

HEAVY METAL EXTRACTION FROM AQUEOUS SOLUTIONS USING IONIC LIQUIDS IMMOBILIZED IN POLYPROPYLENE AND POLYVINYL ALCOHOL BEADS

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Introduction

Heavy metal (HM) pollution of surface and ground water bodies is currently considered as one of the world's most alarming environmental problems. The extraction methods for HM include precipitation, ion-exchange, electrolysis, and adsorption, among others. Each method has its own advantages and disadvantages. In general, these techniques are limited either by selective operation or high operations costs. Ionic liquids (ILs) are a rather novel group of compounds displaying manifold special properties, are considered rather environmental friendly and have been tested for heavy metal extraction quite successfully in the last years (Stojanovic & Keppler, 2012). Amongst others Aliquat 336[®]-based ILs have shown their potential towards metal extraction in the past (eg Kogelnig et al., 2008). Although most of the ILs are hydrophobic substances, their transition into aqueous solution, the so-called "leaching", presents a major drawback regarding their environmental friendliness. Therefore their immobilization in proper matrices has the potential to limit the leaching of ILs (Zhang et al., 2011). The aim of this work was to study the extraction potential of Aliquat 336[®]-based ILs immobilized in polypropylene (PP) and polyvinyl alcohol-alginate (PVA) beads to determine optimal extraction conditions for Hg and Pt with minimized leaching effects.

Methods

The ILs used for the experiments were tricaprylmethylammonium thiosalicylate ([A336][TS]), tricaprylmethylammonium 2-(methylthio)benzoate ([A336][MTBA]), tricaprylmethylammonium 2-(ethylthio)benzoate ([A336][ETBA]) and tricaprylmethylammonium 2-(propylthio)benzoate ([A336][PTBA]). PP beads containing app. 3 % [A336][TS] (PP/TS) and [A336][MTBA] (PP/MTBA) were obtained from Borealis AG, Austria. PVA beads containing app. 3 % [A336][TS] (PVA/TS), [A336][MTBA] (PVA/MTBA), [A336][ETBA] (PVA/ETBA) and [A336][PTBA] (PVA/PTBA) were synthesized using a modified method following Zhang et al.(2011) and Zain et al(2011). Extraction experiments were conducted using different chemical species of Hg and Pt in aqueous solutions of known concentrations. Hg concentrations were determined by CV-AAS, Pt concentrations by GF-AAS. To estimate the leaching effects dissolved organic carbon (DOC) and dissolved nitrogen (DN) values were evaluated as well.

Results

Both Hg and Pt ions were extracted best at pH = 3.5. Immobilized ILs showed different extraction kinetics in the used polymers. Extraction of Hg was influenced by the used species, anion content and bead mass. Pt extraction was influenced by the species and bead mass. Leaching was in general lower for PP beads, leaching of those was during Pt experiments mostly due to cation leaching of the IL, while most of the DOC contributed from PVA beads originated from the polymer matrix. Hg experiments showed for PP

beads almost exclusively leaching of the IL and for PVA beads mostly the polymer matrix. Leaching of the ILs could be reduced up to 90% compared to non-immobilized ILs.

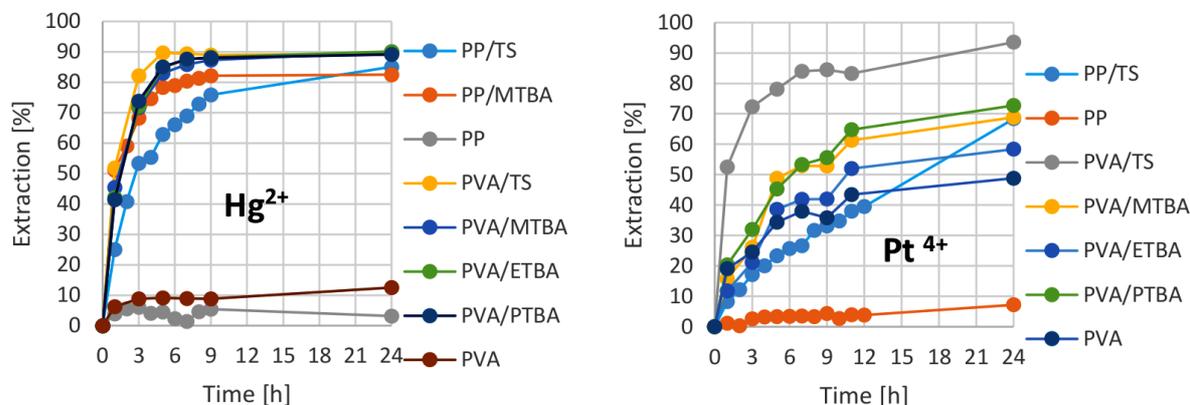


Figure 1. Time-dependent extractions of 100 µg/L Hg²⁺ as Hg(NO₃)₂ (right) and 1 mg/L Pt⁴⁺ as H₂[PtCl₆] (left) under optimized conditions.

Conclusion

PP and PVA beads are suitable immobilization matrices for ILs regarding metal extraction, although PVA beads need further stabilization steps. Extraction efficiencies account up to 90%, the results are well comparable with liquid/liquid extractions, although with slower extraction kinetics. Leaching was reduced significantly.

References

- Kogelnig, D., Stojanovic, A., Galanski, M., Groessl, M., Jirsa, F., Krachler, R., & Keppler, B. K. (2008). Greener synthesis of new ammonium ionic liquids and their potential as extracting agents. *Tetrahedron Letters*, 49(17), 2782-2785.
- Stojanovic A, Keppler BK (2012). Ionic Liquids as Extracting Agents for Heavy Metals, *Separation Science and Technology*, 47:2, 189-203,
- Zain, N. A. M., Suhaimi, M. S., & Idris, A. (2011). Development and modification of PVA–alginate as a suitable immobilization matrix. *Process Biochemistry*, 46(11), 2122-2129. doi:<http://dx.doi.org/10.1016/j.procbio.2011.08.010>
- Zhang, Y., Kogelnig, D., Morgenbesser, C., Stojanovic, A., Jirsa, F., Lichtscheidl-Schultz, I., . . . Keppler, B. K. (2011). Preparation and characterization of immobilized [A336][MTBA] in PVA-alginate gel beads as novel solid-phase extractants for an efficient recovery of Hg (II) from aqueous solutions. *J Hazard Mater*, 196, 201-209. doi:10.1016/j.jhazmat.2011.09.018