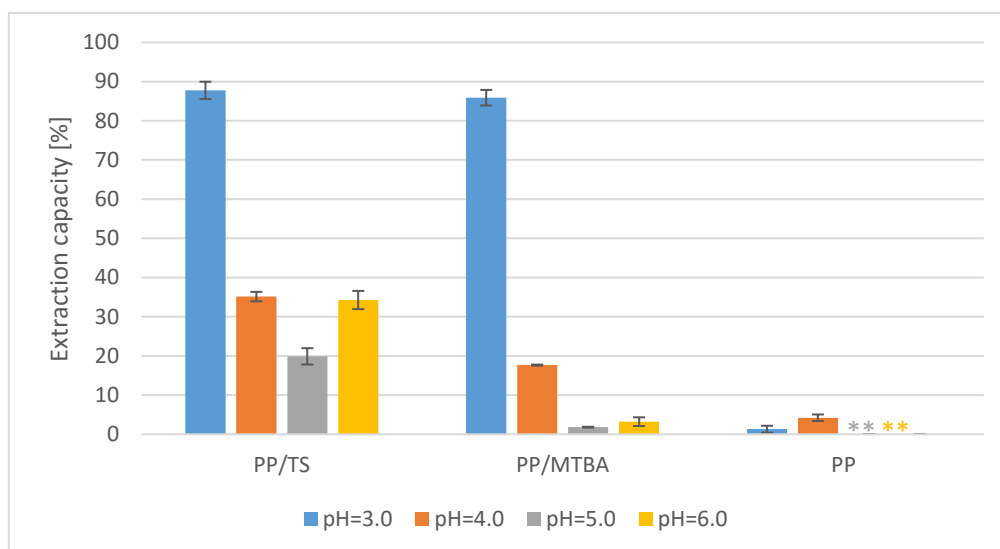*Fig. 29: Mean values ± SD for the extraction capacity of 3 g of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as oxaliplatin solution at pH=3.0, 6.0 and 9.0 after 24 h (n=3). ** = No extraction observed.*

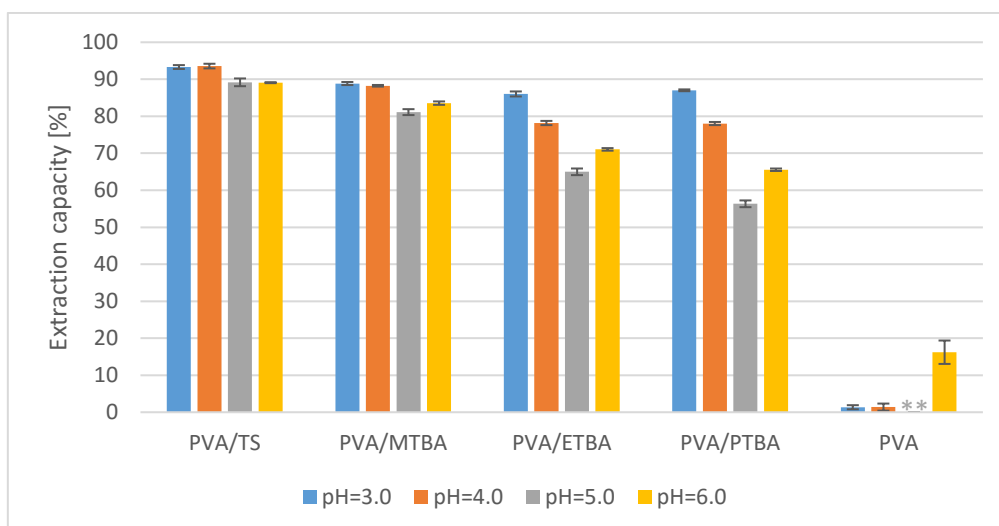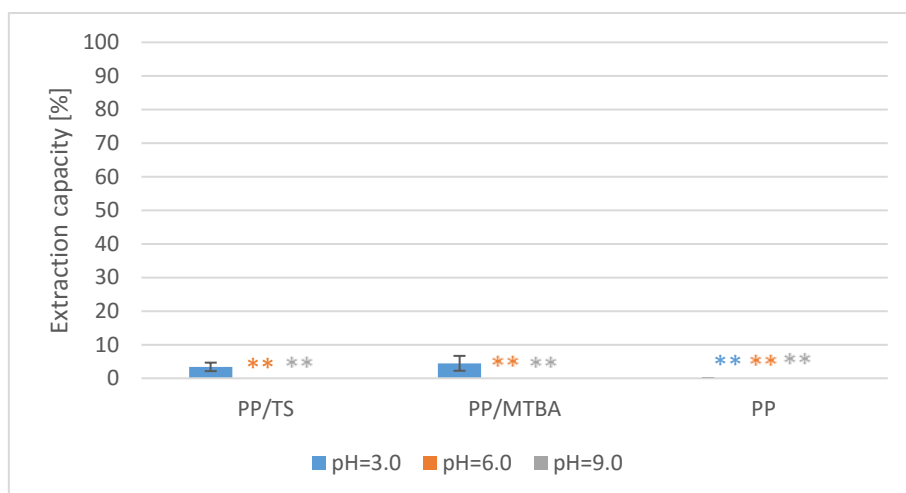*Fig. 30: Mean values ± SD for the extraction capacity of 0.1 g PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as oxaliplatin solution at pH=3.0, 6.0 and 9.0 after 24 h (n=3).*

3.3.4. Time dependency of Pt^{4+} extractions with PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

Observation of time-dependency of the extraction showed that PP/MTBA reached after 9 hours with 82.2 ± 0.5 % the maximum extraction since there was no significant increase after 24 hours (82.5 ± 0.6 %) (Fig. 31). PP/TS reached a steady state between 3 h and 4 h, following a continuous extraction from the 5th hour on (62.9 ± 0.5 %) until the end of the experiment after 24 h with 85.1 ± 0.1 %. The extraction capacity of pure PP beads was constantly below 7 % over the period of the experiment, reaching a value of 3.20 ± 0.67 % after 24 h. When

