TASK SPECIFIC IONIC LIQUIDS FOR SOLVENT BAR MICRO-EXTRACTION OF HEAVY METALS

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Introduction

During the last years the interest in the application of ionic liquids (ILs) in micro-extraction methods has gained increasing attention due to their particular physico-chemical properties. Among the benefits for liquid micro-extraction are their non-volatile nature and their high viscosity, which overcomes instability problems of conventional organic solvents (Zhang et al. 2013). Ionic liquids have been used in liquid micro-extraction of toxic metals. The most recent application is in hollow fiber liquid phase micro-extraction (HFLPME). Despite the interest in HFLPME, it presents some limitations for routine and field use caused by the need of a specific support for the fiber. However, a configuration of solvent bar micro-extraction (SBME) recently appeared to overcome this drawback by thermally sealing both ends of the fiber (López-López et al. 2015).

Tuning the composition of the cation and the anion, including functional groups that act as ligands in their structure, improves the efficiency of ILs for extraction of metals from water samples. These types of ILs are known as "task specific" (TSILs), because they can be considered as design solvents (Sawant et al., 2011).

Methods

Ionic liquids tricaprylylmethylammonium thiosalicylate ([A336][TS]), tricaprylylmethylammonium 2-(methylthio)benzoate ([A336][MTBA]), trihexyl(tetradecyl)phosphonium salicylate ([C101][Sal]), and trihexyl(tetradecyl)phosphonium anthranilate ([C101][Ant]) were synthesized via deprotonation-metathesis reaction from Aliquat® 336 and Cyphos® IL 101 (Sigma-Aldrich) and corresponding Bronsted acids as precursors.

SBME was set-up filling the fiber lumen and pores with the ionic liquid and thermally sealing the fiber ends. Extraction efficiency was calculated as the metal removed from the sample after the extraction experiment. Standard solutions of Ag, Cd, Cr, Cu, Ni, Pb and Pt were prepared using certified standards of 1000 mg L^{-1}. Concentration of the metal in the aqueous solution was quantified by flame and graphite furnace atomic absorption spectroscopy.

Results

A screening of metal extraction (Figure 1) shows that Aliquat® 336 derivatives [A336][TS] and [A336][MTBA] offer the highest extraction efficiency in the case of divalent metals Cu, Cd, Ni, Pb and Pt. However in the case of Cyphos® IL 101 derivatives [C101][Sal] and [C101][Ant] the highest extraction is observed for Ag and Pt. Extraction efficiency observed for Ag with Aliquat 336® can be associated with the presence of $AgCl_n^{(n-1-)-}$ complexes that are exchanged with Cl^- from the ionic liquid. Finally, in the case of Cr, all the used ILs offer extraction yields over 90 % after 24 hours.

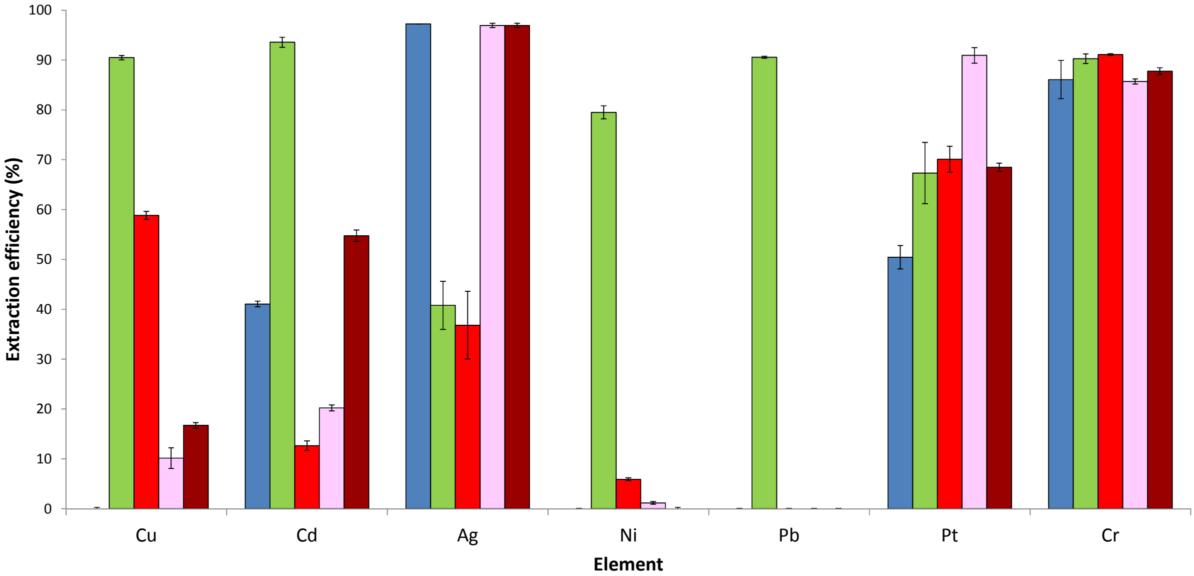

Figure 1. Screening extraction efficiency of Ag, Cd, Cr, Cu, Ni, Pb and Pt by ■ Aliquat® 336, ■ [A336][TS], ■ [A336][MTBA], ■ [C101][Sal], and ■ [C101][Ant]

For [A336][TS], a common behavior was observed for Cd, Cr, Cu, Ni and Pb, with a linear increase of extraction with time up to 5 hours. [A336][MTBA] showed lower capacity than [A336][TS] for Cr and Cu. Regarding Pt, [C101][Sal] showed a stabilization in the extraction profile after 5 hours.

Conclusion

SBME joins the efficiency of the proposed ILs with their stabilization in the porous hollow fiber, leading to the efficient multi-element micro-extraction of Ag, Cd, Cr, Cu, Ni, Pb and Pt.

References

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