EXPLORING NEW SENSORS BASED ON FUNCTIONALIZED MEMBRANES FOR MERCURY MONITORING IN AQUATIC ENVIRONMENTS

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Introduction

Mercury is considered a priority hazardous substance because of its toxicity and widespread occurrence. It is released to the environment through both natural and anthropogenic processes and it is globally distributed. Consequently, environmental Hg monitoring and especially analytical procedures for the determination of the dissolved-bioavailable fraction of Hg in water have attracted great attention.

In the present study we have investigated the use of functionalized membranes incorporated in a special device to allow Hg monitoring from different aquatic systems such as freshwaters and sea water. Thus, we have prepared, characterized, and tested, different membranes composed of an extractant (carrier) and a base polymer such as cellulose triacetate (CTA). These membranes, known as polymer inclusion membranes (PIMs), can be selective to a target species using the appropriate carrier (Almeida et al., 2012). In our work, we have used different ionic liquids (IL) to functionalize the membrane. ILs are generally defined as salts that are liquid below 100º C and consist entirely of ions. Normally, they include an organic cation containing nitrogen or phosphorus and an organic or inorganic anion. Different IL have shown to effectively extract Hg in different matrix, such as trioctylmethylammonium thiosalicylate (TOMATS) impregnated in palm shell activated carbon to extract Hg from contaminated water (Ismaiel et al., 2013), and tetradecyl(trihexyl)phosphonium chloride (TDTHPCl) immobilized in biopolymer capsules for Hg(II) removal from chloride solutions (Guibal et al., 2008).

Methods

Two task-specific IL were synthesized from tricaprymethylammonium chloride (Aliquat 336) in order to use them as carriers: TOMATS and trioctylmethylammonium salicylate (TOMAS). They were prepared by exchanging the chloride anion by thiosalycilate or salicylate, respectively, following the procedure described by Egorov et al., 2010. The phosphonium based IL (tetradecyl(trihexyl)phosphonium chloride) was purchased from Aldrich. PIMs were prepared using CTA as a polymer and the corresponding IL, (50% *wt.* content) as detailed in Fontàs et al., 2014. Both ILs and PIMs were characterized by different techniques such as elemental analysis and IR spectroscopy.

For extractions experiments, small pieces of PIMs were contacted with 25mL 1 ppm Hg(II) in a synthetic freswater solution during 24 hours. Loaded membranes were used to study the elution efficiency of EDTA, thiourea, cysteine or nitric acid solutions.

For monitoring purposes, two different approaches have been investigated. First, functionalized membranes have been used as solid sorbents to extract Hg, and the effect of matrix composition and metal content has been investigated using all IL. On the other hand, PIMs were incorporated in a special device described in Fontàs et al. 2014 in which an aqueous solution was added inside the device to allow the back-extraction of the metal.

Mercury measurement was done using an Advanced Mercury Analyser model AMA-254 for direct analyisis of PIMs and by an ICP-OES for aqueous samples.

Results

Among the different functionalized membranes tested to extract Hg from freshwater samples, the one containing the IL TOMATS showed an extraction efficiency close to 100% whereas a 70% was found when the IL was TOMAS. Thus, a device incorporating a PIM with TOMATS was tested as a sensor for Hg monitoring in Ebro river (Catalonia, NE Spain). Samplers were deployed for 7 days, and the analysis of the membranes revealed the presence of mercury in river water due to industrial activity.

We also investigated the possibility to elute the metal extracted in membranes. In the case of TOMAS, solutions of both 0.1 M and 0.01M EDTA quantitatively recovered the extracted metal. However, in the case of TOMATS, it was necessary to use a 0.1 M cysteine or a 0.1 M thiourea at pH=2 solution to strip the metal.

Moreover, a device including a PIM with TDTHPCl showed to effectively transport Hg from a 1M chloride solution to a 6M HNO_3 acceptor phase (placed inside the device). Using this same configuration, a significant transport of Hg was also achieved using a PIM with TOMAS from a synthetic freswater solution to a 0.1 M EDTA acceptor phase.

Conclusion

From our results we can conclude that functionalized membranes containing ILs can be very useful for Hg monitoring purposes. We can state that PIM with TOMATS can be viewed as an efficient sorbent to collect Hg from freshwaters. However, other membranes with ILs such as TDTHPCl (for high chloride content waters) or TOMAS (freshwaters) allow not only the extraction but facilitates the elution of the metal, which, in turn, can easier Hg analyisis.

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