comparing PVA-alginate beads with immobilized ILs, PVA/TS extracted slightly faster than the other beads until the fifth hour with 89.7 ± 0.3 % (Fig. 32). The extraction capacities began to align after 7 hours for all PVA-alginate beads containing ILs and were after 24 h at 89.4 ± 1.0 % for PVA/TS, 90.0 ± 0.9 % for PVA/MTBA, 90.1 ± 0.3 % for PVA/ETBA and 89.1 ± 0.1 % for PVA/PTBA. The extraction efficiency of PVA beads reached a plateau after 3 h with 8.77 ± 1.19 %, after 24 h a little but noticeable increase was observed with 12.5 ± 0.8 %.
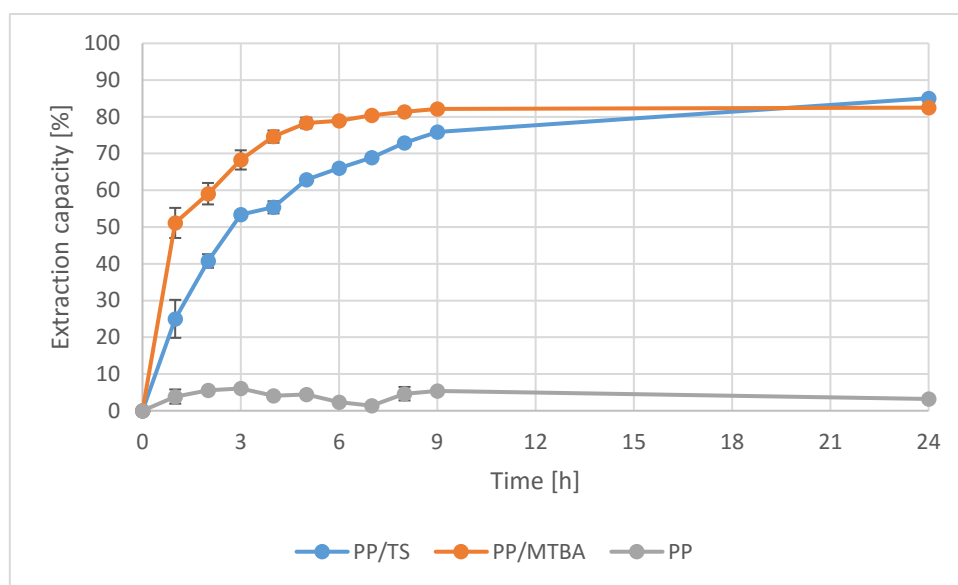
Fig. 31: Mean values ± SD for the extraction capacity of 3 g of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH=3.0 during 24 h (n=3).
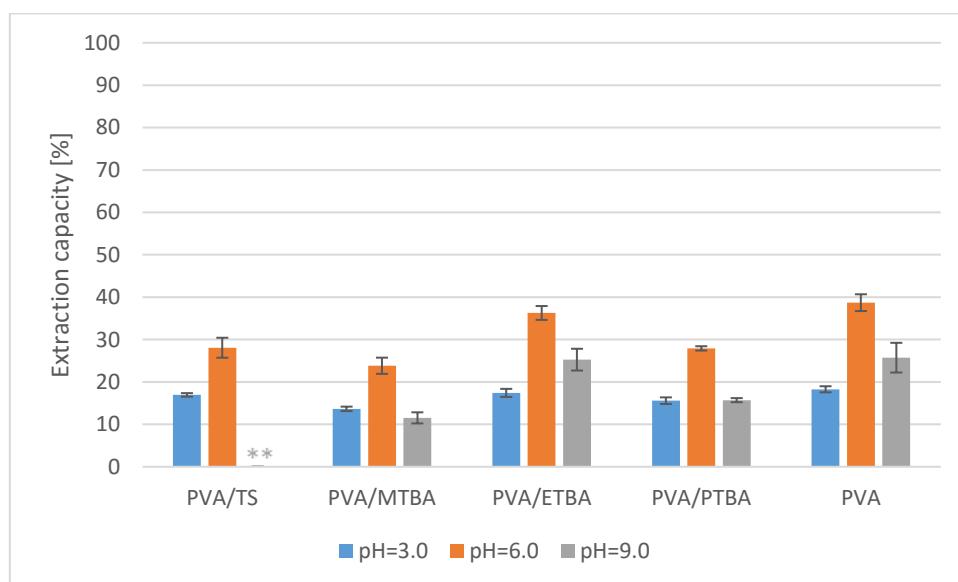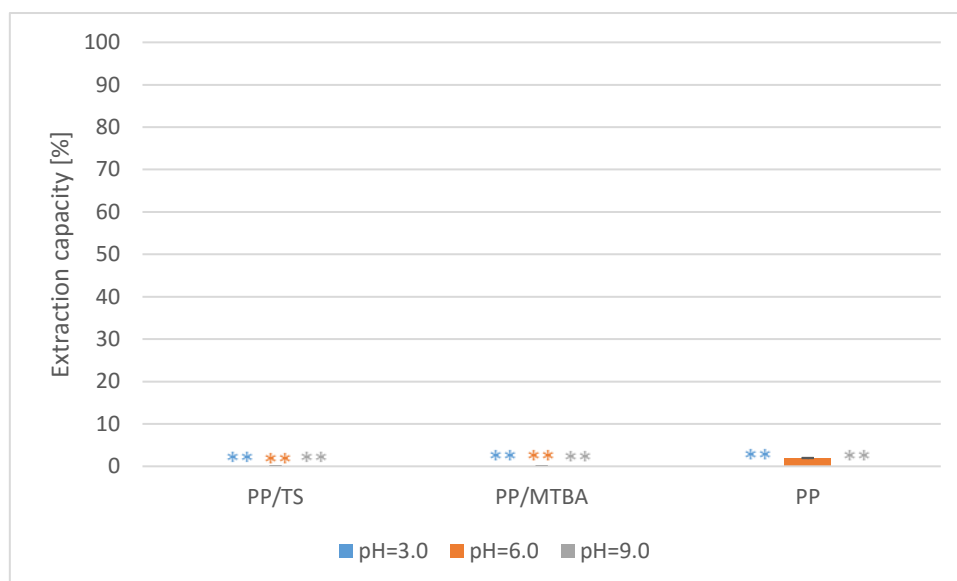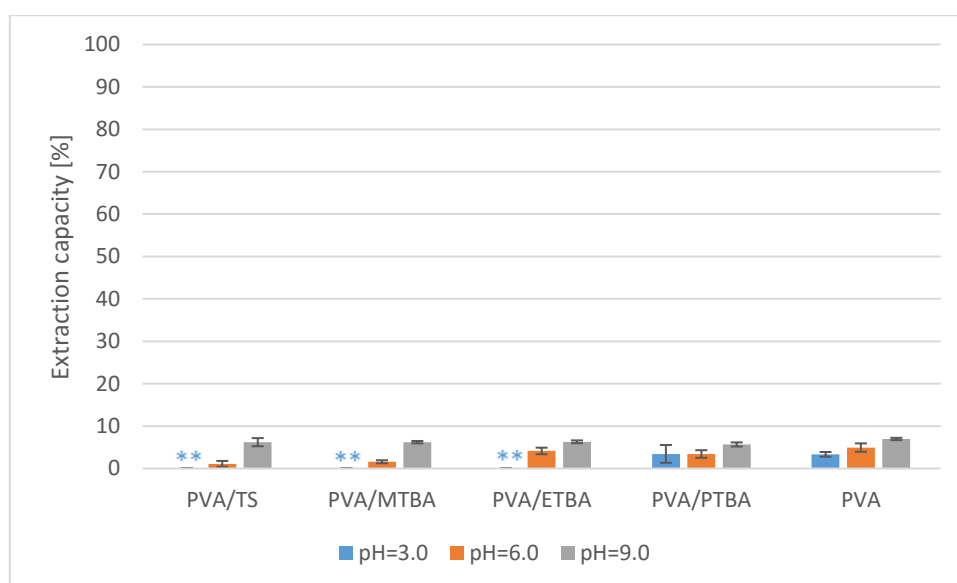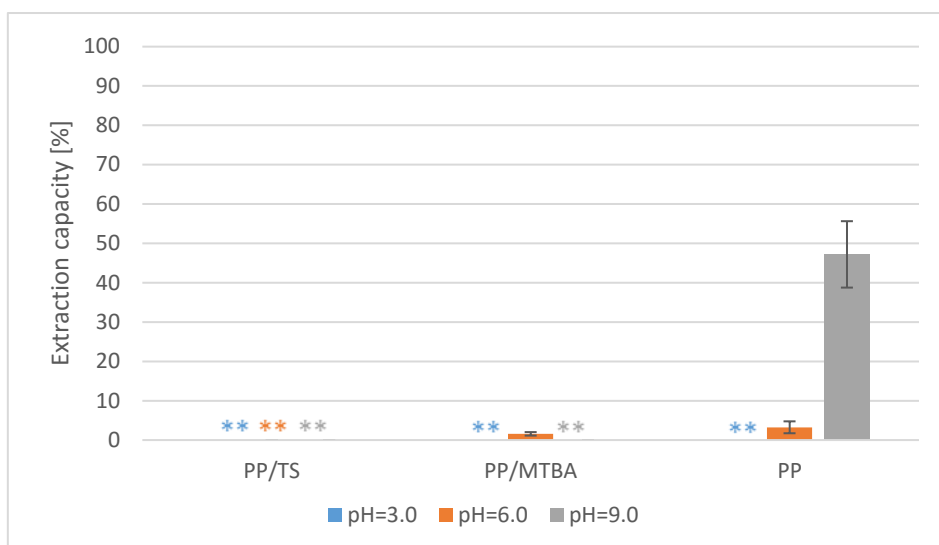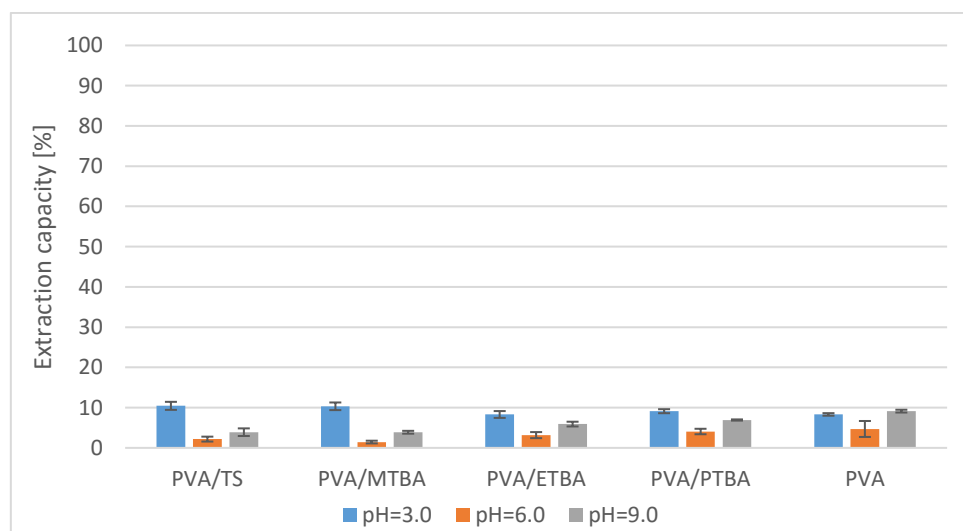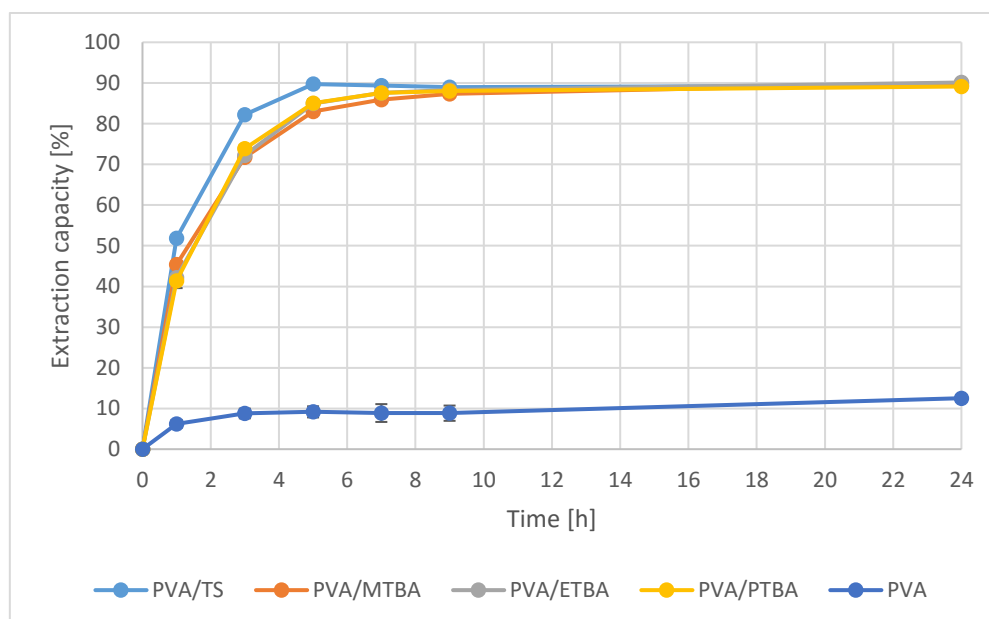

Fig. 32: Mean values ± SD for the extraction capacity of 0.1 g PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as $H_2[PtCl_6]$ solution at pH=3.0 during 24 h (n=3).

3.3.5. Leaching of PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA for Pt^{4+} extractions

DOC increased with increasing bead mass for PP/TS and PP/MTBA beads, highest DOC values were observed at 4 g with 10.7 ± 0.4 mg/L for PP/TS and 26.7 ± 1.4 mg/L (Fig. 33). Pure PP beads showed no correlation regarding DOC and the bead mass, highest DOC values were observed at 1 g with 2.3 ± 0.4 mg/L and 4 g with 1.9 ± 0.3 mg/L. DN rose as expected with increasing bead mass, although PP/TS beads peaked at 3 g with 0.6 ± 0.1 mg/L and then decreased to 0.5 g ± 0.1 mg/L at 4 g, while there was no significant difference at 3 g and 4 g for PP/MTBA beads with 1.0 ± 0.1 mg/L (Fig. 34). Since the only nitrogen source, besides contaminations, was the cation of the ILs, the fraction of the compounds could be estimated: While at 0.1 g total DOC consisted of PP for PP/TS, an increase of bead mass resulted especially in an increase of cation leaching. Except for 0.5 g (0.2 ± 0.4 mg/L) and 1 g (0.2 ± 0.5 mg/L), no anion leached into the aqueous phase (Table 17). The result for PP/TS is similar to PP/MTBA, although the share of the cationic and anionic IL DOC on total DOC is higher (Table 18). An increase in bead mass resulted summarized in an increase of cationic leaching, while anionic leaching was still comparatively low but nonetheless calculable. The highest values for IL leaching were observed at 4 g PP/MTBA beads with 22.1 ± 1.6 mg/L for [A336] and 2.7 ± 2.1 mg/L for [MTBA].
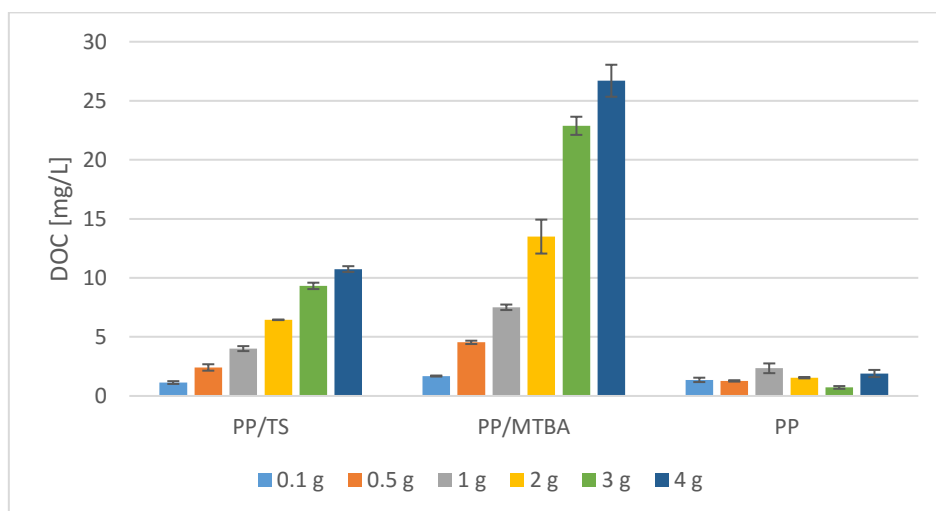
Fig. 33: Mean values ± SD for the DOC of various bead masses of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution at pH=3.0 after 24 h (n=3).
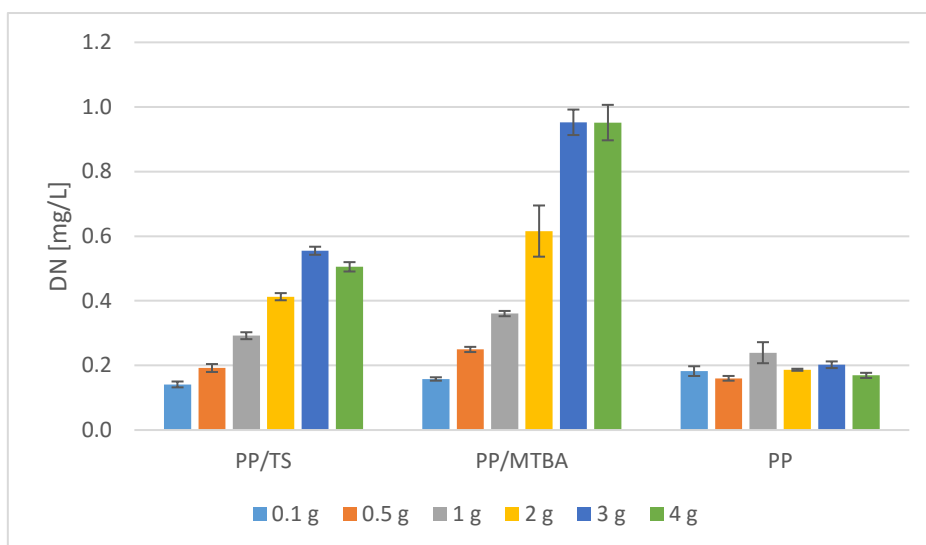
Fig. 34: Mean values ± SD for the DN of various bead masses of PP/TS, PP/MTBA and PP in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution at pH=3.0 after 24 h (n=3).

*Table 17: Mean values ± SD for the total DOC and the share of DOC derived from PP and [A336][TS] after 24 hours of Pt-extraction (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PP [mg/L]	DOC from [A336] [mg/L]	DOC from [TS] [mg/L]
0.1	1.1 ± 0.1	1.4 ± 0.2	*	*
0.5	2.4 ± 0.3	1.3 ± 0.1	0.9 ± 0.3	0.2 ± 0.4
1	4.0 ± 0.2	2.3 ± 0.4	1.5 ± 0.3	0.2 ± 0.5
2	6.4 ± 0.1	1.5 ± 0.1	6.4 ± 0.3	*
3	9.3 ± 0.3	0.7 ± 0.1	10.0 ± 0.4	*
4	10.7 ± 0.2	1.9 ± 0.3	9.5 ± 0.4	*

*Table 18: Mean values ± SD for the total DOC and the share of DOC derived from PP and [A336][MTBA] after 24 hours of Pt-extraction (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PP [mg/L]	DOC from [A336] [mg/L]	DOC from [MTBA] [mg/L]
0.1	1.7 ± 0.1	1.4 ± 0.2	*	0.3 ± 0.2
0.5	4.5 ± 0.1	1.3 ± 0.1	2.5 ± 0.2	0.7 ± 0.2
1	7.5 ± 0.2	2.3 ± 0.4	3.4 ± 0.2	1.8 ± 0.5
2	13.5 ± 1.4	1.5 ± 0.1	12.2 ± 2.2	*
3	22.9 ± 0.8	0.7 ± 0.1	21.2 ± 1.1	1.0 ± 1.4
4	26.7 ± 1.4	1.9 ± 0.3	22.1 ± 1.6	2.7 ± 2.1

PVA-alginate beads showed as expected increasing DOC values with increasing bead mass (Fig. 35). Highest DOC values were observed at 0.2 g with 70.4 ± 1.7 mg/L for PVA/TS, 78.4 ± 1.8 mg/L for PVA/MTBA, 81.0 ± 1.5 mg/L for PVA/ETBA, 78.3 ± 2.2 mg/L for PVA/PTBA and 70.5 ± 5.3 mg/L for PVA. Taking a look at DN, the results were summarized up comparing between

PVA beads low when compared to PP beads containing ILs, ranging between 0.2 and 0.4 mg/L DN (Fig. 36). No nitrogen was detectable during the 0.1 g experiments. Recalculation of the obtained DN values to determine the shares on total DOC showed a high proportion on PVA-alginate (Table 19 – 22). PVA/TS showed almost no IL leaching at all, while the tendency of PVA/MTBA, PVA/ETBA and PVA/PTBA was an increase of anionic leaching with increasing bead mass. Cationic leaching was in general comparatively small, not exceeding 0.1 ± 0.1 mg/L. Highest anionic leaching was observed at 0.2 g with 7.8 ± 5.6 mg/L for PVA/MTBA, 10.4 ± 5.5 mg/L for PVA/ETBA and 7.7 ± 5.7 mg/L for PVA/PTBA.
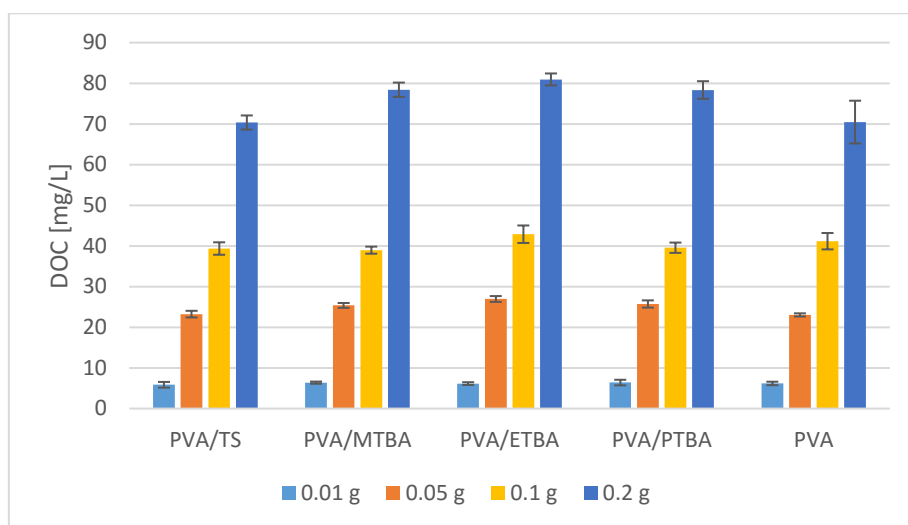
Fig. 35: Mean values ± SD for the DOC of various bead masses of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution at pH=3.0 after 24 hours (n=3).
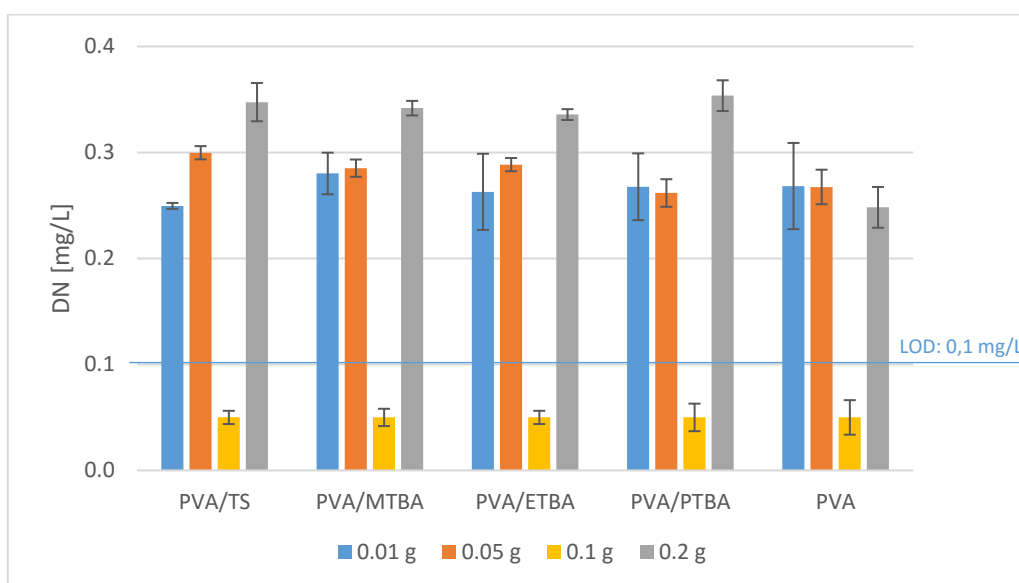
Fig. 36: Mean values ± SD for the DN of various bead masses of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution at pH=3.0 after 24 hours (n=3).

*Table 19: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][TS] after 24 hours of Pt-extraction (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336] [mg/L]	DOC from [TS] [mg/L]
0.01	5.9 ± 0.7	6.2 ± 0.4	*	*
0.05	23.2 ± 0.8	23.0 ± 0.4	0.1 ± 0.1	0.1 ± 0.9
0.1	39.4 ± 1.5	41.2 ± 2.0	*	*
0.2	70.4 ± 1.7	70.5 ± 5.3	*	*

*Table 20: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][MTBA] after 24 hours of Pt-extraction (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336] [mg/L]	DOC from [MTBA] [mg/L]
0.01	6.4 ± 0.3	6.2 ± 0.4	0.1 ± 0.1	0.1 ± 0.5
0.05	25.4 ± 0.6	23.0 ± 0.4	0.1 ± 0.1	2.3 ± 0.7
0.1	40.0 ± 0.9	41.2 ± 2.0	*	*
0.2	78.4 ± 1.8	70.5 ± 5.3	0.1 ± 0.1	7.8 ± 5.6

*Table 21: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][ETBA] after 24 hours of Pt-extraction (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336] [mg/L]	DOC from [ETBA] [mg/L]
0.01	6.1 ± 0.3	6.2 ± 0.4	*	*
0.05	27.0 ± 0.7	23.0 ± 0.4	0.1 ± 0.1	3.9 ± 0.8
0.1	42.9 ± 0.9	41.2 ± 2.0	*	1.7 ± 2.2
0.2	81.0 ± 1.5	70.5 ± 5.3	0.1 ± 0.1	10.4 ± 5.5

*Table 22: Mean values ± SD for the total DOC and the share of DOC derived from PVA and [A336][PTBA] after 24 hours of Pt-extraction (1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] at pH=3.0) (n=3). * = No recalculation possible.*

Bead mass [g]	Total DOC [mg/L]	DOC from PVA [mg/L]	DOC from [A336] [mg/L]	DOC from [PTBA] [mg/L]
0.01	6.4 ± 0.7	6.2 ± 0.4	0.1 ± 0.1	0.1 ± 0.8
0.05	25.7 ± 0.9	23.0 ± 0.4	*	2.7 ± 1.0
0.1	39.6 ± 1.3	41.2 ± 2.0	*	*
0.2	78.3 ± 2.2	70.5 ± 5.3	0.1 ± 0.1	7.7 ± 5.7

3.3.6. Stripping of Pt^{4+} from PP/TS, PP/MTBA, PP, PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA

Lowest Pt^{4+} stripping was observed for beads containing no IL, i.e. PP (7.10 ± 2.40 %) and PVA (10.7 ± 0.59 %) (Fig. 37). Subsequently follow PP beads containing ILs, PP/TS with 24.3 ± 0.4 % and PP/MTBA with 28.5 ± 1.6 %. Highest stripping values were determined for PVA-alginate beads with ILs: PVA/TS with 53.3 ± 2.6 %, PVA/MTBA with 65.6 ± 2.3 %, PVA/ETBA with 63.1 ± 0.6 % and PVA/PTBA with 60.8 ± 1.8 %.
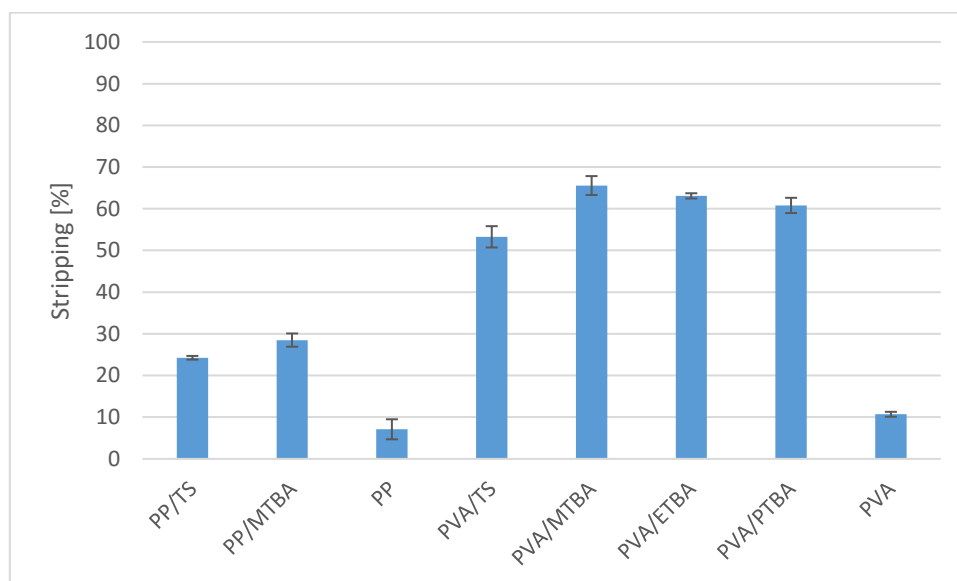
Fig. 37: Hg^{2+}-stripping of 3 g of PP/TS, PP/MTBA and PP and 0.1 g of PVA/TS, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA in a 0.5 M HNO3 solution which have been loaded previously for 24 h in a 1 mg/L Pt^{4+} as H$_2$[PtCl$_6$] solution after 24 h (n=3).

3.4. Change in bead mass

PP/TS beads showed a decrease in mass of 0.14 ± 0.08 %, while PP beads showed an increase of 0.30 ± 0.12 %. All PVA-alginate beads showed a decrease in mass, PVA/TS beads lost 48.33 ± 0.01 %, PVA/MTBA lost 47.79 ± 4.47 %, PVA/ETBA lost 51.28 ± 0.14 %, PVA/PTBA lost 52.21 ± 1.73 % and PVA lost 48.32 ± 1.17 % of the initial mass.

4. Discussion

4.1. Stability of PVA-alginate beads

Stability issues of alginate- (Smidsrød et al. 1990) or PVA-alginate materials in aquatic media are a known problem in literature. This problem has been assessed in various ways: Cruz et al. (2013) used polymer Ca-alginate beads containing the microalgae *Chlorella vulgaris* jointly immobilized with *Azospirillum brasilense* for secondary treatment of municipal wastewater. Their beads lost mechanical strength after 24 h of incubation, bead degradation was tracked by the analysis of the texture and change in the diameter of beads. The addition of polyvinylpyrrolidon, carboxymethyl cellulose or PVA resulted in a weaker gel than their control gel. Bae et al. (2015) used PVA-alginate beads to entrap ammonia-oxidizing bacteria in PVA-alginate beads, trying to pinpoint optimal reaction conditions. Instead of a hardening step in a Na_2SO_4-solution like in this work, a hardening step in KH_2PO_4 was performed. They measured the total chemical oxygen demand in the residual debris after homogenization of the beads and the ammonia-oxidizing activity. They did not only face the issue of bead stability, but also the bioactivity of immobilized bacteria which was inhibited by treatment in saturated boric acid solution. Statistical evaluation showed that for their beads, treatment in saturated $B(OH)_3$ and 1 % $CaCl_2$ (w/v) solution for 3.5 h following hardening in 0.5 M KH_2PO_4 solution for 5.6 h are the optimal conditions. Zain et al. (2011) immobilized the enzyme β-fructofuranosidase in PVA-alginate following basically a similar reaction procedure as stated in this work, in contrast to the previously cited study the hardening solutions which was used is Na_2SO_4. They investigated the solubility of their beads in water and the diffusion coefficients of glucose, which was produced by β-fructofuranosidase from sucrose in their experimental setup. Using a 0.5 M Na_2SO_4 hardening solution resulted in water insoluble beads, increasing the Na_2SO_4 concentration further lead to decreasing diffusion coefficients of glucose. The authors suggested that according to this result, an increase in Na_2SO_4 concentrations lead to less porous beads. To evaluate the stability of PVA beads during the present extraction experiments, measurement of the DOC and DN was chosen, in order to monitor changes in stability by dissolution of beads but also to assess the leaching of ILs quantitatively. The results indicate that the sodium sulfate concentration during the hardening step, when preparing the beads, has the major influence on their stability. Increasing Na_2SO_4 concentrations in the hardening solution lead to a better stability during extraction experiments, up to 1.5 M

Na$_2$SO$_4$. Supersaturation of Na$_2$SO$_4$ has an adverse effect, and lead to the highest degree of dissolution of beads (> 600mg/L DOC). This observation is in accordance with the results of Rodriguez-Navarro et al. (2000), who investigated on the sodium sulfate crystallization from a saturated sodium sulfate solution at room temperature. They report that the presence of micropores in their tested oolitic limestone induced high supersaturation ratios of the sodium sulfate solution before crystallization occurs. The supersaturation lead to a high sodium sulfate crystallization pressure and significant damage to the porous support. DOC decrease of the beads in a supersaturated Na$_2$SO$_4$-solution after 24 h could be explained by coagulation and hardening of particles, which cannot pass the pores of the used filters (which have a size of 0.2 μm) after hardening in a Na$_2$SO$_4$-solution, prior to the DOC measurement.

4.2.   Influence of bead mass on extraction capacities

Bead mass and extraction capacity did not correlate for any of the used beads during Hg extractions, although a trend of increased extraction capacity with increased bead mass is visible. This effect could have been caused for PVA-alginate by the use of the Na$_2$SO$_4$ hardening solution, since Zhang et al. (2011) did not report this observation for their PVA-alginate beads containing [A336][MTBA], but no Na$_2$SO$_4$-solution for hardening was used either in that case. Increase in bead mass resulted in an increase in Hg extraction in the study by Zhang et al. (2011). One possible explanation for the observed behavior of PVA-alginate beads in this work could be the release of sulfate ions into the aqueous solution, which interfere with the extraction mechanism, additional to the observed degradation of beads. This would explain the differing results of the bead mass impact on extraction to Zhang et al. (2011). Since PP beads contain also some additives like elastomers from the production process, those could also have an impact on the extraction by interfering with the extraction process.

Regarding Pt extractions, bead mass did correlate quite well with the extraction capacity for both PP and PVA-alginate beads. An extraction plateau evolved when an extraction capacity of approximately 90% was reached, maybe caused by different kinetics when the concentration of Pt is lowered to 0.1 Pt^{4+} mg/L in the aqueous phase due to a change of the reaction rate resulting in a slower extraction. Further investigations regarding the issue of the impact of the reaction rate would be necessary. In contrast to Hg extractions, fluctuations of the impact of the bead mass on the extraction capacity were small. An explanation to this

observation could be that the used Pt species had a low affinity to interact with sulfate ions or elastomers, if those interfere with the extraction mechanism for Hg.

4.3. pH impact on extraction capacities

The affinity of pure PP beads towards Hg was in general low and showed at pH=3.5 same extraction capacities as PP/MTBA of below 10 %. Because of this observation no further extracting experiments regarding Hg were conducted with PP/MTBA. The chosen concentration of 100 µg/L Hg^{2+} in the feed solution showed a different trend compared to Zhang et al. (2011) who used 10 to 50 mg/L Hg^{2+}, displaying significantly different results. Comparing the impact of the pH on the extraction capacity, Zhang et al. (2011) used Hg^{2+} as $HgCl_2$ in concentrations between 10 to 50 mg/L, showing that from 30 mg/L or above a visible impact on the extraction in a pH-range between 2 to 7 was displayed. It was reported that pH=5.8 showed highest extraction efficiencies for 50 mg/L. In this work, the impact of the pH was evaluated using Hg^{2+} as $Hg(NO_3)_2$ at pH=3.5, 4.0 and 5.0 and showed for every immobilization matrix and IL a different impact. The optimal pH value for PP/TS and PVA/MTBA regarding those extraction experiments was 3.5, for PP 3.5 and 5.0, for PVA/TS and PVA/PTBA 3.5 and 4.0, for PVA/ETBA 4.0 and for PVA 5.0. Extraction capacities for immobilized ILs in PVA-alginate at pH=5.0 were significantly lower compared to extractions at pH=3.5 and 4.0. The lowest extraction capacity for PP/TS was displayed at pH=4.0. Extraction of Hg^{2+} as $HgCl_2$ was observed in this work at a concentration of 100 µg/L and at pH=3.5, but in two different media, 5 % HNO_3 and 3 % HCl. Extraction efficiencies were higher for $HgCl_2$ in 5 % HNO_3 for PP/TS and higher for $HgCl_2$ in 3 % HCl for PVA/PTBA, while no significant difference regarding those two media was for PVA/TS, PVA/MTBA and PVA/ETBA was displayed. The observed differences in extraction due to different pH values may be caused by different charges of ILs, the immobilization matrix or varying Hg species in aqueous solution, which may hinder the metal extraction because of the various possible mechanisms (Janssen et al. 2015). Pure PVA-alginate beads showed best extraction efficiencies at pH=5.0, probably caused by the deprotonation of the material, leading to binding sites with an affinity to heavy metals (Papageorgiou et al. 2006). This effect seems to be already inhibited by small amounts of ILs, which could e.g. protonate the immobilization matrix and prevent thereby higher extraction capacities.

Regarding Pt extractions with $H_2[PtCl_6]$, an increase of the pH lead to a decrease in extraction capacity. Extraction capacities of PP/TS and PP/MTBA depended heavily on the pH in the aqueous solution: pH values of 4.0 and higher lead to a decrease in extraction capacity of more than a half when compared to pH=3.0. PP/MTBA displayed at pH=5.0 and pH=6.0 extraction capacities of below 10 %, while at pH=3.0 approximately 86 % were observed. Extraction with PVA/TS beads worked at all tested pH values quite well, while a trend of decreased extraction was observed with an increasing alkyl chain length of the anion for same extraction conditions. A small increase in extraction capacity at pH=6.0 for PVA-alginate beads might be caused by an improving extraction of PVA-alginate itself, which showed for pure PVA a significant increase at this pH value. PVA/MTBA, PVA/ETBA and PVA/PTBA showed similar progressions of extractions with changing pH, which could be explained with their chemical structure consisting of a alkylthio group with an increasing alkylchain-length, instead of a free thiol group as it is the case for [A336][TS].

4.4. Loading

Regarding the loading, in the study by Zhang et al. (2011) a trend is visible which was observed also in this work: An increase in bead mass resulted almost always in a decrease in loading capacity. Exceptions for this behavior were displayed by PP/MTBA for Pt extractions and PP/TS for Pt and Hg extractions: The loading ranges for Hg extractions of PP/TS overlap at 2 g and 3 g, while for Pt extraction an overlap is displayed for 0.1 g and 0.5 g for both PP/TS and PP/MTBA. The interpretation of this result could mean that when bead masses were used, which were overlapping in the loading range of PP/TS or PP/MTBA beads, all adsorption sites were saturated, but since 0.5 g beads provide more adsorption sites, the loading is higher. Zhang et al. (2011) reported a highest adsorption capacity of 50 mg Hg^{2+}/g IL under their chosen reaction conditions at pH=5.8 and an initial concentration of approximately 50 mg/L Hg^{2+} as $HgCl_2$ for 0.1 g of their PVA/MTBA beads, the loading for PVA/MTBA in this study was for 0.1 g at 520 – 531 µg Hg^{2+}/g IL. The lower loading in this study might have been caused by a different reaction procedure using Na_2SO_4 as a hardening solution, a pH of 3.5 or an initial concentration of 100 µg/L Hg^{2+} as $Hg(NO_3)_2$.

Comparing PP and PVA beads in general, PVA beads display loading ranges for similar loading capacities which are much higher, up to approximately a factor of 100. This effect could be

caused by either the presence of more adsorption sites which are provided by PVA beads or a facilitated binding to adsorption sites due to the swelling of PVA beads during the extraction experiments, which eases the diffusion of heavy metals into the bead. Investigations regarding the amount and distribution of adsorption sites of PP and PVA beads in further experiments could hint towards the reason of those unequally spread loading values.

4.5. Extraction of different Hg species

The Hg species had various effects on the extraction capacity: While PVA/TS displayed a small but significant change to extraction capacity when changing the species to $HgCl_2$, PVA/MTBA, PVA/ETBA, PVA/PTBA and PVA showed decreased extraction efficiencies for $HgCl_2$ in 5 % HNO_3 and 3 % HCl. A significant impact for PP/TS beads could be observed only when $HgCl_2$ was dissolved in 3 % HCl, no significant difference could be observed when comparing the extraction result of $HgCl_2$ in 5 % HNO_3 or $Hg(NO_3)_2$ in 5 % HNO_3. According to Riedel et al. (2011), tri- and tetra-chloro-mercurate-complexes are formed in solutions with high chloride contents. The formation of those complexes could interfere with the extraction mechanism, either because of the negative charge leading to other extraction mechanisms or the structure causing a steric demand which cannot be provided by the IL when compared to dissociated ions. This could explain why PVA/MTBA, PVA/ETBA and PVA/PTBA show a decrease in extraction when the chloride concentration of the aqueous solution is increased: While all of the three stated beads consist of ILs with alkylthio groups, PVA/TS has a thiol group. The alkylthio groups could represent a steric obstacle for tri- and tetra-chloro-mercurate-complexes.

4.6. Time-dependency of extractions

Time-dependency experiments displayed plateaus of various durations for immobilized ILs, this behavior was also described by Zhang et al. (2011). Gupta et al. (2009), who observed similar progresses in their experiments, give an explanation for the adsorption of Cr(VI) on sawdust, which could be adjusted for the present study: After the adsorption sites on the outside of the bead are used, it takes some time until extracted Hg is transported to the inside of the bead and makes room for further metal ions which can adsorb again on the outside. If

the leaching is significantly lowered before those extraction plateaus are reached, an earlier interruption of extractions might be an option. Different extraction behaviors compared to Zhang et al. (2011) could be explained as previously discussed due to the use of the Na_2SO_4 hardening solution or elastomers in the beads.

During Pt extraction experiments, plateaus were observed as well, although except for PP/TS no further significant increase in extraction capacity after a specific extraction time was observed. Compared to the time-dependent extraction of Pt using [A336][TS] and [A336][MTBA] as published previously Fischer et al. (2011), plateaus are reached within 1 hour after the start of the experiment. The provided immobilization matrix in this study might cause a retention of extraction, as discussed previously.

4.7. Extraction of CPCs

PP beads with immobilized ILs showed in general a low affinity to CPCs, cisplatin was extracted with a comparably low extent by PP/TS and PP/MTBA. Extraction of carboplatin was only observable at pH=6.0 with pure PP beads, while oxaliplatin displayed at pH=9.0 a high extraction capacity of 47.2 ± 8.4 % using pure PP beads. Extraction of oxaliplatin by PP/MTBA occurred almost unnoticeably at pH=6.0. Taking a look at immobilized ILs in PVA-alginate, the results indicate that it is unclear whether the ILs extract CPCs at all or if the ILs are just blocking adsorption sites in the matrix. No immobilized IL in PVA-alginate showed better extraction capacities than pure PVA beads for cisplatin and carboplatin, independently of the pH value. Only the extraction of oxaliplatin by PVA/TS, PVA/MTBA and PVA/PTBA resulted in a slightly but significantly higher extraction capacity when compared to PVA, but results were still unsatisfying with approximately 10 % extraction capacity. Interpreting this data, one has to keep in mind that the used CPCs show very different kinetics and products when they are dissolved depending on factors like other present ions or the pH (Miller et al. 1989, Miller et al. 1989). Pharmacokinetics is a different subject due to different species built by biotransformation (Vermorken et al. 1984, van der Vijgh 1991) which are not present in this work because no arrangements were made to have biotransformed products in the extraction solutions. An extreme example is the pharmacokinetics of oxaliplatin, which is undetectable in patient's urine after administration, only concentrations of biotransformed products are higher than the limit of detection (Graham et al. 2000). Other sample preparation techniques,

which could include an aging of CPC stock solutions containing Cl⁻ anions (Lenz et al. 2007), could lead to different extraction results. Further investigations, why pure PP beads extracted oxaliplatin comparatively well, should be conducted.

4.8. Leaching

For Hg extractions, DN values have not been analyzed because of the use of $Hg(NO_3)_2$ and HNO_3 for acidification resulting in fluctuations of DN. As expected, DOC values correlate with increasing bead mass and increasing extraction time. Only one exception is visible in the results, 3 g PP/TS (10.8 ± 0.4 mg/L) show a higher DOC than 4 g (8.0 ± 0.5 mg/L). Two explanations could be thought of, which could cause an increase in DOC: The DOC of 3 g PP/TS was measured at the end of a time-dependency experiment, which means that samples have been taken during the first 12 hours using a pipette, whose tips were in contact with the solution and the material of those tips could dissolve partially. Another explanation could be an increase in mechanical friction due to a continuously lowered reaction volume, because samples were taken every hour during the first 12 hours. This effect is most probably not visible for PVA-alginate beads, because if this effect is caused by the sample taking process, the impact on DOC of this contamination is too low to be able to observed, since measured DOC values are much higher (e.g. DOC of 0.2 g PVA/TS for Hg extractions: 77.0 ± 3.9 mg/L) when compared to PP beads. If the reason for this observed effect regarding PP/TS is mechanical friction, the impact of PVA beads could be lower because either of the smaller bead masses which did not exceed 0.2 g and therefore used less space in the used Erlenmeyer flasks causing less mechanical friction or the elastic properties of the bead-material prevented mechanical friction. Because of the DOC values of the PVA-alginate beads (up to over 90 mg/L), which are compared to PP beads (up to approximately 11 mg/L) higher, an optimization of extraction time is an important factor to preserve emission of bead contents. In this case, only a discrimination between the polymer and the IL is possible due to the lack of DN data.

The comparably low DOC for Hg extractions of PP/TS, when compared to PVA beads, consisted of the immobilized IL. Recalculation of the DOC values which were obtained from PVA beads show that most of the total DOC consists of the matrix material and a low IL share. In the case of PVA/PTBA beads, an IL share was only calculable when 0.01 g beads were used, it was not calculable at higher bead masses. An explanation for the low or not calculable IL share of

PVA/PTBA could be that the hydrophobic IL prefers the bead matrix over the aqueous solution. This might be caused by the structure of the anion, in which the present propylthio group alters the solubility-properties of the IL which prevents leaching into the aqueous solution.

Pt extractions were conducted in an almost "nitrogen-free" environment, in contrast to Hg extraction experiments, which made a differentiation between anionic IL share, cationic IL share and polymer share possible. DOC correlated as expected with the bead mass, but different to Hg extraction experiments pure PP beads showed measurable values as well, although no measurable nitrogen would be expected from those. An explanation could be that the Pt extraction solutions lead to dissolving of PP bead contents like elastomers (since the DOC was below 0.6 mg/L for the respective Hg experiments), which would explain measurable DN quantities in pure PP beads.

Shares on total DOC for Pt extractions revealed for PP/TS that the cation of the IL had the greatest share on total DOC overall, followed by DOC caused by PP, whereas an anionic IL share was only calculable for 0.5 g and 1 g with low values of 0.2 mg/L. Two differences are visible, when comparing DOC shares of PP/TS and PP/MTBA: First, total DOC for PP/MTBA is approximately twice as high when comparing same bead masses of PP/TS. Second, an anionic share is calculable for almost every bead mass, except for 2 g. Especially the first stated observation might have an impact on whether choosing PP/TS or PP/MTBA beads for extractions, because PP/TS beads leach less than PP/MTBA beads when using same bead masses. The shares for PVA beads showed in general a high dissolution of PVA-alginate, followed by leaching of the anion of the respective IL and little shares of [A336]. For PVA/TS beads, a share of cationic and anionic IL leaching was calculable at 0.05 g beads, higher or lower bead masses did not result in any IL leaching. PVA/MTBA, PVA/ETBA and PVA/PTBA displayed increasing anionic leaching with increasing bead mass, which could be a hint towards an anionic exchange mechanism for the extraction of Pt since the leaching of [A336] does not exceed 0.1 ± 0.1 mg/L. In contrast to the leaching results of Hg extraction experiments, PVA/TS shows almost no leaching while PVA/PTBA shows according to recalculation anionic leaching. An increase in anionic leaching could be explained by an incomplete extraction process: An anion exchange occurs, but either no complex with Pt is formed or the Pt-PTBA complex cannot transit back into the immobilization matrix. This assumption is supported by the fact that the respective PVA/PTBA DOC measurements for Hg

extractions revealed only little IL leaching at 0.01 g beads, which could be explained by different occurring mechanisms. Due to a lack of data, which splits the DOC from [A336][TS] into the ionic shares for Hg extractions, only a general assumption can be made that due to an ion exchange mechanism (whether cationic or anionic), higher DOC values were measured than during Pt experiments.

The recalculated data regarding shares on total DOC should be taken with caution, to make it possible simplification assumptions were necessary. Since pure PP and PVA-alginate beads do not share the same physical and chemical properties as beads containing ILs, the impact on the share of the polymer with and without ILs can vary. Also, the exact content of PP and PVA-alginate beads immobilized with ILs is unknown: The information of the manufacturer on the IL content of PP beads is "approximately 3 % IL", while for PVA-alginate due to several production steps over hours IL loss is a probable scenario. Accurate measurements for the determination of IL content in the beads are necessary for more precise calculations.

Data published by Stojanovic et al. (2010) showed that in a mixture of 2 g of [A336][TS] or [A336][MTBA] and either 2 mL of Millipore water or 10 mM $CaCl_2$, the cation of [A336][TS] leaches with an extent of 2.0 mg/L in Millipore water and 2.7 mg/L in 10 mM $CaCl_2$ and the cation of [A336][MTBA] leaches in both aqueous phases with an extent of 0.2 mg/L into the aqueous solution after 5 min. In another study by Leyma et al. (2016), leaching results of 100 mg [A336][ETBA] and [A336][PTBA] with 5 mL of 0.1 M $CaCl_2$-solution were after 24 h 167 mg/L and 110 mg/L (respectively), no differentiation was made between cationic and anionic share in this publication. The comparatively high DOC values for immobilized [A336][TS] and [A336][MTBA], which showed for whether for 2 g PP/TS, PP/MTBA, PVA/TS or PVA/MTBA in this work higher values than the reported ones by Stojanovic et al. (2010), have two explanations: First, the leaching experiment (Stojanovic et al. 2010) conducted ended after 5 minutes, while the DOC of all experiments in this work was measured after 24 h, thus enabling higher DOC values by providing a longer contact time. Second, the leaching in this work was measured at the end of extraction experiments and not in stand-alone leaching experiments as conducted by Stojanovic et al. (2010), which can cause an increase in DOC because of extraction mechanisms. Comparing the DOC values of [A336][ETBA] and [A336][PTBA] with the results reported by Leyma et al. (2016) it has to be kept in mind that leaching was again determined in stand-alone leaching experiments in the publication of and not during

extraction experiments like in this work: 0.2 g of PVA-alginate beads (IL content of 6 mg), which was the highest tested bead mass, displayed total DOC values of up to 90 mg/L. If the calculated share of IL of the respective beads was linearly extrapolated to a value, which would correspond to 100 mg of immobilized IL (and thus the IL mass Leyma et al. (2016) used) in the beads used in this work (simplified by multiplication with a factor of 17), only the immobilization of [A336][PTBA] in PVA-alginate beads during Hg extraction experiments was clearly successful due to no measurable DOC value. Extrapolation of the results for PVA/ETBA during Pt and Hg extractions and for PVA/PTBA for Pt extractions would result in higher calculated DOC. Since no extraction experiments were conducted with more than 0.2 g PVA-alginate beads, it is unclear whether or not the leaching behavior of PVA/ETBA and PVA/PTBA would be the same at higher bead masses.

4.9. Stripping and change in bead mass

Stripping of Hg was in general low for all beads with maximum approximately 11 % of recovery. This might be caused by the high affinity of Hg towards the thiol- and alkylthio groups of the anions of the IL, causing only little releases of the heavy metal after treatment with nitric acid. If the beads are supposed to be reused, more Hg has to be stripped off prior to another use to ensure free binding sites. Further experiments to increase stripping would be necessary, e.g. using different concentrations but 0.5 M HNO_3 for the stripping experiment, stripping of Hg with another chemical or a prolonged stripping experiment which takes longer than 24 h.

The stripping of Pt provided better results than Hg stripping, the recovery from PP/TS and PP/MTBA beads was between 20 % to 30 % and the recovery of PVA-alginate beads with immobilized ILs summarized between 50 % - 70 %. Pure PP and pure PVA-alginate stripping results indicate that the Pt is stripped off ILs to a greater extent than off the immobilization matrix, because PP and PVA-alginate stripping results were comparatively low with 5 % to 10 % when compared to the counterpart with immobilized IL. As stated before, the use of various concentrations of the stripping solution, the use of a different acid or a prolonged reaction time could increase stripping, if the current rates are not high enough.

Nonetheless, prior to the reuse of PVA-alginate beads for extraction experiments, hardening steps should be improved. Currently, the loss in bead mass of PVA-alginate beads is

approximately 50 % after one extraction experiment which takes 24 hours. Not only that leaching is affected by the dissolution of beads, if the mass loss trend cannot be interrupted, after several extraction and stripping rounds beads might not be left anymore. Regarding this issue, PP beads are more suitable: A little decrease in mass was observed for PP/TS beads, while PP beads had a slight increase in mass.

5. Conclusion & outlook

PP beads provide a matrix, which could definitely be used for the immobilization of ILs used for extracting heavy metals from aqueous solutions due to its low leaching behavior. The stability of PVA-alginate beads used for such purposes should be increased, prior to further extraction experiments, because of their comparably high instability in the water phase. Apart from that, both polymers have proven to be usable for metal extraction experiments.

The extraction of Hg and Pt depends highly on the bead mass, pH, species, contact time and the aqueous environment, i.e. in this case the presence of various anions. The release of bead contents into solution could have an impact on the extraction capacity. ILs can show an extraction-prohibiting effect, if the immobilization matrix shows an affinity towards the metal. The extraction of CPCs should be retried with aged solutions to check if the affinity towards immobilized ILs changes.

Minimizing the leaching could be conducted by further optimization through measurement of the time-dependency of extractions. Intermediate extraction plateaus may occur, which could limit the use of beads immobilized with ILs.

If the immobilization matrix is stable, hints towards the extraction mechanism could be assessed via DOC and DN measurements. For exact determination, further analysis of the distribution of the compounds is necessary.

Stripping of metals off used beads was better for PVA-alginate than PP beads, re-extracting experiments should be conducted to test whether the beads could be re-used or not.

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Zusammenfassung

Um die Emission toxischer Schwermetalle zu unterbinden werden unterschiedliche Methoden auf ihre Eignung überprüft. Quecksilber wird größtenteils durch handwerklichen und im kleinen Maßstab betriebenen Goldbergbau sowie Kohleverbrennung in die Umwelt freigesetzt, während Quellen für Platin der mechanische Abrieb von Autokatalysatoren und kanzerostatische Platinverbindungen wie Cisplatin, Carboplatin oder Oxaliplatin aus Krankenhausabwässern darstellen.

Eine Möglichkeit um die genannten Schwermetalle aus wässrigen Lösungen zu entfernen ist die Extraktion mit ionischen Flüssigkeiten (ILs). Die Eigenschaften von ILs können durch funktionelle Gruppen beeinflusst werden, damit diese als Komplexbildner fungieren können. Durch unerwünschte Reaktionen kann es zum sogenannten „leaching" von ILs in wässrige Lösungen kommen, deren toxisches Potential nicht zu unterschätzen ist. Um diese Freisetzung von ILs zu unterbinden, können diese in Polymeren wie Polypropylen oder Polyvinylalkohol-Alginat immobilisiert werden.

Die vier ILs Tricaprylylmethylammoniumthiosalicylat ([A336][TS]), Tricaprylylmethylammonium-2-(Methylthio)benzoat ([A336][MTBA]), Tricaprylylmethylammonium-2-(Ethylthio)benzoat ([A336][ETBA]) und Tricaprylylmethylammonium-2-(Propylthio)benzoat ([A336][PTBA]) wurden im Rahmen dieser Arbeit in Polyvinylalkohol-Alginat Kügelchen immobilisiert. Polypropylen Kügelchen, welche die ILs [A336][TS] und [A336][MTBA] enthalten haben, wurden von Borealis, Linz, Österreich zur Verfügung gestellt.

Es wurde die Extraktionskapazität der oben genannten ILs in Polymerkügelchen für Quecksilber und Platin untersucht. Das Extraktionsausmaß wurde mittels Kaltdampf-Atomabsorptionsspektrometrie und Graphitrohr-Atomabsorptionsspektrometrie anhand Konzentrationsmessungen zu Beginn und nach Ende des jeweiligen Experimentes bestimmt. Der Einfluss der Kügelchenmasse, des pH-Wertes der wässrigen Lösung, der eingesetzten Metallspezies und der Extraktionsdauer wurde festgestellt. Durch Messungen des gelösten organischen Kohlenstoffes (DOC) und gelösten Stickstoffes (DN) wurde das Ausmaß des leaching bestimmt, sowie näherungsweise in welchem Ausmaß die verschiedenen Komponenten der Kügelchen gelöst vorliegen. In weiterer Folge wurde das Freisetzen von

extrahierten Metallen, sogenanntes „stripping" untersucht, um eine potentielle Wiederverwendbarkeit der Kügelchen zu überprüfen.

Die Ergebnisse zeigen, dass bis auf die Extraktionsdauer keine verallgemeinerte Aussage bezüglich optimaler Extraktionsbedingungen gemacht werden kann. Während mit dem zeitlichen Fortschritt der Experimente die Extraktionskapazität gestiegen ist, hatten alle eingesetzten Kügelchen unterschiedlich auf eine Änderung der Kügelchenmasse, des pH-Wertes und der Spezies bzw. verwendeten Säure als Lösungsmittel reagiert. So wurde beispielsweise beobachtet, dass im Vergleich ein Wechsel der Quecksilber-Spezies von $Hg(NO_3)_2$ zu $HgCl_2$ einen geringeren Einfluss auf die Extraktionskapazität hatte als ein Wechsel von $H_2[PtCl_6]$ zu Cisplatin, Carboplatin oder Oxaliplatin: Die Extraktion dieser kanzerostatischen Platinverbindungen war niedrig bis nicht beobachtbar.

Alles in Allem ist festzustellen, dass [A336][TS] im Vergleich zu den anderen ILs die besten Resultate mit bis zu 95 % Extraktionskapazität für Quecksilber und Platin gezeigt hat. Durch die Immobilisierung kam es zu einer relativ langsamen Aufnahme der Metalle in die ILs, und die maximale Extraktion war zwischen 5 und 24 Stunden erreicht. Das leaching konnte durch die Immobilisierung, insbesondere in Polypropylen stark reduziert werden und lag mit Werten unter 10 mg/L C in einem Bereich, der signifikant unter dem für flüssig-flüssig Extraktionen lag. Weitere Forschungen zur Maximierung der Extraktion bei geringem leaching und einer praktikabel scheinenden Reaktionszeit könnten zu Etablierung von praktisch anwendbaren Verfahren beitragen.

Abstract

To prevent the emission of toxic heavy metals, various methods are checked for their suitability. Mercury is released into the environment for the most part by artisanal and small-scale gold mining as well as coal combustion, while sources for Platinum are represented by the mechanical friction of automobile exhaust catalysts and cancerostatic platinum compounds like cisplatin, carboplatin or oxaliplatin from hospital effluents.

One possibility to remove the stated heavy metals from aqueous solutions is the extraction with ionic liquids (ILs). The properties of ILs can be influenced by functional groups, so that those can function as complexing agents. Unwanted reactions can cause the so-called "leaching" of ILs into aqueous solutions, whose toxic potential should not be underestimated. To prevent the release of ILs, they can be immobilized in polymers like polypropylene or polyvinyl alcohol-alginate.

The four ILs Tricaprylylmethylammonium thiosalicylate ([A336][TS]), Tricaprylylmethylammonium 2-(methylthio)benzoate ([A336][MTBA]), Tricaprylylmethylammonium 2-(ethylthio)benzoate ([A336][ETBA]) and Tricaprylylmethylammonium 2-(propylthio)benzoate ([A336][PTBA]) were immobilized as part of this work in polyvinyl alcohol-alginate beads. Polypropylene beads, which contained the ILs [A336][TS] and [A336][MTBA], were provided by Borealis, Linz, Austria.

Investigations on the extraction capacity of the ILs, which were stated above, were made for Mercury and Platinum. The extent of extractions was determined via cold-vapor atomic absorption spectrometry and graphit furnace atomic absorption spectrometry, based on concentration measurements in the beginning and in the end of the respective experiment. The impact of the bead mass, the pH-value of the aqueous solution, the used metal species and the duration of the extraction was observed. By measurement of the dissolved organic carbon (DOC) and dissolved nitrogen (DN), the extent of leaching was determined as well as an approximation to which extent the various bead components dissolved. Further investigations were made on the release of extracted metals, so called "stripping", to check a potential reusability of the beads.

The results demonstrate that except for the duration of the extraction, no general statement can be made regarding optimal extraction conditions. While an increase in the extraction

capacity with temporal progress was observed, the beads reacted differently towards a change regarding bead mass, pH-value and species or acid as solvent. For example, a change of the Mercury species from $Hg(NO_3)_2$ to $HgCl_2$ had a lower impact on the extraction capacity when compared to a change from $H_2[PtCl_6]$ to cisplatin, carboplatin or oxaliplatin: The extraction of those cancerostatic platinum compounds was low to not observable.

Overall, [A336][TS] showed the best results in comparison to the other ILs with up to 95 % extraction capacity for mercury and platinum. The immobilization lead to a relatively slow uptake of the metals into the ILs, the maximum extraction was achieved between 5 and 24 hours. Leaching could be reduced by immobilization, especially in polypropylene and was with values below 10 mg/L C in a range, which was significantly below those for liquid-liquid extractions. Further research for maximizing the extraction with low leaching and a reaction time, which seems feasible, could lead to the establishment of practically applicable procedures.